

Prog. Polym. Sci. 24 (1999) 793-873

PROGRESS IN POLYMER SCIENCE

Anionic polymerization of (meth)acrylate esters in the presence of stabilizers of active centres

P. Vlček*, L. Lochmann

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague, Czech Republic

Received 1 January 1999; accepted 22 March 1999

Abstract

The controlled polymerization of polar vinyl monomers like acrylic and methacrylic esters is often complicated owing to their chemical structures. As (meth)acrylate polymers are a class of technologically important and useful materials, a great amount of attention has been focused on the polymerization of these monomers is a controlled fashion to give materials with well defined structures and desired properties. This review summarizes recent work on ligated anionic polymerizations of (meth)acrylate esters. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Anionic polymerization; Ligated polymerization; Methacrylates; Acrylates; Block copolymers; Active centre stabilization; Alkali metal ester enolates; Alkali metal alkoxides; Lithium chloride; Alkylaluminiums

Contents

1

	Intro	duction		795
	1.1.	Side re	actions in the polymerization process	795
	1.2.	Other 1	nethods for (meth)acrylate polymerization	797
	1.3.	Stabiliz	zer-assisted anionic polymerization - general approach	798
2.	Alka	li metal	ester enolates, their reactions and use in model oligomerizations studies	799
	2.1.	Prepara	ation and properties of alkali metal ester enolates	800
	2.2.	Infrare	d spectra of alkali metal ester enolates	801
	2.3.	Interac	tions of alkali metal ester enolates with alkali metal <i>tert</i> -alkoxides	802
	2.4.	NMR a	and quantum chemistry studies of lithium ester enolates and their complexes	803
		2.4.1.	Self-aggregation of ester enolates	803
		2.4.2.	Complexes of ester enolates with LiCl or lithium 2-(2-methoxyethoxy)ethoxide	805
		2.4.3.	Complexes with alkali metal <i>tert</i> -alkoxides	808
	2.5.	Conder	nsation and transmetallation reactions of alkali ester enolates	815
		2.5.1.	Condensations and their significance in (meth)acrylate anionic polymerization	815

* Corresponding author. Tel.: + 420-2-20403250; fax: + 420-2-367981.

0079-6700/99/\$ - see front matter @ 1999 Elsevier Science Ltd. All rights reserved. PII: S0079-6700(99)00017-9

E-mail address: vlcek@imc.cas.cz (P. Vlček)

		2.5.2. Transmetallation between lithium ester enolates and carboxylic acid esters	816
	2.6.	Addition of ester enolates onto methacrylate monomers, oligomerization studies	817
		2.6.1. Products of MMA oligomerization	817
		2.6.2. Kinetics of MMA oligomerization	821
	2.7.	Addition of ester enolates onto tert-butyl acrylate, oligomerization studies	824
		2.7.1. Products of the <i>t</i> -butyl acrylate oligomerization	824
		2.7.2. Effect of additives on the <i>tert</i> -butyl acrylate oligomerization	826
		2.7.3. Stability of active centres in <i>tert</i> -butyl acrylate oligomerization	827
3.	Poly	merization of methacrylates in the presence of alkali metal <i>tert</i> -alkoxides	827
	3.1.	Polymerization initiated by neat alkali metal <i>tert</i> -alkoxides	827
	3.2.	Polymerization initiated by alkali metal ester enolates, effect of <i>tert</i> -alkoxides	830
	3.3.	Microstructure of poly(methacrylate)s, effect of alkali metal <i>tert</i> -alkoxides	832
4.	Poly	merization of acrylate esters assisted with <i>tert</i> -alkoxides	834
	4.1.	tert-Butyl acrylate	835
	4.2.	2-Ethylhexyl acrylate	837
		4.2.1. Polymerization with butyllithium and/or lithium <i>tert</i> -butoxide	837
		4.2.2. Polymerization with lithium ester enolates	839
	4.3.	Butyl and ethyl acrylates	841
	4.4.	Polymerization of acrylates in the presence of lithium 3-methyl-3-pentoxide	847
	4.5.	Synthesis of block copolymers with (meth)acrylate blocks	847
5.	Othe	r types of stabilizing additives (ligands) and their effect on (meth)acrylate polymerization	850
	5.1.	Alkali metal halides	850
		5.1.1. Homopolymers and functionalized polymers	850
		5.1.2. Block and random copolymerization	852
		5.1.3. Microstructure of polymers, effect of LiCl	856
	5.2.	Bidentate lithium alkoxides	858
		5.2.1. Homopolymerization of acrylates	858
		5.2.2. Block and random copolymerization	859
	5.3.	Alkylaluminiums	862
		5.3.1. Homopolymerization of methacrylates	862
	_	5.3.2. Mechanistic studies	864
6.	Conc	clusion remarks	869
Ac	know	ledgements	869
Re	eterenc	es	869

Nomenclature

butyl methacrylate
tert-butyl methacrylate
2,3-epoxypropyl methacrylate
2-dimethylaminoethyl methacrylate
ethyl acrylate
butyl acrylate
tert-butyl acrylate
2-ethylhexyl acrylate
buta-1,3-diene
butyl isopropenyl ketone
tert-butyl isopropenyl ketone

BuLi:	butyllithium
s-BuLi:	sec-butyllithium
t-BuLi:	<i>tert</i> -butyllihium
MIB-Li(Na):	methyl 2-lithio(sodio)isobutyrate
tBIB-Li:	tert-butyl 2-lithioisobutyrate
EIB-Li(K):	ethyl 2-lithio(potassio)isobutyrate
tBPr-Na(Li):	tert-butyl 2-sodio(lithio)propionate
tBLTMG:	di-tert-butyl 2-lithio-2,2,4-trimethyl glutarate
MLTMG:	di-methyl 2-lithio-2,2,4-trimethyl glutarate
<i>t</i> -BuOLi(Na,K):	Li(Na,K)-tert-butoxide
3-MPeOLi:	Li 3-methyl-3-pentoxide
MEEOLi:	Li-2-(2-methoxyethoxy) ethoxide
αMeSt:	α -methylstyrene
DPHLi(K):	1,1-diphenylhexyllithium(potassium)
DPMLi:	(diphenylmethyl)lithium
DPMPLi:	1,1-diphenyl-3-methylpentyllithium
TPDLB:	1,1,4,4-tetraphenyl-1,4-dilithiobutane

1. Introduction

Now being one of the new and modern fields of polymer chemistry, ordered polymer systems find a number of important practical applications. Block copolymers, in particular, show special properties utilizable in many cases, e.g. as compatibilizers in polymer blends [1] or hydrophilic/hydrophobic copolymers applicable to steric stabilization of dispersions [2]. As only well defined macromolecules exhibit required properties, a significant amount of interest is devoted to methods of controlled synthesis of polymers. For this purpose, ionic processes, in particular anionic polymerization, with a more or less living character of active species are commonly used [3]. Block copolymers composed of styrene and diene blocks can be relatively simply prepared in this way and some of them are commercially available (e.g. Kratons, Shell Co.). Polystyrene or polydienes can also be functionalized by termination of the living polymer with an appropriate agent [4,5] giving the product with terminal, e.g. carboxy or hydroxy groups.

On the contrary, the controlled polymerization of polar vinyl monomers, such as acrylic and methacrylic esters is much more complicated owing to their chemical structures. As the (meth)acrylate polymers offer a wide scale of useful materials [6] a great amount of attention has been devoted to the polymerization of these monomers in a controlled manner producing tailor-made poly((meth)acrylate)s with well-defined structures and predetermined properties.

This review reports briefly on the ligated anionic polymerization of methacrylate esters which is one of the methods for their more or less controlled polymerization.

1.1. Side reactions in the polymerization process

In principle, the conjugated unsaturated system C=C-C=O of the (meth)acrylate molecule can react



Scheme 1.

with the ion-pair of the organometallic initiator $(R^- M^+)$ or a living chain-end in several ways [7,8], see Scheme 1.

In the methacrylate polymerization, 1,2-addition onto the carbonyl double bond leads, after splitting off an alkoxide, to the reactive alkyl isopropenyl ketone, with possible addition of the second initiator molecule giving a tertiary alcohol. 1,4- and 3,4-additions, being formally possible, give enol or keto-forms of active centres of polymerization, which have an enolate structure [9] (see below).

Side reactions in the initiation step of the polymerization have been studied in a number of works [7,8,10-12]. By NMR analysis, BIK was detected in PMMAs prepared with BuLi the content of which depends on polymerization medium. In contrast to BuLi, *tert*-butyl magnesium bromide with a bulky alkylgroup reacts in toluene at low temperatures with monomer in a 1,4- or 3,4-fashion, giving poly-(methacrylate)s with narrow MWDs and extremely high contents of isotactic [13,14] microstructure. Polymerization initiated by the combination *t*-BuLi/R₃Al gives in toluene highly syndiotactic polymer [15]. Neither of the stereospecific polymers contains ketone units and they have the same chemical structure. Therefore, both of these polymerizations are initiated with the *t*-Bu⁻ carbanion and initiation proceeds without the side reactions mentioned above. The initiating systems were successfully used for polymerization of a number of acrylic-type monomers [16].

In termination reactions, the ion-pair of the growing chain-end reacts similarly to the initiator with a carbonyl group either of the monomer or polymer yielding the chain terminated with the isopropenyl ketone group in the first case or branched polymer in the latter. These terminations are of minor importance. The most important termination reaction of the growing polymer is the condensation



Scheme 2.

P. Vlček, L. Lochmann / Prog. Polym. Sci. 24 (1999) 793-873



Scheme 3.

reaction of the living chain-end with the carbonyl group of the antepenultimate unit of the own chain ("back-biting reaction") forming in the first step a "dormant" cyclic complex and in the second step, after the splitting off an alkoxide, inactive cyclic oxo ester [17] (Scheme 2). In acrylate polymerization, the cyclic product exists predominantly in an enolized form containing conjugated unsaturated system C=C-C=O [18] (Scheme 3). The enolized oxo ester absorbs in UV region (260 nm); this can be utilized for assessment of the extent of back-biting reaction, e.g. in SEC analysis with a UV detection [19].

1.2. Other methods for (meth)acrylate polymerization

It is worth noting some of polymerization methods which have been developed recently as a consequence of an effort devoted to controlled polymerization of (meth)acrylate monomers. Nevertheless, they are not the subject of this article, so that they are mentioned very briefly.

Most important of these processes is group transfer polymerization (GTP) discovered by DuPont scientists [20] which is, in principle, a repeated Michael reaction of activated silyl ketene acetal with (meth)acrylate monomer. The reaction is initiated by 1-methoxy-1-(trimethylsiloxy)-2-methylpropene (MTS) and catalyzed either by nucleophilic or by electrophilic compounds. The former are convenient for polymerization of methacrylates [21–24], while the latter gives better results in the polymerization of acrylic esters [25], which complicates preparation of methacrylate/acrylate block copolymers [26,27]. The GTP is preferred for the synthesis of methacrylate block copolymers [22,28], macromonomers [25] and functionalized poly(methacrylate)s [29]. The process is hardly compatible with a controlled polymerization of non-polar vinyl monomers, so that the preparation of, e.g. styrene/MMA diblock polymer is rather complicated [30]. GTP of acrylates catalyzed by an electrophile gives often non-homogenous products [31] or polymers with broadened MWD and, especially at ambient temperatures, the process loses its living character [32]. Good results were obtained in HgI₂-catalyzed GTP of BuA [33,34]. The mechanism of GTP is not completely clear and has been the subject of discussions [29,35–39].

A favourable effect of a bulky counterion was utilized in the metal-free polymerization (MFP) of acrylic esters initiated by tetraalkylammonium thiolates [40] or, better, by carbanion salts derived, for instance, from dialkylmalonates [41], mostly at room temperature. The method is limited to rather low-molecular-weight products, however, using specially synthesized initiators, α -functionalized polyacry-lates can be easily prepared [42–44]. An overview of various types of initiators for the preparation of functionalized polymers by MFP and GTP is given in the literature [45].

Another promising way to controlled poly((meth)acrylate)s is a polymerization initiated by



Scheme 4.

metaloporphyrine derivatives [46]. A number of initiators have been designed; some of them require activation by visible light [47] (the process is very slow in the dark), others polymerize monomer rapidly without irradiation [48]. The reaction rate can be enhanced by the addition of sterically hindered Lewis acids [49–51] ("high-speed" living polymerization) the active centres remaining living for a long time [52]. Being virtually free of side reactions, the process offers poly(methacrylate)s with high molecular weights [53] and narrow MWDs. As some of the systems initiate ring-opening polymerization, a number of block copolymers of vinyl and heterocyclic monomers [54] can also be prepared.

Similarly, polymerization initiated with rare earth metal initiators, mostly of the lanthanocene type [55], affords at 0°C in toluene poly((meth)acrylate)s with very narrow MWDs in quantitative yields without perceptible participation of side reactions [56–58]. The metals (La, Sm, Y, etc.) are in an oxidation state II or III. Owing to a very low extent of self-termination, the initiators are well applicable to the synthesis of block copolymers composed of methacrylate and acrylate blocks [59]. Moreover, organolanthanides initiate the ring opening polymerization of lactones [60] and some of them are also useful for the polymerization of non-polar vinyl monomers [61] (ethylene) so that the systems are applicable to the synthesis of a wide spectrum of block copolymers [62].

1.3. Stabilizer-assisted anionic polymerization - general approach

The methods mentioned in Section 1.2 allow more or less "living" polymerization of (meth)acrylate monomers to products with tailored structures including block copolymers. However, they are hardly compatible with the anionic polymerization of non-polar vinyl monomers (e.g. styrene) lacking carbonyl-conjugated groups which can be polymerized only by strong nucleophiles. Highly basic carbanions complicate (meth)acrylate polymerization (see Section 1.1) so that an idea arose to modify the nucleophilic character of the organometallic initiator or living polymer (polystyrene, polydiene) and minimize in this way the extent of side reactions. The basic strategy followed here was to depress the reactivity of a living chain-end toward the carbonyl group of (meth)acrylate and the acid α -hydrogen in acrylate. This can be performed by tailoring the environment of the propagating chain-end by electronically wellbalanced ligands which cause steric hindrance and, at the same time, lower the nucleophility of the growing carbanion remaining reactive enough to add another monomer molecule or reagent. At present, the following stabilizing additives (ligands) are mainly used for (meth)acrylate polymerization: (i) alkali metal *tert*-alkoxides (the oldest-type ligand); (ii) alkali metal halides (prevailingly LiCl); (iii) alkali metal polydentate alkoxides (dual ligands); and (iv) alkylaluminiums.



2. Alkali metal ester enolates, their reactions and use in model oligomerizations studies

Anionic polymerization of (meth)acrylates is a complex process involving a range of partial reactions and equilibria. To obtain more detailed information about the individual steps of the polymerization, model studies were performed with low-molecular-weight compounds the results of which were used to design real polymer syntheses. The active centre in (meth)acrylate polymerization is assumed to have a structure of alkali metal ester enolate of the following general formula (Scheme 4, see also Section 1.1): Therefore, ester enolates were used as model compounds for the study of the polymerization process. Although the negative charge is predominantly located on the oxygen atom (enol form), the reactions of the ester enolate proceed mostly at the carbon atom (keto form).



Scheme 6.



Fig. 1. IR spectra of 10% solutions in benzene; full line, isopropyl 2-lithioisobutyrate; dotted line, isopropyl isobutyrate. (Reproduced with the kind permission of J Organomet Chem 1973;50:9.)

2.1. Preparation and properties of alkali metal ester enolates

Alkali metal isobutyrate ester enolates can be prepared in good yield and purity by the metalation of isobutyrate acid esters with substituted alkali metal amides in a hydrocarbon medium at room temperature [63] according to Scheme 5. The enolates are colourless, air-sensitive substances, soluble in THF and, some of them, even in hydrocarbon solvents (e.g. ethyl or isopropyl 2-lithioisobutyrates). In solution, they are aggregated [64] to various degrees [65] (see below). At temperatures near 0°C and under an inert atmosphere, the solid isobutyrate ester lithium enolates are stable for up to several years, whereas the corresponding sodium or potassium derivatives are considerably less stable. To verify whether the ester enolates correspond to the true growth centre of methacrylate polymerization, the product of metalation of di-*tert*-butyl 2,2,4-trimethylglutarate (dimer of *t*-BuMA) and the product of the addition of *t*BIB-Li onto *t*-BuMA were compared (Scheme 6) [63]. Analyses and IR spectra of both the compounds were found to be identical.



Fig. 2. IR spectra of lithiated MMA dimer (M = Li); (1): in benzene; (2): in THF. (Reproduced with the kind permission of Makromol Chem 1982;182:1361.)

Table 1

H - CH ₂	$- \begin{array}{c} CH_{3} \\ l \\ C \\ l \\ COOR \end{array} \right _{n} CH_{n}$	CH3 I2 — C — M COOR		Absorptions (cm ⁻¹)	
N	R	М	In benzene	In benzene with <i>t</i> -BuOM	In THF
0	Me	Li	1692	1683	1676
0	<i>t</i> -Bu	Li	1677	1670	1659
0	Et	Li	1684	_	1679
0	Et	Na	1663	1665	1666
0	Et	Κ	1651	_	1652
1	Me	Li	1645,1711	1660,1713	1640,1714,1731
1	Me	Na	1640,1712	1641,1710	1640,1720,1736
1	Me	K	1630,1714	1628,1714	1626,1717,1736
2	Me	Li	(1717,1733) ^a	(1718,1735) ^a	(1718,1734) ^a
3	Me	Li	~1645 (1718,1736) ^a	~1655, (1716,1735) ^a	_
4	Me	Li	\sim 1645, (1717,1733) ^a	-	-

Characteristic IR absorptions of alkali metal mono- and oligo-ester enolates in the region $1600-1800 \text{ cm}^{-1}$. (Reproduced with the kind permission of Makromol Chem 1982;182:1361)

2.2. Infrared spectra of alkali metal ester enolates

IR spectra of ester enolates sensitively reflect their various interactions, especially in the range of the carbonyl group stretching vibrations [63,66,67]. The IR spectra of isopropyl isobutyrate and its lithio derivative are compared in Fig. 1. The lithio ester enolate is manifested by a single narrow peak in the carbonyl group region with a wavenumber lower by about 50 cm⁻¹ than that of the parent ester and by a new strong absorption below 600 cm^{-1} , where stretching vibrations of C–Li and O–Li bonds are located. Beside these major changes, some other frequency shifts can be observed in the spectrum of the lithio enolate—see Fig. 1.

An IR spectrum of MLTMG, i.e. model of the MMA living dimer, is more complicated than that of the simple enolate [67]. In a benzene solution of a living dimer (Fig. 2, curve 1), two adsorption bands with a shoulder were found in the carbonyl group region, the lower frequency band being assigned to the enolate structure. The absorption of the second carbonyl group, i.e. in γ -position with respect to Li-atom, did not appear in the position expected for the non-metalated ester, its frequency being lower by about 25 cm⁻¹. This shift was explained by coordination of the γ -ester group to the enolate group, as indicated in Fig. 2. The extent of coordination, intra- or inter-molecular type, is high and only a few ester groups are non-coordinated, which is demonstrated by a shoulder at 1753 cm⁻¹ in the spectrum. The band of the γ -ester group coordinated to Li of the enolate group is direct proof of cyclic complex formation between the Li of the enolate and the ante-penultimate ester group of a living PMMA chain as was proposed by Cram [68] many years ago as a necessary condition for isotactic chain growth.

The alkali ester enolates are solvated by strong donor solvents, like THF, which is also reflected in the IR spectrum [67]. The solvation causes absorption band shifts in the region of the carbonyl group vibrations as well as in the region below 600 cm^{-1} . In addition, in the spectrum of the living PMMA

Table 2

IR spectra of dimer and Li-dimer in the absence and presence of *t*-BuOLi in the range $1600-1800 \text{ cm}^{-1}$ (Li-Dimer: Dimethyl-2-lithio-2,2,4-trimethylglutarate; s: strong; w: weak; sh: shoulder). (Reproduced with the kind permission of Lochmann L, Dsc Thesis, Inst Macromol Chem, Prague (1997))

		Benzene			THF		
System		ν , cm ⁻¹	E_{1710}/E_{1730}		ν , cm ⁻¹	E_{1710}/E_{1730}	
Dimer		1734(s)	_		1733(s)	_	
Dimer		1733(s)	_		1733(s)	_	
+t-BuOLi			_			_	
Li-Dimer	1640(s)	1730(w,sh)	1.4	1641(s)	$1733(s)^{a}$	0.8	
	1708(s)			1713(w)			
Li-Dimer +	1656(s)	1730(w,sh)	2.8	1640(s)	$1732(s)^{a}$	1.6	
t-BuOLi	1710(s)			1713(s)			
Li-Dimer	1658(s)	1730(w,sh)	2.8	1640(s)	$1730(s)^{a}$	1.9	
+3t-BuOLi	1711(s)			1711(s)			

^a Measured 20 min after metallation.

dimer (Fig. 2, curve 2) a decrease in the intensity of the band of the γ -ester group coordinated to Li and an increase in the intesity of the non-coordinated γ -ester group were both observed. A possible explanation is that THF competes with the γ -ester group in coordination to the enolate Li atom, suppressing in this way the latter. This effect leads to a lower formation of a cyclic complex, which is in accordance with the well-known fact that PMMA prepared by Li initiators in the presence of THF or other polar solvents exhibits a lower content of isotactic triads [69,70].

Characteristic adsorption bands of some ester enolates are summarized in Table 1. Their frequencies are influenced by the effects of both the metal and solvent type decreasing in the order Li > Na > K and, being generally lower in THF than in benzene solutions. The lithiated higher MMA oligomers, like trimer, tetramer and pentamer, are unstable at room temperature even in benzene solutions. Their spectra recorded 30 min after the preparation exhibited only two bands around 1700 cm⁻¹ corresponding to the products of ester enolate condensation, cyclic ketoesters.

2.3. Interactions of alkali metal ester enolates with alkali metal tert-alkoxides

These interactions can be of two types:

(A) If both the ester enolate and alkoxide contain the same alkali metal, the interaction results in complex (cross-aggregate) formation [63,71]. The adducts can be best studied using Li compounds; they are manifested in IR spectra by a shift of an ester enolate group absorption (see Table 1) and by a shift of an alkoxide band around 950 cm⁻¹. Some of the Li enolate–*tert*-alkoxide complexes can be isolated. A more detailed information on these interactions was obtained by NMR analysis (cf. Section 2.4). The complexes are formed from monoester enolates as well as from oligoester enolates, e.g. MLTMG (living MMA dimer)—see Table 2. In the IR spectra of the latter cross-aggregate, another interesting feature was observed. In the both benzene and THF [67] solutions, the intensity ratio of the band of the coordinated (1710 cm⁻¹) and non-coordinated (1730 cm⁻¹) γ -ester group increases in the presence of *t*-BuOLi. This means that the coordination, i.e. formation of the cyclic complex according to Cram [68]



Scheme 7.

is enhanced by the alkoxide addition. This corresponds well with a slightly higher content of isotactic triads of PMMAs prepared by some of Li initiators in the presence of Li *tert*-alkoxide [72,73] (cf. Section 3.3). The supermolecular structure of the ester enolate–*tert*-alkoxide cross-aggregates was confirmed by molecular mass measurements, by the VPO method [64] and by NMR spectral analysis (see Section 2.4). They probably contain the mixed structural units shown in Scheme 7.

(B) If a Li ester enolate is mixed with a heavier alkali metal alkoxide, lithium—heavier metal interchange takes place according to Scheme 8. This reaction gives rise to an ester enolate of the heavier alkali metal and to a Li alkoxide and is complete within a few minutes at room temperature [66,74,75]. Similarly to the Li compounds, a mixed cross-aggregate of both the starting components is obviously formed in the first step of this interchange. The mentioned interchange of alkali metal and organolithium compound containing, besides Li enolate group, also the C–Li bond (BuLi) or N–Li bond (lithium diisopropylamide). Again, organic compounds of a heavier alkali metal and lithium alkoxides are formed in these systems. The effect of alkali metal *tert*-alkoxides on the reactions of ester enolates and on (meth)acrylate polymerization will be discussed below.

2.4. NMR and quantum chemistry studies of lithium ester enolates and their complexes

The lack of information on the real structures of the active species in anionic polymerization of polar vinyl monomers—except for Seebach's and Bywater's works [76–78]—led to the study of model lithium ester enolate compounds.

2.4.1. Self-aggregation of ester enolates

Lithium ester enolates form self-aggregates in solutions similar to other organolithium compounds. It was determined by VPO that isobutyrate lithium ester enolates are self-aggregated in THF and benzene to a degree of 2-7 [64,65].

In the first study of the MIB-Li in THF [79] based mainly on the ⁷Li NMR spectroscopy, it was found, that this compound exists as tetrameric or dimeric self-aggregates with a relatively slow rate of

 $(CH_3)_2CLi\ COOC_2H_5\ +\ RO\ M \ \rightarrow \ (CH_3)_2CM\ COOC_2H_5\ +\ RO\ Li$

(M = Na, K, Rb, Cs)

Scheme 8.

803

P. Vlček, L. Lochmann / Prog. Polym. Sci. 24 (1999) 793-873

(MIB-Li)₄ + 2*n*S
$$\xrightarrow{k_1}$$
 2(MIB-Li. S_{*n*})₂
(S = solvent)

re-arrangement assisted by the solvent according to Scheme 9. With an increasing concentration of the solution and increasing temperature (193–233 K) the content of the tetramer increases. Thus, in a 0.2 M solution at temperatures higher than 213 K as well as in 2.0 M solution at 197 K, MIB-Li forms exclusively tetramer. The same problem was studied in more detail using ¹³C, ¹H, ⁶Li and ⁷Li NMR and Raman spectroscopy [80]. Here, the number of signals in the Li spectrum is higher than in the former study and the same fact can be observed in the ¹³C NMR spectrum. As these differences can hardly be attributed to the chemical inhomogeneity of samples (i.e. products of MIB-Li self-condensation), it is clear that the ester enolate forms in THF solutions more than two self-aggregates. A variety of signals in all NMR spectra as well as in Raman spectra of MIB-Li in THF indicate the existence of two isomeric trimers at low temperatures, in addition to the dimer and tetramer. All these self-aggregates are in dynamic equilibria according to the equations in Scheme 10 in which D denotes dimer, Te tetramer, Tr1 and Tr2 trimers and S is THF. Thermodynamic data for the individual equilibria are given in Table 3. The values for the D–Te equilibrium are in a very good agreement with those published elsewhere [79]. Concerning the rates of the equilibria, the highest rate is exhibited by the D-Te exchange and the exchange rate decreases in the order D-Tr > Te-Tr > Tr1-Tr2. The rates of interconversion, however, seem to be slow enough to interfere in the initiation step of the polymerization process. The temperature dependences of the equilibria are expressed by van't Hoff plots in Fig. 3, which were made from both signals of carbonyl and α -C atom in ¹³C NMR spectra in the temperature interval 197–223 K. Using MNDO and ab initio calculations, an optimized geometry of the aggregates of MIB-Li was modeled [81], as is shown in Fig. 4. MNDO molecular parameters of the most stable forms of the MIB-Li aggregates (see Table 4) indicate that non-solvated dimer is most stable near the keto form whereas the higher self-aggregates (trimer and tetramer) shift the keto-enol equilibrium toward the enolate. When solvated with two molecules of dimethyl ether (DME), however, the dimer has also predominantly enolate character.

Consequently, it follows from spectral studies as well as from theoretical calculations that MIB-Li exists as three energetically similar self-aggregates even in solvating media and, in addition, the Li atom coordinates with both C and O anions; the enol form of the ester enolate seems to be more stable.

(1)
$$2 [D.nS] \xrightarrow{K_{24}} Te + 2nS$$

(2) $3 [D.nS] \xrightarrow{K_{23}} 2 [Tr.mS] + (3n - 2m)S$
(3) $4 [Tr.mS] \xrightarrow{K_{34}} 3 Te + 4mS$
(4) $[Tr2.m_1S] \xrightarrow{K_{33}} [Tr1.m_2S] + (m_2 - m_1)S$

Scheme 10.

804

Table 3

י ויוי ת		$A T (1 + 1 + 1^{-1})$	$A = (1 + 1^{-1} + 1^{-1})$
Equilibrium no	Equilibrium constant	ΔH_{ij} (kcal mol)	ΔS_{ij} (cal mol K)
(1)	K_{24}	2.2	12.3
(2)	K_{23}	3.9	17.3
(3)	K_{34}	-1.5	1.1
(4)	K_{33}	0.2	1.4

Enthalpies ΔH_{ij} and entropies ΔS_{ij} calculated for equilibria (1)–(4) in Scheme 10. (Reproduced with the kind permission of Makromol Chem Phys 1994;195:3039)

2.4.2. Complexes of ester enolates with LiCl or lithium 2-(2-methoxyethoxy)ethoxide

In the anionic polymerization of MMA in THF with an alkali metal counterion [82–84], the reaction rate decreases with an increasing concentration of active species as a consequence of association phenomena of the living chains according to Scheme 11. The existence of associated living chains was confirmed by viscosity measurements [85] documenting an increase in the fraction of aggregates with increasing concentration of the living chain ends. Different reactivities of aggregated and non-aggregated chains lead to a multiplicity of active species and, consequently, to the bimodal MWD of the polymer, assuming a sufficiently low rate of interconversion of chains compared with a rate of polymerization [83]. This is the case of *t*-BuA having a very high rate of propagation. If LiCl is added to the system, (see Section 5.1), it forms mixed cross-aggregates of the salt with the living chain ends, which competes with self-aggregation of the growing polymer. In this way, the cross-aggregates (P*LiCl) with a molar ratio 1:1 or 1:2 are "non-associated" polymer chains with high reactivity. As an addition of an equimolar amount of LiCl causes a slight increase in an overall polymerization rate and a further addition of the salt depresses the reaction rate, it can be assumed that the reactivities of the individual mixed cross-aggregates are different. It was concluded, mostly on the basis of Li-NMR spectra, that the



Fig. 3. van't Hoff plots for individual self-aggregation equilibria of MIB-Li in THF (see Scheme 10) based on ¹³C NMR spectra. (Reproduced with the kind permission of Makromol Chem Phys 1994;195:3039.)



Fig. 4. MNDO optimized geometries of MIB-Li self-aggregates in THF: (a) dimer (a) and its solvate with two molecules of dimethyl ether (b); (b) trimer 1 (a), trimer 2 (b); (c) tetramer (two projections). (Reproduced with the kind permission of Collect Czech Chem Commun 1994;59:1699.)

Table 4

MNDO molecular parameters of most stable forms of MIB-Li aggregates (dimer to tetramer) and the solvate [D 2DME]. (Reproduced with the kind permission of Collect Czech Chem Commun 1994;59:1699)

Parameter	D	[D 2DME]	Tr1	Tr2	Te
Heat of formation $(kJ mol^{-1})$	-1137.1	-1607.9	-1697.1	-1730.4	-2171.6
Stabilization energy $(kJ mol^{-1})$	-95.8	-116.9	-92.9	-104.0	-70.1
Bond length (ppm)					
C1–C2	154	145	140	145	139
C1–O	125	127	131	127	132
C2–Li	215	210	301	206	312
0-Li	316	203	208	206	220
Bond angle					
C1–O–Li (°)	82.9	143.0	109.4	102.5	113
Torsion angle (°0)					
C2-C1-O-Li	0.0	51.5	23.9	6.3	0.0
O-C1-C2-Me ¹	114.7	176.0	179.9	172.8	179.8
O-C1-C2-Me ²	-114.7	27.9	0.5	21.9	0.6
Net atomic charge					
0	-0.39	-0.48	-0.47	-0.49	-0.46
C1	0.47	0.51	0.38	0.53	0.37
C2	-0.49	-0.51	-0.40	-0.52	-0.37
Li	0.33	0.30	0.37	0.40	0.38

equilibrium between non-aggregated (free) ion pairs and those complexed with various numbers of LiCl units is faster than the equilibrium between non-aggregated and self-aggregated ion pairs without LiCl. This seems to be corroborated by the results of NMR study of aggregation of MIB-Li with LiCl [86] as well as with other types of complexing ligands [87]. However, the results of the following studies [88,89] of complexes of *t*BLTMG with LiCl or MEEOLi by ¹H, ⁷Li and ¹³C NMR spectroscopy as well as MNDO theoretical calculations have not verified the idea of a fast equilibrium between free, non-aggregated centres and those complexed with added ligand. An addition of one equivalent of LiCl to MIB-Li solutions leads to the formation of a highly stable equimolar complex, the additional salt forms mixed cross-aggregates with a higher content of LiCl. The assumed processes can be expressed by Scheme 12 [86]. If an excess of LiCl over MIB-Li is 3 or higher, uncomplexed LiCl was found in the reaction mixture, the concentration of which depends on both the mole ratio LiCl/MIB-Li and the



Scheme 11.



Scheme 12.

temperature. In this way, LiCl supports the formation of only one type of active species, which has a very favourable effect on the MWD of the prepared polymer.

Similarly, MIB-Li forms a unique complex with bidentate ligand [90] MEEOLi (cf. Section 5.2), which stabilizes efficiently active centres in the low-temperature polymerizations of (meth)acrylates. ⁷Li and ¹³C NMR spectra showed fast complexation of MIB-Li even with a small addition of MEEOLi, documented by the immediate disappearance of the signal of the MIB-Li dimer. An equimolar mixture of the both components exhibits in a ⁷Li spectrum a residual signal of a MIB-Li tetramer and a new, slightly broadened signal of the complex, which is only the signal of the mixture MIB-Li:MEEOLi 1:2. Thus, the formation of the cross-aggregate (MIB)₁Li₃(MEEO)₂ can be reasonably assumed, which is corroborated by ¹³C NMR spectra. As has been found, this complex is very stable in the temperature range from -60 to 0°C moreover, emerges in polar THF as well as in non-polar toluene. With the molar ratio MEEOLi:MIB-Li increasing above 2, signals of "free", i.e. non-complexed alkoxide can be clearly seen in the ¹³C NMR spectra, so that no "higher" cross-aggregates of MIB-Li and MEEOLi are formed even at 0°C. Comparing the results of this study and that of the complex of MIB-Li with other types of Li-binding ligands (e.g. crown ethers and cryptands) [87], the authors assume that the Li^+ cation is strongly coordinated by the chelating MEEOLi ligand. This weakens the interaction between the bulky "gegenion" and the MIB anion and also influences its negative charge delocalization. Thus, the cross-aggregate MIB-Li/MEEOLi 1:2 was described as a "ligand-promoted-loose mixed complex" $MIB^{-}[Li_3(MEEO)_2]^+$.

2.4.3. Complexes with alkali metal tert-alkoxides

As follows from foregoing studies by other methods [63,66,67], alkali metal ester enolates form crossaggregates with alkali metal *tert*-alkoxides, which are considered to be responsible for the enhanced stability of the polymerization centres (see Sections 2.5, 3 and 4). In contrast to LiCl, *t*-BuOLi replaces gradually molecules of MIB-Li in its tetramer forming complexes with molar ratios MIB-Li:*t*-BuOLi 3:1, 2:2 and 1:3 [91]. The rate of formation as well as the stability of the individual complexes are

 $(MIB)_{3}Li_{4}(t-BuO)_{1} < (MIB)_{2}Li_{4}(t-BuO)_{2} < (MIB)_{1}Li_{4}(t-BuO)_{3}$

Scheme 13.

 $2[(MIB-Li)_{3} (t-BuOLi)_{1}] + (t-BuOLi)_{4} \xrightarrow{\Delta H_{1}} 3[(MIB-Li)_{2} (t-BuOLi)_{2}]$ $[(MIB-Li)_{2} (t-BuOLi)_{2}] + (t-BuOLi)_{4} \xrightarrow{\Delta H_{2}} 2[(MIB-Li)_{1} (t-BuOLi)_{3}]$

Scheme 14.

dependent on the molar ratio of MIB-Li:*t*-BuOLi and on time. The first replacement of MIB-Li in its tetramer by *t*-BuOLi proceeds in fact immediately, the complex 3:1, however, is not stable and is rapidly re-arranged into complexes with higher *t*-BuOLi contents. The equilibrium concentration of the 1:3 complex (MIB-Li:*t*-BuOLi) is reached after relatively long storage times at -15° C, it is, however, stable for hours even at room temperature. Thus, the stability of the cross-aggregates increases according to the Scheme 13, whereas the rate of their formation decreases in the same order.

The re-arrangement of the complexes is assumed to proceed in the sense of the following equilibria (Scheme 14), with different enthalpies ($\Delta H_1 = -1.51$, $\Delta H_2 = -1.02$ kcal mol⁻¹). These values were calculated from equilibrium contents of individual cross-aggregates in the mixtures with varying molar ratios of MIB-Li:*t*-BuOLi. The order of stability of individual aggregates is corroborated by the results of theoretical MNDO calculations [91] of their heats of formation (ΔH) and their stabilization energies (ΔH_s) as indicated in Table 5. Concerning the geometry of individual complexes, the core of each cross-aggregate is formed by the cubic structure in which Li and O atoms alternate. The Li–O distance slightly varies, the complexes with lower *t*-BuOLi contents are less tightened. This conclusion corresponds to the energy minima obtained from MNDO calculations, from which also the optimum geometries of the complexes were predicted (see Fig. 5). From both ¹H and ¹³C NMR spectra, a slight non-equivalence of two *tert*-butyl groups in the complex (MIB-Li)₂/(*t*-BuOLi)₂ can be seen, so that this cross-aggregate is assumed to exist in two different forms. In Fig. 5 and Table 5, they are depicted as (2:2) and (2:2)a, respectively.

In another paper by Wang et al. [92], the same problem was studied, the results being, however,

Mole ratio [MIB-Li]:[t-BuOLi]	ΔH (kcal mol ⁻¹)	$\Delta H_s \ (\mathrm{kcal}^{-1})^{\mathrm{a}}$
(4:0) ^b	-518.02	16.52
(3:1)	-481.96	19.99
(2:2)	-445.12	23.27
(2:2) ^b	-441.63	22.40
(1:3)	-407.05	26.24
(0:4) ^c	-366.96	28.70

Heats of formation ΔH and stabilization energies ΔH_s for aggregates of MIB-Li and *t*-BuOLi predicted by MNDO. (Reproduced with the kind permission of Magn Res Chem 1994;32:S8)

^a Per molecule in the aggregate.

^b Tetramer of MIB-Li.

Table 5

^c Tetramer of *t*-BuOLi.



Fig. 5. Optimized geometries of the MIB-Li/t-BuOLi complexes predicted by MNDO quantum calculations. (Reproduced with the kind permission of Magn Res Chem 1994;32:S8.)

different to some extent. Probably because of a shorter storage time of the measured mixtures, the complex formation was found to be favourable in the order $(MIB)_2Li_4(t-BuO)_2 > (MIB)_3Li_4(t-BuO)_1 > (MIB)_1Li_4(t-BuO)_3$.

*t*BIB-Li is supposed to be in THF solution in a tetrameric form irrespective of concentration $(0.1-0.8 \text{ mol } 1^{-1})$ and temperature (203-273 K) [93]. From colligative measurements [64], an average self-aggregation degree of about 2.3 was estimated. In the presence of TMEDA, however, *t*BIB-Li forms dimeric self-aggregates as follows from X-ray scattering studies [94]. One has to consider that a highly coordinating agent such as TMEDA partly saturates the coordination ability of the enolate so that

$$(tBIB-Li)_{4} + 3 (t-BuOLi)_{4} \xrightarrow{\Delta H_{13}} {}_{4} [Li_{4} (tBIB) (t-BuO)_{3}]$$

$$(tBIB-Li)_{4} + (t-BuOLi)_{4} \xrightarrow{\Delta H_{22}} {}_{2} [Li_{4} (tBIB)_{2} (t-BuO)_{2}]$$

$$3 (tBIB-Li)_{4} + (t-BuOLi)_{4} \xrightarrow{\Delta H_{31}} {}_{4} [Li_{4} (tBIB)_{3} (t-BuO)]$$

Scheme 15.



Scheme 16.

formation of larger self-aggregates is virtually impossible. In THF, the enolate tetramer coordinates with tetrameric *t*-BuOLi according to Scheme 15 in which the respective enthalpy values ΔH_{13} , ΔH_{22} and ΔH_{31} are -59.47, -3.76 and +37.89 kJ mol⁻¹, respectively. Thus, formation of the [Li₄ (*t*BIB)₃ (*t*-BuO)] cross-aggregate seems to be unlike, which is in agreement with the results of NMR relaxation measurements. Similar results were obtained in a study of the cross-aggregation of *t*BIB-Li with 3-MPeOLi; again, no complex [Li₄ (*t*BIB)₃ (3-MPeO)] was observed in NMR spectra and, moreover, the rate of complex formation was lower in this case than that in the former one. The



Fig. 6. Optimized structures of the MLTMG/MMA transition complexes TMMALi^{*}, TMMALi⁺ and the resulting living trimer TMMALi predicted by MNDO for the isotactic bonding of MMA to "closed" form of MLTMG. (Reproduced with the kind permission of Macromol Theory Simul 1997;6:437.)



Scheme 17.

stabilities of the complexes are relatively high even at room temperature and seem to be almost equal irrespective of the type of alkoxide. This could lead to a conclusion that the chemical structure of the alkoxide should have no effect on its stabilization efficiency in a polymerization system. However, polymerization studies gave opposite results, see Section 4.4.

The following NMR and theoretical study of the model of living dimer of *t*-BuMA, i.e. *t*BLTMG, (see Scheme 16) offered similar, but extended results [95]. It has been found, in agreement with previous infrared studies [66,67], that this model compound exhibit a strong tendency for the Li atom to be coordinated with the C5 carbonyl on a C5 atom forming in this way a closed intramolecularly complexed form. The linear, non-coordinated form of *t*BLTMG exists simultaneously with the closed (coordinated) one, the former is, however, stabilized by a formation of a dimeric aggregate similarly as the simple 2-lithioisobutyrates discussed above. From the ¹H, ⁷Li, and ¹³C NMR spectra, it can be concluded that



Fig. 7. ¹H NMR spectra of *t*BLTMG (i) and its mixtures with *t*-BuOLi at -20° C in THF-*d*₈. *t*BLTMG: *t*-BuOLi ratio (m/m): 1:1 (ii); 1:2 (iii); 1:3 (iv). (Reproduced with the kind permission of Makromol Chem 1983;184:2021.)





the relative populations of the "open" (linear) and "closed" (cyclic) forms, i.e. non-coordinated and coordinated γ -ester groups, depend on the concentrations of solution as well as on temperature. As the content of the "open" form increases with increasing temperature, it can be reasonably assumed that the intramolecular coordination, i.e. "closed" form is restricted to higher temperatures, while the formation of higher self-aggregates, formed from two "open" molecules is preferred. It follows from the measurements of relaxation times using ⁷Li NMR spectra that the interchange reaction between "open" and "closed" forms must be very slow, in particular, in comparison with a rate of polymerization process. This can be expected owing to a number of desolvation and dissociation steps in the interchange of both these forms. The results of the spectral study are in agreement with theoretical MNDO and ab initio calculations for both the model dimers, i.e. *t*BLTMG and MLTMG [96]. The most stable form of *t*BLTMG, in particular under conditions of real polymerization, corresponds to the closed (or coordinated form) which is given in Fig. 6. The γ -coordinated form of MLTMG was found to bind up two units of a polar solvent (dimethyl ether or THF); however, such solvation does not interfere with the intramolecular coordination of the Li counterion with the carbonyl on a C5 atom (see Scheme 17) and, in addition, the tendency to coordination does not depend on the structure of ester alkoxy group.

*t*BLTMG cross-aggregates with *t*-BuOLi in a similar way as its simple enolate analogue *t*BIB-Li. The process was studied by NMR spectroscopy and by theoretical methods [97]; the ¹H NMR spectra of *t*BLTMG alone and its mixtures with the *t*-BuOLi in various molar ratios are shown in Fig. 7. The assignment of the signals correspond to the superscripts in Scheme 16, signals 14 belonging to protons of *t*-BuOLi.

According to differences in NMR spectra, cross-aggregates are formed having *t*BLTMG: *t*-BuOLi molar ratios either 2:2 or 1:3 and, similarly to the system *t*BIB-Li/*t*-BuOLi, no complex with a ratio of 3:1 was observed even in mixtures with low contents of *t*-BuOLi. Most probably, this is due to the steric requirements of the bulky *t*-Bu ester group.

As the model compounds do not fully correspond to the real polymerization system, an NMR study of a MMA oligomerization mixture was performed [91]. The mole ratio of MMA:MIB-Li:*t*-BuOLi was 2:1:3 and the initiation complex ester enolate–alkoxide was used either fresh or after ageing at -70° C. The structure of both the living oligomers prepared with fresh or equilibrium initiators was found to be independent of ageing, which was corroborated by polymerization experiments. Again, the end-group of the living oligomer was found to be coordinated with the penultimate carbonyl, in this case, however,

P. Vlček, L. Lochmann / Prog. Polym. Sci. 24 (1999) 793-873

2(CH₃)₂CM COOR (CH₃)₂COOR + ROM

Scheme 19.

interaggregated with one molecule of the *t*-BuOLi. The structure of this complex is proposed in Scheme 18. From the ¹H NMR spectrum, the mole ratio of the growing centre: *t*-BuOLi is 1:2.1 which indicates that approximately half of the alkoxide forms a 1:3 complex and half a 2:2 comlpex. The residual *t*-BuOLi is probably bound up in its self-aggregates or coordinated with the products of the self-termination reaction. An oxo ester structure of the self-termination product was found in the NMR spectra of a reaction mixture after 4 h of ageing at -20° C.

The investigation of the character of the growing species in anionic MMA polymerization was extended to ab initio SCF, MNDO and AM1 calculations for an early step of the process with the aim to obtain more insight into the stereoregularity of a monomer addition [98]. Again, MLTMG was taken as a model of the active centre being either in an "open" non-coordinated form or an intramole-cularly coordinated "closed" form [95,96]. The possibilities for approach and addition of another MMA unit were calculated. It was found that on the non-coordinated active centre ("open" form) both the arrangements, i.e. iso- and syndio- are possible. However, syndiotactic addition is energetically preferred whereas isotactic growth can proceed exclusively on the coordinated ("closed") form of the active centre. Both of these forms of growing centres are present in nonpolar as well as in polar solvents and the relative population of them depends on reaction conditions and on the polarity of the solvent. Therefore, the resulting microstructure of product is probably a consequence of a dynamic equilibrium between "open" and "closed" forms of active centres. In the isotactic arrangements, a monomer unit joins the growing chain-end, i.e. coordinated form of MLTMG, via a stabilized "pre-addition complex" (TMMALi^{*}) followed by "addition complex" (TMMALi⁺) and, finally, the extension of the corresponding chain (coordinated form of the living trimer—TMMALi) as shown in Fig. 6.

It can be concluded from the results discussed in this section that the model growing centre of (meth)acrylate polymerization has the following features [97]:

- 1. Cubic structure is the probable form of the complex composed of four Li and four O atoms held together by a system of polycentric electron deficient bonds of low covalency.
- 2. The system is relatively stable, its mutual exchanges are, in comparison with the rate of real polymerization, slow and its stability is enhanced by the presence of Li *tert*-alkoxide.
- 3. Owing to the weak covalency of the polycentric bonds, an additional bonding of the monomer or γ -ester group is possible.



Scheme 20.

```
(CH<sub>3</sub>)<sub>2</sub>CM COOR + (CH<sub>3</sub>)<sub>2</sub>CHCOOR (CH<sub>3</sub>)<sub>2</sub>CH COC(CH<sub>3</sub>)<sub>2</sub>COOR + ROM
```

Scheme 21.

4. Coordination of the lithium ester enolate group with the γ -ester group is promoted in the presence of lithium containing ligands (*tert*-alkoxide).

Consequently, various types of growing centres probably exist simultaneously in the anionic polymerization of (meth)acrylates, even in solvating media.

2.5. Condensation and transmetallation reactions of alkali ester enolates

2.5.1. Condensations and their significance in (meth)acrylate anionic polymerization

Two types of ester enolate condensation reactions are of importance in the sense of this review: Autocondensations of ester enolates, (A), see Schemes 19 and 20, and the condensation of ester enolates with non-metalated carbonyl compounds (B), see Scheme 21.

(A) Autocondensations can be either a bimolecular reaction (Scheme 19) leading to linear ketoester or a unimolecular reaction (Scheme 20) giving rise to cyclic ketoesters. The first type of autocondensation occurs prevailingly with mono- or di-ester enolates [67,99] and determines the stability of enolate solutions, whereas the latter type predominates with longer oligo- and poly(ester enolates) restricting the life-time of growing chain-ends, cf. Section 1.1. The rates of autocondensations of some ester enolates, expressed by reaction half-times, are listed in Table 6. The effect of the solvent type is clearly seen because the autocondensation in THF is much faster than in hydrocarbon solvents. This fact makes possible an easy isolation of pure alkali metal ester enolates in hydrocarbon media (cf. Section 2.1).

Table 6

Autocondensation rates of alkali metal mono- and oligo-ester enolates (at 25° C, 0.15 mol l^{-1} ; molar ratio [enolate] : [*t*-BuOM] = 1:1). (Reproduced with the kind permission of Makromol Chem 1982;182:1361)

н – Сн ₂ –	$\begin{array}{c} \begin{array}{c} CH_3 \\ I \\ C \\ I \\ COOR \end{array} \end{array} \begin{array}{c} CH_2 \\ R \end{array} - \begin{array}{c} CH_2 \\ CH_2 \end{array} - \begin{array}{c} CH_2 \\ R \end{array} $	$ \begin{array}{c} CH_3 \\ -C - M \\ -C OOR \end{array} $	Autocondensa	tion half-times (min)	
n	R	М	In benzene	In benzene, with <i>t</i> -BuOM	In THF
0	Me	Li	≫10	-	1380 ^a
0	Et	Li	≫10	_	4200,1440 ^a
0	Et	Na	>10	_	220
0	Et	Κ	>10	_	40
1	Me	Li	1400	4000	140
1	Me	Na	420	3000	28
1	Me	Κ	380	1500	10
2	Me	Li	≪1	≪1	≪1
3	Me	Li	≪1	<2	_
4	Me	Li	<1	-	_

$(CH_3)_2CHCOC(CH_3)_2COOEt + t-BuONa$ (CH₃)₂CNa

(CH₃)₂CNaCOOEt + (CH₃)₂CHCOOt-Bu

Scheme 22.

Also, the effect of a counterion is evident; lithium ester enolates are considerably more stable than the potassium derivatives.

A dramatic increase in the autocondensation rate (over five orders of magnitude) appeared in the order mono-, di-, tri- and tetra(ester enolates). Obviously, this change in the rate is associated with the change of reaction mechanism and a very fast intramolecular formation of six-membered cyclic trimer by the autocondensation of poly(ester enolate)s with a number of units three or more (see back-biting reaction).

(B) In the condensations of isobutyrate alkali metal ester enolates with non-metalated isobutyrates, the same solvent- and counterion effects apply as in the respective autocondensations; however, the reaction rates are considerably higher [99]. This reaction may cause a termination of propagation by monomer, cf. Section 1.1. The effect of *tert*-alkoxides on enolate condensations was also investigated [67,99] and it was found, that the alkoxide generally lowers the rates of condensations by a factor from 3 to 8 for metallated MMA dimers (Table 6). The retardation effect of alkoxides depends on their structures, counterions and concentrations, so that, e.g. potassium *tert*-butoxide was found to slow down the enolate autocondensation more intesively than its lithium analogue. This effect of the alkoxides may be a consequence of their cross-aggregation with enolates, the product of which is less reactive in the condensations (see Section 2.2). Moreover, it cannot be excluded that the alkoxide also acts by its mere presence because it is one of the condensation products.

It is well known that the ester enolate condensations are equilibrium reactions and, therefore, reactions according to Schemes 22 and 23 can be expected to occur. Actually, in the reaction of linear or cyclic ketoesters and sodium *tert*-butoxide, a cleavage of the ketoester into the compounds on the right-hand side of Schemes 22 and 23 could be proved [100]. The products of the cleavage were estimated by IR spectroscopy and determined by GLC after hydrolysis. The cleavage was also confirmed by the fact that the reaction mixture of ketoester and *t*-BuONa immediately initiates MMA polymerization, in contrast to the alkoxide alone (see Sections 3 and 4.2). The number of polymer chains produced in this process approximately corresponds to the extent of the cleavage. The cleavage is considerably slower than MMA propagation and, therefore, it is not significant in the propagation of polymer. However, it could play some role in the so called "reviving" of dormant active centres (see above).

- 2.5.2. Transmetallation between lithium ester enolates and carboxylic acid esters
 - In contrast to methacrylates, the acrylate esters contain an acid hydrogen in an α -position and,



816



```
(CH<sub>3</sub>)<sub>2</sub>CLiCOOt-Bu + CH<sub>3</sub>CH<sub>2</sub>COOt-Bu
```

(CH₃)₂CHCOOt-Bu + CH₃CHLiCOOt-Bu

Scheme 24.

consequently, metal transfer from the enolate group onto another molecule of non-metalated ester is possible. As this reaction corresponds to chain transfer in acrylate anionic polymerization, the metal transfer was studied using model compounds [101] according to Scheme 24. Mixtures of either *t*BIB-Li with *tert*-butyl propionate or *t*BPr-Li with *tert*-butyl isobutyrate were deuterolyzed with (CH₃)₃ COD under various conditions and after different time intervals. In the forward reaction in Scheme 24, the metal transfer of only 1% was found and, moreover, when lithiated propionate reacted with the non-metalated isobutyrate, no metal transfer was observed (Table 7). These findings do not support the idea of an easy chain transfer in the anionic polymerization of acrylates. It should be noted here that the extent of side reactions in the anionic polymerization of *tert*-butyl (meth)acrylate is generally low [102–104]; nevertheless, in studies of real acrylate polymerization systems (cf. Section 4), the same conclusions were made.

2.6. Addition of ester enolates onto methacrylate monomers, oligomerization studies

2.6.1. Products of MMA oligomerization

The addition of alkali metal ester enolates on an activated C=C double bond in (meth)acrylate esters is the propagation reaction of the polymer chain. First, the reaction of an isobutyrate ester sodium enolate and the corresponding methacrylate was investigated [99,105,106] at low methacrylate/enolate molar ratios and under conditions shown in Scheme 25. The products of these reactions were, after protolysis, isolated and characterized as different linear methacrylate oligomers and products of ester enolate condensation, i.e. predominantly cyclic ketoesters. As the addition of ester enolates to methacrylates is very fast, a flow tube reactor was used allowing an instantaneous mixing of the components and sampling of the reaction mixture in various time intervals starting up with 20 ms [105]. After protolysis,

Table 7

Temperature (°C)	Time min	Contents	Contents of esters and of their deuterated analogs			
°C		tBPr	t BPr d_1	tBIB	tBIBd ₁	
tert-Butyl2-lithioisob	utyrate + <i>tert</i> -but	ylpropionate				
25	2	86	0.1	75	85	
25	32	60	0	47 ^a	21	
-30	1	100	0.3	88	84	
-30	185	82	0.3	88	84	
-75	63	100	1.0	92	85	
-75	305	100	0.7	91	91	
tert-Butyl2-lithioprop	ionate + <i>tert</i> -buty	lisobutyrate				
-75	10	100	88	100	0.04	
-75	300	87	84	97	0.2	

Contents of starting compounds and of their deuterated analogs after the reaction according to Scheme 24 and deuterolysis. (Reproduced with the kind permission of Polym Prepr (Am Chem Soc, Div Polym Chem) 1988;29(2):29)

^a An appreciable amount of ketoesters was formed through a condensation reaction; they were easily transmetallated.



 $[MIB-Na]_0 = 0.1 \text{ or } 0.3 \text{ mol/l}; x = 1,2 \text{ or } 4; \text{ flow tube reactor, time } 0.02-1.4 \text{ s, temperature: } 20, 8 \text{ or } 0^\circ\text{C}; [t-BuONa]_0/[MIB-Na]_0 = 0 \text{ or } 3$

Scheme 25.

the samples were analyzed by GLC and GPC and, based on these results, conversion-time curves were calculated for individual components of the reaction mixture [105,106]. The curves are shown in Fig. 8 where the solid-line curves correspond to the conversion of MMA. Only traces of methyl isobutyrate could be detected in the mixture even at the shortest time intervals, which indicates a very fast reaction of ester enolate with methacrylate. The composition of the reaction mixture considerably depends on the reaction conditions and the ketoester, i.e. "cyclic trimer", as the result of a self-termination reaction is a prevailing product in many cases. The type of solvent strongly affects the rates of individual reactions to various extents causing pronounced changes in the composition of the reaction mixture. In THF (Fig. 8(a)), the MMA conversion is fast and also the rate of autocondensation of the linear sodium trimer is high giving rise to the cyclic trimer as the most populated product. On the contrary, in a toluene–THF mixture (5:1 v/v; Fig. 8(c)), the cyclization reaction is much slower and the ester enolate persisted for a longer time than in the foregoing case.

The effect of alkali metal *tert*-alkoxides on the reaction of ester enolates can be seen in Fig. 9 where the composition of the oligomerization mixtures obtained in the absence or presence of *t*-BuONa are compared. In the presence of the alkoxide under otherwise identical conditions, oligomerization is generally slower but the concentration of a cyclic trimer is low and sodium linear trimer is the main reaction product (Fig. 9(a)). Without the alkoxide (Fig. 8(a)), the oligomerization produces mainly cyclic trimeric ketoester at the same reaction time.

From the total amount of all oligomers formed in the reaction, the initiating efficiency F of alkali metal ester enolate was calculated [106]. It depends on the reaction medium decreasing in the order THF > toluene/THFmixtures > toluene, see Table 8. *t*-BuONa increases the enolate efficiency, as follows from a comparison of F values obtained from the oligomerizations in toluene/THF mixture in the presence or absence of the alkoxide. Data in Table 8 document a good agreement between calculated and experimentally found average molecular weights of the reaction products in oligomerization with a high enolate efficiency; in reactions with a lower enolate efficiency, the real average molecular weight of the products is commensurately higher.



Fig. 8. Composition of oligomerization mixture MMA/MIB-Na vs. reaction time according to Scheme 25. Conditions: $[MMA]_0 = 0.20 \text{ mol } 1^{-1}$; $[MIB-Na]_0 = 0.10 \text{ mol } 1^{-1}$: (a) in THF at 23°C; (b) in THF at 3°C; (c): in toluene-THF mixture 5:1 (v/v) at 23°C. (—): MMA; (---): dimer (3a); (---): linear trimer (3b); (---): tetramers (3c); (----): tetramers (3d); (---): cyclic trimer (5); (-----): mixture of higher oligomers (3e). (Reproduced with the kind permission of Makromol Chem 1983;184:2021.)

Beside autocondensation, also depolymerization of alkali metal oligoester enolates proceeds in their THF solutions, leading to a lower oligomer and methacrylate monomer. This monomer molecule can then react with another ester enolate forming a higher oligomer again; the process can be characterized as "disproportionation" [107]. According to Scheme 26, the decomposition of MLTMG (lithio-MMA dimer) proceeds via depolymerization giving MIB-Li and MMA (reaction 1). Then, MMA reacts with the so far unreacted MLTMG yielding lithio-MMA trimer (reaction 2). At the same time, all present lithioester enolates undergo autocondensations to linear or cyclic ketoesters. Consequently, the final reaction mixture contains after hydrolysis a small amount of methyl 2,2,4-trimethyl-3-oxopentanoate (through reaction 4) and methyl isobutyrate in addition to the main product, dimethyl 2,4,6,6-tetra-methylcyclohexanone-2,4-dicarboxylate (cyclic MMA trimer) formed by reaction 3. Formation of the cyclic MMA trimer (self-termination reaction) is the fastest reaction in this system and this is obviously the reason for the product distribution found in this case.

Similarly, trimethyl 2-lithio-4,6-dimethylheptane-2,4,6-tricarboxylate (linear lithio MMA trimer) is transformed almost exclusively into cyclic trimer (reaction 3), most probably because of optimum steric



Fig. 9. Composition of oligomerization mixture MMA/MIB-Na vs. reaction time in the presence of *t*-BuONa. Conditions: $[MMA]_0 = 0.20 \text{ mol } 1^{-1}$; $[MIB-Na]_0 = 0.10 \text{ mol } 1^{-1}$; $[t-BuONa]_0 = 0.30 \text{ mol } 1^{-1}$; 23° C; (a) in THF; (b) in toluene-THF mixture 5:1 (v/v); (c) in toluene. For meaning of other symbols, see Fig. 8. (Reproduced with the kind permission of Makromol Chem 1986;187:1473.)

$[\mathbf{MMA}]_0 \ (\mathbf{mol} \ \mathbf{l}^{-1})$	$[t-BuONa]_0 \pmod{l^{-1}}$	Solvent	F (%)	Total M_n of product	
				Calc	Found
0.2	0	THF	100	355	319
0.2	0	tol/THF ^a	49	322	433
0.2	0.3	THF	100	346	306
0.2	0.3	tol/THF	87	425	417
0.2	0.3	Tol	24	361	918
0.4	0	tol/THF	61-93	572	578
0.4	0.3	tol/THF	53-96	524	522
0.1	0	tol/THF	47	212	239
0.1	0.3	tol/THF	52	213	253

Efficiency of MIB-Na, F, in the reaction with MMA at 23°C. (Reproduced with the kind permission of Makromol Chem 1983;184:2021)

^a tol/THF = toluene/THFmixture 5:1 (v/v).

Table 8



conditions. The disproportionation of the lithio MMA tetramer in THF leads to both the MMA cyclic trimer and tetramer, besides a mixture of higher MMA oligomers, probably cyclic and linear. The results confirm the fact that the reaction of MMA with ester enolates is a reversible process.

2.6.2. Kinetics of MMA oligomerization

To describe the initial phase of methyl methacrylate anionic polymerization, Scheme 27 can be designed, where M denotes the monomer, k are the respective propagation or depolymerization rate constants and k_c stand for the condensation rate constants. From the time-conversion data for the



Scheme 27.

821



Fig. 10. Calculated time–conversion plots and experimental points of individual products of the MMA oligomerization with MIB-Li. Conditions: $[MMA]_{0=}0.10 \text{ mol } 1^{-1}$; $[MIB-Li]_0 = 0.05 \text{ mol } 1^{-1}$. M = MMA; $P_1 = MIB-Li$; $P_2 = dimer$; $P_3, P_4 = linear trimer, tetramer; P_3^c, P_4^c = cyclic trimer, tetramer. (Reproduced with the kind permission of Makromol Chem 1990;191:1657.)$



Fig. 11. Dependence of the rate constants of propagation k_i (A) and cyclization k_{ci} (B) on the chain length *i* of the living oligomers in the absence and presence of *t*-BuOLi. Conditions: $[MMA]_0 = 0.40 \text{ mol } 1^{-1}$; $[MIB-Li]_0 = 0.20 \text{ mol } 1^{-1}$; $[t-BuOLi]_0 = 0.60 \text{ mol } 1^{-1}$; THF; 20°C. (Reproduced with the kind permission of Makromol Chem 1990;191:2253.)





individual reaction products, the corresponding rate and equilibrium constants [108] were calculated and used for the construction of the theoretical conversion curves. The calculated curves together with the experimental data for the oligomerization of MMA ($M_0 = 0.10 \text{ mol } 1^{-1}$) initiated with the MIB-Li $(C_0 = 0.05 \text{ mol } 1^{-1})$ are shown in Fig. 10. The calculated rate constants for the addition of MMA onto different lithio ester enolates and for their cyclizations are given in the heading of Fig. 10. A good agreement of the calculated curves with the experimental results is apparent [82,108]. As can be seen from Fig. 11(A) (propagation) and Fig. 11(B) (cyclization), the rate constants of both these reactions markedly depend on a polymerization degree of the oligomer. In the propagation reactions of the shortest oligomers, the largest differences between the rate constants have always been observed, becoming smaller with increasing length of the oligomer. Thus, MIB-Li reacts with MMA almost 100 times faster than the higher oligomers, among which differences are much smaller. The lower reactivity of lithiated dimer (P₂^{*} in Scheme 27) in comparison with the MIB-Li (P₁^{*} in Scheme 27) can be explained by a coordination of the penultimate ester group to Li of the enolate group which is, clearly, possible only in lithiated dimer or higher oligomers [82] (Scheme 28). As to the rate constant of cyclization (Fig. 11(B)), again, the highest k_c value was always found for the shortest oligomer, i.e. lithiated trimer in this case. This fact may likely have sterical reasons.

It was shown above that the alkali tert-alkoxides lower the rates of both the ester enolate addition and



Flow tube reactor, in THF at 20°C, time: (a) 0.02-1.4 s, (b) 60-1800 s, followed by hydrolysis

Scheme 29.



Fig. 12. SEC eluograms of reaction mixtures of *t*-BuA oligomerization. Conditions: $[t-BuA]_0 = 0.20 \text{ mol } 1^{-1}$; $[tBIB-Li]_0 = 0.10 \text{ mol } 1^{-1}$; THF; 20°C; reaction time (a) 0.06 s, (b) 1800 s. (—) RI signal (linear + cyclic oligomers); (---) UV signal (cyclic oligomers only). (Reproduced with the kind permission of Makromol Chem 1993;194:625.)

condensation reactions. This effect was also observed in oligomerization experiments [108] the results being quantitatively demonstrated in Figs. 10 and 11. The propagation as well as cyclization rate constants are actually lowered in the presence of *t*-BuOLi, but not to the same extent. As can be seen, the cyclization rate constant is lowered by the alkoxide about 10 times more than that of propagation. This finding means that addition of *tert*-alkoxide markedly increases the ratio of propagation to termination rate constants, which consequently, should exert a favourable effect on the process of anionic (meth)acrylate polymerization.

2.7. Addition of ester enolates onto tert-butyl acrylate, oligomerization studies

2.7.1. Products of the t-butyl acrylate oligomerization

In model oligomerization of *t*-BuA, similar to that of MMA, *t*BIB-Li reacted with two molar equivalents of *t*-BuA in THF in a flow tube reactor [105] at room temperature [18]. The reaction was very fast, so that within less than 20 ms, both the starting components were completely converted into the products (Scheme 29). After a short reaction time (0.06 s), the reaction mixture contained over 95% of linear oligomers and the content of ketoesters—probably mostly cyclic—was lower than 5%. An SEC eluogram of the reaction mixture is shown in Fig. 12(a). This finding is in contrast with the results of a similar study of MMA oligomerization, where ketoesters were major products even at short reaction times indicating a low tendency of growing *t*-BuA to participate in a back-biting reaction [102–104]. After



Fig. 13. SEC eluograms (RI signal) of *t*-BuA oligomers formed by *t*BIB-Li within 0.34 s in the absence and presence of additives. Polymerization conditions: $[t-BuA]_0 = 0.20 \text{ mol } 1^{-1}$; $[tBIB-Li]_0 = 0.10 \text{ mol } 1^{-1}$; THF; 23°C; $[\text{LiCl}]_0 = [t-BuOLi]_0 = 0.30 \text{ mol } 1^{-1}$: (a) without additives; (b) in the presence of LiCl; (c) in the presence of *t*-BuOLi. (Reproduced with the kind permission of Makromol Chem 1993;194:625.)

1800 s, the reaction mixture is more complicated containing a number of side products. Di-*tert*-butyl 5,5-dimethyl-6-oxocyclohexane-1,3-dicarboxylate (cyclic trimer P_3^*) was isolated from this mixture and characterized [18]. UV, IR and ¹H NMR analyses gave a direct evidence that this cyclic ketoester is enolized (see Scheme 3). UV spectra of the side products in the reaction mixture were identical with that of the cyclic trimer and, therefore, their structures are probably similar. As the enol form of the trimer absorbs at 260 nm, its amount could be determined semiquantitatively using both UV and RI detectors in the SEC analysis. The data are shown in Fig. 12 where the dashed curves represent UV signals and solid correspond to the RI detection. It can be seen from Fig. 12(b) that the amount of UV absorbing compounds in the reaction mixture attained about 70% within 1800 s. The enol hydrogen in the cyclic trimer (Scheme 3) is markedly more acidic (pK about 11) than the α -hydrogen of a simple carboxylic acid ester. Therefore, at least a part of the living oligomers are protonated by the enolized ketoesters giving an inactive product. Consequently, the autocondensation of one living chain-end can thus cause termination of up to two growth centres.



Fig. 14. SEC eluograms of *t*-BuA oligomers formed from the first (---) and second (—) additions of *t*-BuA into *t*BIB-Li in THF at 23°C in the absence of additives (a); in the presence of LiCl (b); in the presence of *t*-BuOLi (c). Time interval between additions: 300 s; for other reaction conditions, see Fig. 13. (Reproduced with the kind permission of JPS, Polym Chem Ed 1979;17:1727.)

It follows from the SEC eluograms (Figs. 12 and 13), that the di-*tert*-butyl 2,2-dimethylglutarate (*t*-BuA dimer, P₂) makes a large part of the reaction product [109–110]. Obviously, the rate of reaction of the monomer with the living dimer is much slower than that with the higher *t*-BuA oligomers and this fact strongly affects the MWD of the products (M_w/M_n about 2). Another reason for the broadened MWD can be additionally found in the concept of "multi-state propagation mechanism" suggested by Müller [84], or earlier by Coleman [111] which is based on the multiplicity of active species in a dynamic equilibrium.

2.7.2. Effect of additives on the tert-butyl acrylate oligomerization

A favourable effect of alkali *tert*-alkoxides on the methacrylate polymerization was discussed in the foregoing section. Similar properties of some Li salts, namely LiCl, was described by Teyssié et al. [112]. The influence of both these additives (ligands) on the *t*-BuA polymerization process was studied in more detail [109,110]; see Fig. 13.

The presence of *t*-BuOLi in the *t*-BuA polymerization system causes a pronounced decrease in the rates of all partial reactions to a higher extent than that in the MMA polymerization. Similarly, the alkoxide affects the reactivity of various *t*-BuA oligomers to a different extent, again, in dependence on

their polymerization degrees (DP). This follows from a SEC eluogram of the *t*-BuA oligomerization mixture (Fig. 13(c)) which indicates a very high content of *t*-BuA dimer exceeding the dimer amount formed in the absence of *t*-BuOLi (Fig. 13(a)). In addition to the dimer, a number of high *t*-BuA oligomers with DP values up to 80 were obtained. Based on these results, it can be assumed that the reactivity of the living *t*-BuA dimer towards the monomer was lowered by the interaction with the alkoxide more than those of other higher oligomers. Therefore, only a few living chains can get over the dimer stage and, consequently, the MWD of the reaction products is broad with M_w/M_n ratio about 3.5.

The effect of LiCl on the *t*-BuA oligomerization is in an opposite sense, as can be seen in Fig. 13(b). The content of dimer is lower than in the oligomerization without additive or in the presence of *t*-BuOLi and the reaction products exhibit very narrow MWD values with a M_w/M_n ratio of 1.15. Evidently, by the interaction with LiCl, the reactivity of the dimer increases to the level, which is comparable with those of the higher oligomers. This result of the *t*-BuA oligomerization is in agreement with the polymerization experiments of Teyssié [112].

2.7.3. Stability of active centres in tert-butyl acrylate oligomerization

The stability of living *t*-BuA chains was studied by a two-step polymerization technique [109,110]. After mixing the first dose of t-BuA with tBIB-Li, a second monomer dose was added within a time interval ranging from 1.4 to 1800 s. The protonized reaction mixtures were analyzed by SEC and the eluograms are shown as full lines in Fig. 14. The dashed lines relate to the oligomerization of the first dose only so that the difference between the full and dashed curves represents the oligomers formed from the second monomer dose. The time interval between the doses was 300 s in this case. The upper eluograms (Fig. 14(a)) correspond to the mixtures prepared without any additive and it can be seen that the second *t*-BuA dose gave rise to oligomers with considerably higher DPs and, at the same time, most of the first dose products remained virtually unchanged. From the DP of the oligomers formed from the second monomer dose it was calculated that, in THF at room temperature, only 9% of the originally present living chains "survived" within the given time interval. In the presence of LiCl (Fig. 14(b)), similar results were obtained; however, the DPs of chains formed from the second t-BuA dose was markedly lower. In this case, about 30% of the original centres were found to be active after 300 s. If t-BuOLi was present in the oligomerization mixture, different results were obtained (Fig. 14(c)). After the second monomer dose addition, all oligomers from the first dose exhibit approximately equal enhancement no formation of a separated population of higher oligomers being observed. This result can be understood assuming that most of the living chains from the first dose retain their activity over the given time interval and are still capable of propagating. Although the fraction of "surviving" centres could not be calculated using the procedure mentioned earlier; nevertheless, it is evidently high. These results show that a portion of living t-BuA oligomers remain live after 300 s and, moreover, this fraction can be markedly increased by stabilizing the additives, in particular, t-BuOLi.

3. Polymerization of methacrylates in the presence of alkali metal tert-alkoxides

3.1. Polymerization initiated by neat alkali metal tert-alkoxides

Alkali metal *tert*-alkoxides were used for the first time by Trekoval and Lím [113] as initiators for the anionic polymerization of MMA. In non-polar solvents, they polymerize methacrylates quantitatively

828

Table 9

Effect of polar solvent addition on the microstructure of PMMA prepared in toluene at 20°C using various initiators (I:initiator; MIB: BIBmethyl or butyl isobutyrates; X_p : yield of polymer). (Reproduced with the kind permission of Trekoval J, PhD Thesis, Inst Macromol Chem, Prague (1970))

$[\text{MMA}]_0 \text{ (mol } l^{-1}\text{)}$	$[I]_0 \pmod{l^{-1}}$	Polar solvent		<i>X</i> _p (%)	Triads (%)		
		Туре	$mol \ l^{-1}$		Iso	Hetero	syndio
Li tert-hexoxide							
5.61	0.083	_	_	15	84	12	4
1.81	0.097	_	_	23	83	12	5
Li tert-butoxide							
2.80	0.025	_	_	19	82	13	5
1.88	0.011	MIB	1.76	58	82	13	5
1.88	0.017	MIB	5.74	62	80	15	5
3.77	0.016	MIB	4.00	29	82	13	5
4.74	0.024	MIB	3.08	29	80	14	6
1.85	0.011	BIB	1.20	99	82	13	5
0.64	0.011	BIB	2.15	100	86	11	3
4.86	0.050	THF	4.40	11	58	21	21
BuLi							
8.45	0.045	_	_	30	52	25	23
0.10	0.012	_	_	22	71	17	12
0.74	0.022	MIB	2.77	100	29	30	41
0.93	0.005	THF	0.86	40	17	36	47

even at room temperature; however, the reaction is much slower than that initiated by BuLi and only a small part of the added alkoxide is efficient in the initiation reaction. Consequently, the idea arose that the unreacted alkoxide interacts with the growing chain-end forming a "protective complex" which is responsible for a relatively high stability of active species and for a quantitative monomer conversion [114,131]. Separately and additionally, coordination of alkali metal alkoxides to active centres of anionic polymerization was proved in a number of studies, see Section 2. It should be noted that Wiles and Bywater also found favourable but much less distinct effects of Li methoxide, ethoxide, and proposide in the polymerization of MMA initiated with BuLi in toluene [115]. Later on, various alkali metal alkoxides were used for the anionic oligomerization and polymerization of MMA [116-119] under different conditions. As the alkali metal *tert*-alkoxides form self-aggregates in nonpolar solvents [64], it was assumed that in the first reaction step the monomer "activates" the alkoxide aggregates, which are then able to add onto the C=C methacrylate bond [120]. Thus, the rate of polymerization distinctly increased with increasing initial monomer concentration. The same, but even more expressive effect was observed if solvating compounds, such as isobutyrate or pivalate esters or piperidine were added [121,122]. In contrast to the polymerization initiated by BuLi [70], the microstructure of PMMAs prepared by t-BuOLi exhibited lower sensitivities to the solvating power of the polymerization medium [114] (see Table 9). Moreover, the degree of branching γ according to

$$t$$
-BuO-(MMA)_n-H $\xrightarrow{(CH_3)_3Sil}$ (CH₃)₃SiO-(MMA)_n-H $\xrightarrow{H^+}$ HO-(MMA)_n-H

Scheme 30.
Polymerization of MMA with EIB-Li in toluene in the presence of various *tert* butoxides (conditions: $[MMA]_0 = 0.63 \text{ mol } 1^{-1}$; 60 min; 20°C; mole ratio $[MMA]_0/[EIB-Li]_0$). (Reproduced with the kind permission of JPS, Polym Chem Ed 1974;12:2091)

t-Butoxide	<i>t</i> -Butoxide/enolate (m/m)	Yield (%)	$M_{ m w}/M_{ m n}$
a	_	41	_
Li ^a	1	53	3.63
Na ^a	1	82	1.87
K ^a	1	92	1.76
Na ^b	1	36	2.05
Na ^b	3	90	1.85
Na ^b	5.5	100	1.60

^a See Ref. [120].

^b See Ref. [140].

Shultz's calculations, was found to be distinctly lower for PMMAs prepared by *t*-BuOLi [123] than for those prepared by BuLi; this fact can be a consequence of the complex formation between the living chain-end and the residual alkoxide which restricts the reactivity of the chain end toward the carbonyl group of the polymer.

As the polymerization is initiated by *tert*-butoxide anion, *tert*-butyl alcohol can be used as a chain transfer agent. By this method, methacrylate oligomers with well-controlled chain length having acceptably narrow MWDs can be purposefully prepared [124,125]. These oligomers, as well as higher-molecular-weight polymers, bear starting *tert*-butoxy groups from the initiator which can be selectively



Fig. 15. Conversion of MMA in the polymerization of the first and second doses of MMA with the system *t*BPr-Na + x t-[BuONa] vs x. Conditions: [MMA]_{first} = [MMA]_{second} = 0.63 mol 1⁻¹; mole ratio [MMA]_{first}/[*t*BPr-Na] = 120; toluene; 20°C; time interval between the first and second doses was 15 min; overall polymerization time was 75 min. (Reproduced with the kind permission of JPS, Polym Chem Ed 1979;17:1727.)



Fig. 16. Transformed non-normalized SEC elution curves of PMMAs: (1) polymer formed by the polymerization of the 1st MMA dose only; (2) polymer formed by the polymerization of the 1st and 2nd doses added within a time interval of 4 min; (3) time interval 15 min. Elution curves were corrected for zone spreading of the fractions. For conditions see Fig. 15. (Reproduced with the kind permission of Macromolecules 1994;27:4902.)

converted [126], e.g. via trimethylsilyloxy end-group [127], to hydroxy groups according to Scheme 30. Thus, poly(methacrylate)s prepared by a neat *tert*-alkoxide are excellent precursors for α -hydroxylated polymers. Also, the alkoxides are less sensitive to protic impurities and their preparation and purification are rather simple, so that they were successfully used for the anionic polymerization of various methacrylate esters [128–130] at room temperature.

3.2. Polymerization initiated by alkali metal ester enolates, effect of tert-alkoxides

As follows from the oligomerization studies (cf. Section 2), the properties of alkali metal ester enolates, in particular, their fast reactions with methacrylates characterized by a minimum of side reactions, allow them to be ideal initiators for the anionic polymerization of (meth)acrylate monomers. This assumption was confirmed by the polymerization of MMA initiated with EIB-Li [131] giving at room temperature a polymer in good yield and with a more or less broadened MWD (Table 10). Also, a favourable effect of the alkoxides was fully confirmed here. In the presence of alkoxide, a higher limiting conversion of a monomer was reached and the obtained polymer had a narrower MWD than that prepared with a neat ester enolate in the absence of the alkoxide (Table 10). The effect of the alkoxide increases with increasing concentration and also depends on the metal counter-ion and, to some extent on the structure of the alkoxide. The *t*-BuONa and *t*-BuOK or bulkier 3-MPeOLi (see Section 4.4) are more effective than the *t*-BuOLi. This is obviously associated with the lithium–heavier alkali metal interchange (see Scheme 8) and with the finding that heavier alkali metal ester enolates exhibit in MMA

Microstructure of PMMA prepared using ester enolates as initiators, effect of *tert*-butoxides. (Reproduced with the kind permission of Collect Czech Chem Commun 1977;42:1355)

Initiating system ^a		Triads (%)	
	Iso	Hetero	syndio
EIB-Li	71	21	8
EIB-Li + t-BuOLi	74	19	7
EIB-Li + 3t-BuOLi	74	19	7
tBPr-Na	50	40	10
<i>t</i> BPr-Na + <i>t</i> -BuONa	28	39	33
<i>t</i> BPr-Na + <i>t</i> -BuONa	19	37	44
EIB-K	28	51	21
EIB-Li + t-BuOK	28	51	21
EIB-Li + t-BuONa	50	34	16
EIB-K + t-BuOK	30	49	21

^a In toluene at 20°C.

polymerization more advantageous ratios of rate constants of propagation and self-termination (k_p/k_t) . It is also known that the heavier alkali metal alkoxides incline more to various interactions than the lithium analogues [132].

Generally, alkali metal *tert*-alkoxides enhance the ratio k_p/k_t , so that their effect on polymerization can be regarded as a stabilization of living growth centres. The concentration dependence of the stabilizing activity of the alkoxide was tested in two-dose experiments using the system *t*-BuONa/*t*BPr-Na at various mole ratios [133] (Fig. 15). MMA was polymerized in toluene at room temperature and the second monomer dose was added 15 min after the addition of the first. The limiting conversion and MWD of the polymer were then separately determined for the products of the first and the second monomer doses. When initiated by the ester enolate alone, the limiting conversion of the first dose was 50% only and the second dose did not polymerize at all. With an equimolar mixture of both the components, the first MMA dose polymerized up to 96% conversion and the second one to about 3%. When the ratio of alkoxide/enolate was 2, the first MMA dose polymerized completely and 30% of the second monomer dose was also converted to polymer. The conversion of the second monomer dose increases steeply with increasing alkoxide concentration up to the alkoxide/enolate ratio of about 4; further increase in the alkoxide content had a much less pronounced effect.

Fig. 16 shows SEC eluograms of PMMAs prepared under conditions mentioned above with the initiating complex alkoxide/enolate, mole ratio 6:1, with various time intervals between the monomer doses. Curve 1 corresponds to a polymer prepared from one monomer dose only, curve 2 represents a two-step polymerization, wherein the time interval between mononer doses was 4 min, and curve 3 is the same but with the time interval of 15 min. The last eluogram is clearly bimodal and its lower-molecular-weight peak corresponds to the polymer formed from the first dose only. The low-molecular-weight part of this product represents the chains self-terminated within the given time interval and the high-molecular part was formed by the "survived" centres. Curve 2 (4 min interval between the doses) is unimodal with a maximum at higher molecular weights than curve 1 and is only slightly broadened towards the lower-molecular-weight region. This indicates that with a six-fold excess of alkoxide and at room

Solvent	Y ^a		Triads (%)	
		Iso	Hetero	syndio
THF	1/0	1	21	78
	1/1	1	19	80
	1/10	1	19	80
Toluene	1/0	88	9	3
	1/1	86	9	5
	1/10	87	9	4
Toluene/THF ^b	1/0	17	25	58
	1/1.25	31	24	45
	1/3	57	11	32
	1/10	57	11	32

Effect of *t*-BuOLi on stereoregularity of PMMA prepared with DPMLi in various solvents at -78° C. (Reproduced with the kind permission of Macromolecules 1994;27:4902)

^a Mole ratio DPMLi/t-BuOLi.

^b 9:1 (v/v).

temperature, most of active centres formed from the first monomer dose remain active after 4 min. It was found in a separate experiment that polymerization of MMA under the conditions mentioned above is completed within 15 s so that the lifetime of active centres is sufficient for quantitative polymerization of a second monomer, which is a basic condition for synthesis of block copolymers (see Section 4.5). This example demonstrates that, due to the stabilizing effect of *tert*-alkoxides, methacrylate block copolymers can be prepared even at room temperature.

If polymerization of (meth)acrylates is initiated with *t*BIB-Li, the resulting polymer chains bear a starting *tert*-butyl isobutyrate unit which can be selectively hydrolysed to a carboxylic group. Again, the method via a trimethylsilyl ester is the most convenient [127] being very selective and allowing the remaining the ester groups along the chain, e.g. methoxy- or butoxycarbonyl, to be untouched. Thus, the method leads to poly((meth)acrylate)s quantitatively functionalized with one carboxy group in the α -position of each polymer chain [126]. ¹³C NMR spectra of the functionalized polymethacrylate and its precursor are virtually identical, the only difference being the total disappearance of the peak at 25.83 ppm (*t*-Bu group) and the emergence of signal at 176.98 ppm which belongs to the free COOH groups.

3.3. Microstructure of poly(methacrylate)s, effect of alkali metal tert-alkoxides

As the microstructure of anionically prepared poly(methacrylate)s depends, among other things, on the metal counterion [69,70], the effect of *tert*-alkoxides on the stereospecific growth in the MMA polymerization was investigated with respect to (i) permanent coordination of the alkoxide to the growth centres and (ii) metal-metal interchange according to Scheme 8 (Table 11) [72]. The addition of *t*-BuONa to the polymerization of MMA initiated with a sodium ester enolate causes a distinct decrease in the isotactic triad content in the product in favour of syndiotactic ones. As the *t*-BuONa itself (see above) gives highly syndiotactic PMMA, this finding proves the above mentioned permanent coordination of active centers with the added alkoxide. On the contrary, the microstructure of PMMA polymerized

Rate constants of propagation (k_p) and self-termination (k_t) ; number-average degrees of polymerization, (P_a) ; concentrations of active centres, $([P^*])$; initiator efficiencies, $(f = [P^*]/[I]_0)$; and M_w/M_n ratios in the polymerization of *t*-BuA in THF at 20°C, initiated with *t*BIB-Li in the absence and presence of LiCl and *t*-BuOLi. (Reproduced with the kind permission of Makromol Chem 1992;193:101)

	No additive	LiCl	t-BuOLi
$k_{app,0} (s^{-1})^{a}$	48.0	14.4	0.23
$10^{-3} k_{\rm p} (1 {\rm mol}^{-1} {\rm s}^{-1})$	42.5	11.4	0.17
$k_{\rm t} ({\rm s}^{-1})^{\rm b}$	0.75	0.75	0.25
$10^3 k_t / k_p \pmod{1^{-1}}$	0.02	0.07	0.68
$k_{\rm t} ({\rm s}^{-1})^{\dot{c}}$	6.0	2.8	_
$10^3 k_t/k_p \ (\text{mol } 1^{-1})^c$	0.14	0.25	_
P _n	177	158	146
$10^3 [P^*] (mol 1^{-1})$	1.13	1.27	1.37
F	0.28	0.32	0.34
$M_{\rm w}/M_{\rm n}$ (crude polymer mixture) ^d	1.35	1.08	1.77

^a Initial slope of the first-order time-conversion plot: $k_{app,0} = k_p[P]_0$.

^b Determined from the fraction of β -ketoester end-groups by UV spectroscopy: $\ln[(A_0 - A)/(A_0 - A_{\infty})] = k_t t$, where A is absorbance at 265 nm.

^c Determined from the curvature of time-conversion plots.

^d At full monomer conversion.

with lithium or potassium ester enolates can be only moderately affected by an addition of the corresponding alkoxide [73]. If, however, a heavier metal alkoxide interacts with the lithium enolate before polymerization, the microstructure of the formed PMMA nearly corresponds to that of PMMAs prepared with heavier metal enolates themselves. Again, this fact proves metal-metal interchange between enolate and alkoxide according to Scheme 8.

Lithium initiators in toluene impart to PMMA a prevailingly isotactic microstructure depending only slightly on the other reaction conditions (initiator type, temperature, etc.) [72]. The effect of the added Li*-tert*-alkoxide is also rather small in this case. In THF, a highly syndiotactic product is formed. If, however, MMA is polymerized by DPMLi in a mixture toluene/THF 9/1 (v/v), the originally low content

Table 14

 M_n and M_w/M_n values of poly(*t*-BuA) prepared by anionic polymerization. Effects of additives and method of preparation (conditions: $[t-BuA]_0 = 0.20 \text{ mol } 1^{-1}$; $[tBIB-Li]_0 = 0.004 \text{ mol } 1^{-1}$; $[LiCl]_0 = [t-BuOLi]_0 = 0.012 \text{ mol } 1^{-1}$; in THF at 20°C; time 5 min). (Reproduced with the kind permission of Makromol Chem 1992;193:101)

Additive	Flow tub	e reactor			Tank read	ctor	Ampoule	es		
	Crude m	ixture	Precip. p	olymer	Precip. po	olymer	Crude m	ixture	Precip. p	olymer
	M _n	$M_{\rm w}/M_{\rm n}$								
_	20 930	1.42	28 700	1.17	29 300	2.03	15 600	2.52	24 300	1.87
LiCl	19 530	1.10	20 980	1.06	30 800	1.69	9500	2.16	-	_
t-BuOLi	17 600	1.79	31 440	1.26	13 600	3.38	14 600	3.88	-	-



Fig. 17. Effect of *t*-BuOLi concentration on the microstructure of PMMA prepared by DPMLi in toluene/THF mixture 9/1 (v/v) at -78° C.

of isotactic PMMA can be distinctly enhanced by the addition of *t*-BuOLi as is seen from the data in Tables 12–14. Isotacticity of the polymer increases with increasing concentration of the alkoxide up to the DPMLi/*t*-BuOLi ratio of 3; further addition of the alkoxide has no effect (Fig. 17). As the alkoxide forms with a living chain complexes of various composition (cf. Section 2.3), it can be assumed that these complexes control stereochemistry of the growing polymer. Thus, in a medium of moderate polarity, aggregation/complexation equilibria play an important role because ligand-complexed non-aggregated and aggregated species can produce different types of stereospecific addition of monomer. This is roughly described in Scheme 31, where (P^{*}) and (P)^{*}_{agg} represent free and associated species, respectively, *L* is ligand and *M* monomer, *m* and *r* are *meso*- and *racemo*-arrangements. The other ligands act in this sense in a rather different way as will be mentioned in Section 4. In principle, this idea is based on the "multistate mechanism" according to Coleman [111] and Müller [83,84].

4. Polymerization of acrylate esters assisted with *tert*-alkoxides

The anionic polymerization of acrylic esters is more complex than that of methacrylates as a consequence of their high tendency for side reactions, including a reaction of organometallic initiator with the



Scheme 31.

Polymerization of EtHA with BuLi; effect of solvent, temperature, and alkoxide addition ($[EtHA]_0 = 0.961$; $[BuLi]_0 = 0.0096$; $[t-BuOLi]_0 = 0.0577 \text{ mol } l^{-1}$). (Reproduced with the kind permission of JPS, Polym Chem Ed 1990;28:2917 and 1992;30:1511)

Solvent	Temperature (°C)	Time (min)	$X_{\rm p}~(\%)$	$M_{\rm n} \times 10^{-3}$ (calc)	$M_{\rm n} \times 10^{-3}$ (SEC)	$M_{\rm w}/M_{\rm n} \times 10^{-3}$
Toluene ^a	-78	60	36	6.6	13.6	7.57 ^b
Toluene	-78	120	100	18.4	55.3	2.50
Toluene	-60	60	100	18.4	48.7	3.51
Toluene	-20	60	95	17.5	44.1	3.33
Heptane	-60	120	95	17.5	158.6	2.57
Heptane	-20	60	85	15.6	37.0	3.83
THF	-60	60	67	12.4	19.0	2.70
THF ^a	-60	100	13	2.4	11.9	3.50
$(3:7)^{c}$	-60	100	80	14.8	27.5	2.22
$(5:5)^{c}$	-60	120	87	16.1	26.0	2.48
(9:1) ^c	-60	30	99	18.4	28.5	2.08

^a Initiated with neat BuLi without *t*-BuOLi.

^b Polymodal MWD.

^c Mixture toluene/THF (v/v).

acid hydrogen in the α -position [7]. In fact, untill recently, only the polymerization of acrylate esters having α -branched alkoxy groups was successful [102,135], whereas the polymerization of *n*-alkyl acrylates self-terminated at low conversions giving inhomogeneous products with broad MWD values [103]. Therefore, an attempt was made to use alkoxide-containing complex initiators for a controlled synthesis of polyacrylates, in particular those with less or non-branched alkyl groups which—among others—are used in a number of technological applications [6].

4.1. tert-Butyl acrylate

The investigation of *t*-BuA polymerization in THF at room temperature using the above mentioned flow tube reactor was focused mainly on the kinetics of the process and on the yields and MWD of the product [19,110]. The polymerization initiated by tBIB-Li at room temperature with or without additives is very fast, reaction half-times being 0.01 s for the system without additive, and 0.05 or 3 s for the systems containing LiCl or t-BuOLi, respectively. The rate of self-termination was estimated using UV absorption at 260 nm, which is caused by the enolized form of cyclic ketoester (see above). The rate constants of propagation and self-termination, k_p and k_t , obtained from these data are summarized in Table 13. The DP of the formed polymer depends linearly on the monomer conversion, however; M_n values indicate low initiating efficiency of the enolate (about 30%), which can be only slighly influenced by the additives. The MWDs of the products are narrow even when measured in crude polymerization mixtures, the M_w/M_n values being 1.42, 1.10 and 1.79, respectively, for polymers prepared without any additive and in the presence of LiCl and t-BuOLi, respectively (Table 14). The dependence of MWDs of the polymers on the composition of the initiator is the same as was described in the oligomerization studies (cf. Section 2.7). Experiments in a flow tube reactor were compared with polymerizations performed in ampoules or in a stirred tank reactor (see below) under otherwise identical conditions with the reaction time 300 s (Table 14). Considering the sum of the polymer soluble and insoluble in a



Fig. 18. Conversion curves of the EtHA polymerizations at -60° C: (1) initiated with BuLi in THF; (2) with the complex BuLi/ *t*-BuOLi 1:6 in THF; (3) in toluene/THF mixture 3/7; (4) 5/5; and (5) 9/1. For other conditions, see Table 15. (Reproduced with the kind permission of JPS, Polym Chem Ed 1992;30:1519.)

precipitant, the conversion of the monomer was 100% in all cases. MWD of the polymer prepared in the flow tube reactor is distinctly narrower than those of the products synthesized in a tank reactor or in ampoules. This is obviously due to a very rapid mixing of reaction components in a flow tube reactor having a considerable effect on the polydispersity of the product in such a rapid polymerization. In polymerizations with lower reaction rates, e.g. at low temperatures, the effect of mixing is not as significant.

Table 16

Temperature (°C)	Time (min)	Conversion	n (%)	SEC	
		EtHA	t-BuOLi	$M_{\rm n} \times 10^{-1}$	$M_{\rm w}/M_{\rm n}$
20	0.5	3.7	_	11.1	1.72
20	60	28.6	_	4.6	1.88
0	5	17.5	6	12.6	1.76
0	180	60.1	24	8.5	1.84
-20	10	10.9	5	25.7	1.90
-20	300	89.3	17	16.5	2.26
-60	10	1.9	_	8.3	2.15 ^a
-60	290	10.6	8	11.8	4.08 ^a

Polymerization of EtHA initiated with *t*-BuOLi in THF ($[EtHA]_0 = 0.96$; [t-BuOLi $]_0 = 0.058 \text{ mol } 1^{-1}$). (Reproduced with the kind permission of JPS, Polym Chem Ed 1992;30:1519)

^a Polymodal MWD.



Fig. 19. Conversion curves of the EtHA polymerization initiated with *t*-BuOLi in THF at various temperatures: (1) 20°C; (2) 0° C; (3) -20° C; (4) -60° C, conditions see Table 16. (Reproduced with the kind permission of JPS, Polym Chem Ed 1992;30:1519.)

4.2. 2-Ethylhexyl acrylate

4.2.1. Polymerization with butyllithium and/or lithium tert-butoxide

First experiments were performed using BuLi as an initiator in the presence or absence of *t*-BuOLi and the effects of the reaction temperature and medium were studied [136,137]. In neat toluene or heptane, monomer is converted virtually quantitatively, though the formed polymers have broad MWDs and the effectivity of BuLi is low, as estimated from molecular weights (Table 15). In neat THF, conversion is limited to a low degree and the best results were obtained in a mixture toluene/THF, containing 10% v/v THF only. The conversion curves in Fig. 18 clearly indicate a non-negligible extent of self-termination in all referred experiments which is, however, distinctly dependent on the reaction medium used. Polymerizations were performed in a stirred tank reactor allowing for a rapid mixing of pre-cooled reaction components and sampling at chosen time intervals. From the ¹H and ¹³C NMR and IR spectra of



Fig. 20. Dependence of M_n of poly(EtHA) prepared by *t*-BuOLi on the monomer conversion at -20° C (1) and 0° C (2), for other conditions, see Table 16.



Fig. 21. Conversion curves of the EtHA polymerization at -60° C: (1) initiated with a neat *t*BIB-Li in THF; (2) with the *t*BIB-Li/*t*-BuOLi complex 1:3 in THF and (3) in toluene/THF mixture 9:1. [EtHA]₀ = 0.961 mol 1⁻¹; [*t*BIB-Li]₀ = 0.0096 mol 1⁻¹. (Reproduced with the kind permission of Makromol Chem 1993;194:841.)

poly(EtHA), prepared in a mixture toluene/THF 9/1, it seems very likely that the chain propagation is self-terminated mainly by a "back-biting" reaction. This is corroborated by the fact that the polymers absorb in the UV region at 260 nm. Terminal unsaturation in the polymer molecule possibly caused by transmetallation of monomer in α -position or by termination via the reaction of the propagating chainend with carbonyl group of the monomer was not found in the spectra and does not seem probable. Also, the polymer does not contain *tert*-butyl groups in detectable amounts. This means that the polymerization is initiated exclusively by BuLi and, moreover, transesterification of polymer or monomer by the alkoxide can be neglected.

Regardless of the foregoing findings that *t*-BuOLi virtually does not initiate MMA polymerization at low temperatures [122], the polymerization of EtHA by neat *t*-BuOLi was studied in a separate paper [138]. It follows from the results in Table 16 and Fig. 19 that the polymerization initiated with alkoxide proceeds much more slowly than with BuLi and the reaction rate distinctly decreases with decreasing reaction temperature. In addition, the molecular weight of the polymer decreases (see Fig. 20) with increasing monomer conversion which, together with the time dependence of the alkoxide consumption,

Run	$[EtHA]_0 \ (mol \ l^{-1})$	$[M]_0/[I]_0$	Time (s)	<i>X</i> _p (%)	$M_{\rm n} \times 10^{-3}$ (theor)	$M_{\rm n} \times 10^{-3} ({\rm SEC})$	$M_{\rm w}/M_{\rm n}$
1	0.240	14	60	100	2.73	3.7	1.13
2	0.240	25	60	100	4.75	7.6	1.04
3a	0.240	50	40	67	6.31	13.6	1.08
3	0.240	50	120	100	9.35	21.0	1.07
4	0.721	75	120	>99	13.96	25.2	1.08
5	0.961	100	120	>99	18.55	34.2	1.07
6	1.201	125	300	>99	23.17	40.1	1.08
7	0.961	160	600	99	29.59	55.0	1.15

Molecular weight control in polymerization of EtHA initiated with complex *t*BIB-Li/*t*-BuOLi 1:3. (Reproduced with the kind permission of Makromol Chem 1993;194:841)

Table 17



Fig. 22. Dependence of the M_n values of poly(EtHA) prepared with the complex *t*BIB-Li/*t*-BuOLi 1:3 (m/m) on the ratio [EtHA]₀/[*t*BIB-Li]₀. For conditions, see Table 17. (Reproduced with the kind permission of Makromol Chem 1993;194:841.)

indicates a slow initiation reaction. Thus, the alkoxide in the complex initiating systems actually acts as a stabilizing additive only whereas its direct participation in the initiation step is negligible.

4.2.2. Polymerization with lithium ester enolates

If initiated with a less nucleophilic ester-enolate, namely *t*BIB-Li at low temperatures, the polymerization of EtHA gives markedly better results [139]. Again, the favourable effect of the alkoxide addition is clearly seen by comparing the conversion curves 1 and 2 in Fig. 21; nevertheless, the extent of selftermination strongly depends on the polarity of the polymerization medium. Under optimized reaction conditions, i.e. initiation with the complex *t*BIB-Li/*t*-BuOLi 1:3 (m/m) at -60° C in the mixed solvent toluene/THF 9/1 (v/v), the molecular weight of pEtHA can be controlled by varying the [EtHA]₀/[*t*BIB-Li]₀ ratio in a range exceeding one order of magnitude [140], keeping MWD narrow as documented in Table 17. The molecular weight of the formed polymer (determined by SEC [141]) linearly increases



Fig. 23. M_n of poly(EtHA) vs. monomer conversion. The numbers of plots correspond to the runs in Table 17. (Reproduced with the kind permission of Polym Bull 1993;31:393.)

Run	Temperature (°C)	<i>X</i> _p (%)	$M_{\rm n} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$	$k_{\rm p} \mathrm{l} \mathrm{mol}^{-1} \mathrm{s}^{-1}$	$k_{\rm t} \times 10 \ {\rm s}^{-1}$	$k_{\rm p}/k_{\rm t} \times 10^{-3} \rm l \ mol^{-1}$
1 ^a	-72	100	26.1	1.13	4.72	0.48	9.79
2^{a}	-60	100	21.3	1.05	13.58	4.79	2.3
3 ^b	-60	100	20.6	1.09	10.11	5.36	1.89
4^{a}	-40	79	36.2	1.23	24.08	14.71	1.64
5 ^b	-40	90	35.4	1.24	26.74	13.46	1.99
6 ^a	-20	42	26.7	1.31	42.54	52.54	0.81
7 ^b	-20	77	18.0	1.31	31.26	39.07	0.80
8 ^b	0	50	7.9	2.06	~ 50	~ 200	0.25

Effect of reaction temperature on the polymerization of EtHA initiated with tBIB-Li/t-BuOLi complex. (Reproduced with the kind permission of Collect Czech Chem Commun 1993;58:2565)

^a [EtHA]₀ = 0.24 mol 1⁻¹; [*t*BIB-Li]₀ = 4.8 mmol 1⁻¹; time 10 min; mole ratio [*t*BIB-Li]₀/[*t*-BuOLi]₀:1/3. ^b [EtHA]₀ = 0.24 mol 1⁻¹; [*t*BIB-Li]₀ = 4.8 mmol 1⁻¹; time 10 min; mole ratio [*t*BIB-Li]₀/[*t*-BuOLi]₀:1/10.

with increasing the molar ratio of the starting concentrations of monomer and initiator; this plot is demonstrated in Fig. 22.

The plot also indicates non-quantitative but virtually constant efficiency of the initiator in the chosen range of concentrations. From the ratios of calculated vs. determined M_n values, the average initiator efficiency of \sim 50% can be estimated. The MWD of the formed polymer does not depend on the monomer conversion (Table 17, runs 3a, 3) and its molecular weight linearly increases with the monomer conversion (see Fig. 23). These facts indicate a very low extent of self-termination during propagation and, at the same time, a sufficiently higher rate of initiation than that of propagation. In the ${}^{13}C$ NMR spectra of the p(EtHA) with a relatively low molecular weight (Table 17, run 1), the signal of the tertbutyl group methyls at $\delta = 26.11$ ppm as well as the band of the isobutyrate carbonyl group at $\delta =$ 174.14 are clearly present. The intensity of the former relative to the adjacent CH_2 signals of the 2-ethylhexyl groups corresponds to the monomer /initiator ratio 19.35, which is in an excellent agreement with the value obtained from $M_{\rm p}$ determined by SEC (see Table 17, run 1). Consequently, the transmetallation reaction between initiator and monomer can been excluded because such a reaction would introduce terminal vinyl groups into the polymer, lowering at the same time the content of isobutyrate units. This corresponds to the results of model reaction of Li ester enolate and non-metalated ester [101]. Moreover, no signals for the vinyl group were observed in the spectrum. The reliability of such measurements of the initial group content was verified by the ¹³C NMR spectra of PMMA, prepared with t-BuONa initiation. Here again, the CH₃ signals of the tert-butoxy group appear at $\delta = 26.11$ ppm and their intensity corresponds to the number-average molecular weight of the respective polymer. Thus, under the reaction conditions given above, initiation proceeds exclusively by tBIB-Li whereas the

$$I^{*} + M \xrightarrow{k_{i}} P_{2}^{*} \xrightarrow{M} P_{3}^{*} \xrightarrow{M} P_{4}^{*} \xrightarrow{M} P_{4}^{*} \xrightarrow{M} etc.$$

$$\downarrow k_{t3} \qquad \downarrow k_{t4}$$

$$P_{3}^{t} \qquad P_{4}^{t}$$

Scheme 32.

Table 18

P. Vlček, L. Lochmann / Prog. Polym. Sci. 24 (1999) 793-873

$$[M] = ([M]_0 - [I^*]) \exp(-\{1 - \exp(-k_t t)\} k_p [I^*] / k_t)$$

Scheme 33.

alkoxide lowers the rate of self-termination and does not participate in the initiation step directly. This conclusion is corroborated by the results of the EtHA polymerization initiated by a neat *t*-BuOLi [138] as discussed above.

EtHA polymerization initiated with the *t*BIB-Li/*t*-BuOLi complex was investigated also at various temperatures [142] mainly for reasons of possible applications. The results are summarized in Table 18. The rates of both propagation and self-termination were calculated on the basis of Scheme 32 which is in fact a simplified Müller's Scheme 27. Here, I^* denotes effective initiator, M monomer, P_j^* living chains, P_j^* terminated chains, k_i , k_{pj} and k_{ij} rate constants of initiation, propagation and self-termination reactions, respectively. In Scheme 32, the initiation step was assumed instantaneous, i.e. k_i equal to infinity, all propagation (k_{pj}) and termination (k_{ij}) constants independent of j which is in agreement with the fact that MWD of the polymers is narrow and rather independent of the monomer conversion. To simplify mathematical treatment, it was also assumed that the living dimer P_2^* self-terminates with the same rate as longer chains; the error due to this assumption is negligible. Under these assumptions, the following equation for the monomer concentration [M] at reaction time t was obtained (Scheme 33). If the self-termination is caused mainly by the back-biting reaction mentioned above, i.e. chain cyclization, the result of the polymerization depends on the rates of competing propagation and cyclization reactions, which are given by the equations in Scheme 34, where [C^*] denotes the concentration of active species.

However, in acrylate polymerization, self-termination probably also involves protonization of living chains by acidic hydrogen of the above mentioned enol form of the cyclic oxo ester [18,19]. In contrast to monomolecular cyclization, this type of self-termination is a bimolecular reaction and thus does not follow Scheme 33 exactly. Its rate depends on the equilibrium fraction of the enol form in the system and on the rate of protonation reaction, which is assumed to be very fast. This consideration is based on the results of the foregoing *t*-BuA polymerization study [19] where a difference was found between the rate constants of self-termination calculated either from the curvature of semilogarithmic conversion curves or from the absorbance of the products at 260 nm. Moreover, the concentration of oxo ester groups was found to be lower than the total concentration of all polymer chains.

4.3. Butyl and ethyl acrylates

Compared with EtHA, BuA is expected to have a higher tedency for side reactions, in particular, for self-termination by back-biting reaction. Thus, this monomer was studied [143] using the information obtained in the foregoing EtHA polymerization. Initiated with neat *t*BIB-Li in a mixed solvent toluene/ THF 9:1, polymerization of BuA proceeds to a very low monomer conversion only, producing polymer with a very broad MWD, see Fig. 24, so that a high extent of self-termination can be reasonably assumed. A three- or ten-fold excess of *t*-BuOLi over the initiator leads to a dramatical improvement;

$$r_{p} = k_{p} [C^{*}] [M];$$
 $r_{t} = k_{t} [C^{*}]$
propagation autotermination

Scheme 34.



Fig. 24. $\ln[M]_0/[M]$ vs. time plots of the polymerization of BuA in toluene/THF mixture 9/1 at -60° C initiated with (1) *t*BIB-Li; (2) *t*BIB-Li/*t*-BuOLi 1:3; (3) dtto 1:10. (Reproduced with the kind permission of Polym Bull 1993;31:393.)

Table I	9
---------	---

Effect of reaction temperature, solvent and composition of initiating complex on the BuA polymerization of butyl acrylateinitiated with complex *t*BIB-Li/*t*-BuOLi ([BuA]₀ = 0.351 mol l; [*t*BIB-Li]₀₌7.02 mmol l; time 10 min (runs 1–5), 5 min (runs 6–15)). (Reproduced with the kind permission of Polym Bull 1993;31:393)

Run	A^{a}	B^{b}	Temperature (°C)	<i>X</i> _p (%)	$M_{\rm n} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$	$k_{\rm p}$ (1.mol ⁻¹ s ⁻¹)	$\begin{array}{c} k_{\rm t} \times 10^3 \\ ({\rm s}^{-1}) \end{array}$	$k_{\rm p}/k_{\rm t} \times 10^{-1}$ (1 mol ⁻¹)
1 ^c	10	10/0	-60	>99	11.5	2.67 ^d			
2	10	19/1	-60	100	12.2	1.18			
3	10	9/1	-60	100	11.0	1.23			
4 ^e	10	0/10	-60	67	11.8	1.73			
5^{f}	10	19/1	-60	100	5.6	1.12			
6	10	19/1	-69	100	14.6	1.18	15.71	6.0	2.62
7	10	19/1	-59	100	11.3	1.13	26.17	15.3	1.74
8	10	19/1	-41	93	12.1	1.38	55.55	76.2	0.73
9	10	19/1	-22	90	10.0	1.55	52.36	95.6	0.55
10	10	9/1	-71	100	13.0	1.21	12.64	3.5	3.61
11	10	9/1	-62	100	10.8	1.14	24.84	15.8	1.71
12	10	9/1	-40	58	18.1	1.71	51.88	99.9	0.52
13	3	9/1	-69	100	13.6	1.27	17.40	5.8	3.00
14	3	9/1	-60	100	13.2	1.22	22.67	13.6	1.78
15	3	9/1	-41	70	12.8	1.79	41.84	108.0	0.39

^a Mole ratio [*t*-BuOLi]₀/[*t*BIB-Li]₀.

^b Toluene/THF (v/v).

^c In toluene, initiated with EIB-Li.

^d Polymodal MWD.

^e In THF.

 f [BuA]₀ = 0.213 mol l.



Fig. 25. $\ln[M]_0/[M]$ vs time plots of the BuA polymerization in various solvents. The numbers of plots correspond to the runs in Table 19. (Reproduced with the kind permission of Macromolecules 1994;27:4881.)

the monomer is quantitatively converted to the polymer with a narrow MWD, slightly narrower if the alkoxide concentration is higher. The polarity of the reaction medium distinctly affects the course of polymerization, which is documented by Table 19 and Fig. 25. In neat toluene, the non-linear shape of the semilogarithmic conversion curve indicates slow initiation reaction and, consequently, the formation of polymer with a broad and polymodal MWD. Similarly to the EtHA polymerization, highly polar THF supports self-termination by a back-biting reaction so that the BuA polymerization stops at a low monomer conversion producing polymer with a broad MWD. As can be seen from Fig. 25, Runs 2 and 3, lowering the content of polar THF in reaction mixture from 10 to 5% (v/v) leads to a slightly lower extent of self-termination and to the formation of products with a narrower MWD.

Under the optimized reaction conditions, i.e. Li-*t*BIB:*t*-BuOLi mole ratio 1:10 and in a mixed solvent toluene/THF 19/1 (v/v) at -60° C, reaction orders of the polymerization with respect to the initial concentrations of monomer and active centers were determined to be unity [144]. The initial

Table 20

Influence of starting concentrations of monomer $[M]_0$ and initiator $[I]_0$ on the anionic polymerization of butyl acrylate (reaction conditions: $[tBIB-Li]_0/[t-BuOLi]_0 = 1 : 10$; toluene/THF = 19/1 (v/v); $T = -60^{\circ}C$; time 5 min). (Reproduced with the kind permission of Macromolecules 1994;27:4881)

Run	$[M]_0 \ (\mathrm{mol} \ \mathbf{l}^{-1})$	$[I]_0 \;(\text{mmol } l^{-1})$	$X_{\rm p}(\%)$	$M_{\rm n} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$	$k_{\rm p} ({\rm l}{ m mol}^{-1}{ m s}^{-1})$	$k_{\rm t} \times 10^{-3} \ ({\rm s}^{-1})$	$k_{\rm p}/k_{\rm t} \times 10^{-3} \; ({\rm mol}^{-1})$
1	0.098	7.02	100	2.8	1.09	25.15	_	_
2	0.213	7.02	100	5.9	1.07	21.61	1.5	14.31
3	0.315	7.02	100	11.3	1.13	26.17	10.0	2.42
4	0.729	7.02	92	17.7	2.07	30.06	41.3	0.73
5	0.351	0.23	12	5.6	1.53	24.49	26.2	0.94
6	0.351	0.35	90	26.5	1.52	22.53	15.4	1.47
7	0.351	11.70	100	6.6	1.09	29.20	23.7	1.33



Fig. 26. $\ln[M]_0/[M]$ vs time plots of the BuA polymerization at: (1) -70° C; (2) -60° C; (3) -40° C; for other conditions see, Table 19. (Reproduced with the kind permission of Polym Prepr (Am Chem Soc, Div Polym Chem) 1997;38(1):491.)

concentrations of the monomer and initiator varied in the range 0.098-0.729 and $0.0003-0.0117 \text{ mol } 1^{-1}$, respectively. The reaction orders were calculated from the rate equation assumed for the initial stage of polymerization (Scheme 33) with instantaneous rate of initiation and virtually zero rate of self-termination. It was also found, that k_p virtually does not depend on the starting concentrations of reaction components whereas k_t distinctly increases with increasing monomer concentration (Table 20). The idea that this phenomenon can be caused by the increasing polarity of the medium due to a higher monomer concentration has not been experimentally verified because substitution of part of the monomer by its saturated analogue (isobutyrate) did not affect markedly the rate of self-termination. Moreover, in the systems with higher $[M]_0/[I]_0$ ratios, the limiting conversion decreases and MWD of the product broadens, so that the best results gives the systems in which this ratio does not exceed 50. Both these facts indicate that the polymerization is complicated by a number of processes some of them being not yet known.

The temperature dependence of k_p and k_t together with limiting conversions and molecular weights for BuA polymerization are summarized in Table 19. Similarly to EtHA, also in this case, k_t is more temperature-dependent than k_p , so that with increasing reaction temperature the extent of self-termination

duced wi	duced with the kind permission of Polym Prepr (Am Chem Soc, Div Polym Chem) 1997;38(1):491)									
Run	<i>T</i> (°C)	$Y (\mathrm{mol})^{\mathrm{a}}$	$X_{\rm p}$ (%)	$M_{\rm n}$ (calc)	SEC ^b					
					M _n	$M_{\rm w}/M_{\rm n}$				
1	-60	1:10	80	4114	15100	1.43				
2	-69	1:10	100	5143	11800	1.09				
3	-70	1:3	62	3188	14800	1.57				

Polymerization of ethyl acrylate with *t*BIB-Li/*t*-BuOLi complex ($[EtA]_0 = 0.35 \text{ mol } l^{-1}$; $[EtA]_0/[tBIB-Li]_0 = 50:1$). (Reproduced with the kind permission of Polym Prepr (Am Chem Soc, Div Polym Chem) 1997;38(1):491)

^a [*t*BIB-Li]₀/[*t*-BuOLi]₀ mole ratio.

Table 21

^b Calculated with Mark–Houwink constants for PMMA.



Fig. 27. Semilogarithmic conversion plots of EtA polymerization initiated with *t*BIB-Li/*t*-BuOLi complex. The numbers of plots correspond to the runs in Table 21.

increases markedly. At -40° C, the limiting conversion of BuA is only 90% and MWD of the formed polymer broadens attaining the value of $M_w/M_n = 1.38$. The increasing extent of self-termination at higher reaction temperature is also clearly seen from the semilogarithmic conversion plots in Fig. 26, and, it is even more distinct if the polymerization is performed in a medium with higher polarity (cf. Section 2.5.1). The variation of the ratio of initiator components does not markedly affect the course of polymerization (see Table 19).

The polymerization of EtA was studied under the same conditions as that of BuA, discussed above. In toluene/THF mixture 19/1 (v/v), initiated with the complex *t*BIB-Li/*t*-BuOLi 1:10, EtA polymerizes at -70° C quantitatively with a high reaction rate, producing polymer with a narrow MWD [145]. Higher reaction temperature as well as a lower excess of the alkoxide over the initiator both lead to a low



Fig. 28. Arrhenius plots of k_p (a) and k_t (b) of the polymerization of BuA (1) and EtHA (2) initiated with the system *t*BIB-Li/*t*-BuOLi 1:3 (EtHA) or 1:10 (BuA) in toluene/THF mixture 9/1 (EtHA) or 19/1 (BuA). (Reproduced with the kind permission of Polym Bull 1995;34:1.)

Run	Ester	A^{a}	Temperature (°C)	Time (s)	$X_{\rm p}~(\%)$	SEC	
						$M_{\rm n} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$
1	EtHA ^b	1/1	-40	300	75	14.8	1.63 ^c
2	EtHA	1/2	-40	600	>99	15.8	1.16
3	EtHA	1/3	-40	1200	>99	27.9	1.23
4	EtHA	1/3	-20	600	87	14.8	1.71
5	EtHA	1/6	-20	300	99	10.0	1.33
6	BuA^d	1/10	-40	600	100	9.6	1.19
7	BuA	1/3	-40	600	>99	10.6	1.28
8	BuA	1/10	-20	600	>99	9.0	1.32

Polymerization of acrylic esters with the system *t*BIB-Li/3-MpeOLi. (Reproduced with the kind permission of Polym Bull 1995;34:1)

^a Mole ratio [*t*BIB-Li]₀/[3-MPeOLi]₀.

^b [EtHA]₀ = 0.48 mol l^{-1} ; [*t*BIB-Li]₀ = 9.6 mmol l^{-1} ; toluene/THF 9/1 (v/v).

^c Bimodal MWD.

^d [BuA]₀ = 0.35 mol l^{-1} ; [*t*BIB-Li]₀ = 7.0 mmol l^{-1} ; toluene/THF 19/1.

limiting monomer conversion, lowering the initiator efficiency and broadening MWD (Table 21). The semilogarithmic conversion plots in Fig. 27 document the non-negligible extent of self-termination even under optimized conditions, in particular, at higher monomer conversion. The increasing extent of self-termination with increasing reaction temperature and/or in a system with lower *t*-BuOLi concentration is also apparent from the plots. From the results of Run 2 in Table 21, initiator efficiency can be roughly estimated to be about 50%, i.e. the same as that found in the foregoing polymerizations of EtHA and BuA.

It is obvious from a comparison of the results of the polymerizations [139,140,142–147] of EtHA, BuA, and EtA, as well as from results of the foregoing studies of acrylate anionic polymerization



Fig. 29. MWD curves of poly(EtHA) prepared by *t*BIB-Li in the presence of various concentrations of 3-MPOLi. The numbers of curves correspond to the runs in Table 22. (Reproduced with the kind permission of Polym Prepr (Am Chem Soc, Div Polym Chem) 1997;38(1):446.)

Table 22

[102–104] that the tendency for a back-biting self-termination increases markedly with decreasing length and branching of the alkoxy group in the acrylate ester. Thus, the rate constants k_p and k_t in the polymerization of BuA depend on reaction temperature more steeply than in EtHA polymerization, which is documented by Arrhenius plots in Fig. 28.

4.4. Polymerization of acrylates in the presence of lithium 3-methyl-3-pentoxide

As low-temperature polymerizations bring about complications and additional costs when applied in technology, an attempt was made to find out an initiation system with a stabilizing efficiency high enough for temperatures over -50° C. For this reason 3-MPeOLi was tested [148] instead of t-BuOLi in a combination with tBIB-Li. The results of EtHA and BuA polymerizations initiated with this system at -40 and -20° C are summarized in Table 22. The addition of 3-MPeOLi lowers the overall polymerization rate more than t-BuOLi, see Figs. 21 and 29, so that, e.g. in the presence of three-fold excess of 3-MPeOLi over the initiator, EtHA is completely consumed at -40° C after 20 min (see run 3, Table 22) and the product has the M_w/M_n ratio 1.23. Equimolar amounts of 3-MPeOLi (run 1 in Table 22) has not sufficient stabilization efficiency in the EtHA polymerizations at -40° C, so that the attainable conversion is 75% only and the formed polymer had a broad MWD with a clear hint of bimodality. A sample, which was withdrawn from the reaction mixture and protonized before the limiting conversion was reached had distinctly bimodal MWD (curve 1, Fig. 29). This phenomenon indicates the simultaneous existence of terminated and non-terminated active centres in the system, so that the given MWD curve is a superposition of the "living" and "dead" fractions. Similar MWD curves were calculated theoretically from kinetic equations for EtHA polymerization assuming non-zero rate of selftermination [149].

To prepare poly(EtHA) with a comparable MWD at -20° C, the content of 3-MPeOLi in the initiating system must be enhanced because a three-fold excess of the alkoxide does not sufficiently stabilize the active centres at this temperature. If, however, the polymerization is initiated with the system [*t*BIB-Li]₀: [3-MPeOLi]₀ = 1 : 6, virtually all monomer is converted to the polymer with a narrow MWD (see Table 22, runs 4 and 5).

As has been shown earlier, BuA requires a more efficient stabilization of the active species to reach a "living" polymerization process, especially, at relatively higher temperatures. At -40° C, initiating systems with ten- or three-fold excess of the alkoxide polymerize BuA quantitatively within 10 min; those with a mole ratio [*t*BIB-Li]₀/[3-MPeOLi]₀ of 1/10, however, give the polymer with a narrower MWD. The same system, when used at -20° C, gives the monomer conversion over 99% within the same time interval as in the former case producing a polymer with slightly broadened MWD. The results are given in Table 22, runs 6-8, indicating that the stabilizing efficiency of alkali metal *tert*-alkoxides depends, at least to some extent, on their chemical structure and bulkiness.

4.5. Synthesis of block copolymers with (meth)acrylate blocks

It was shown in Section 3.2 that in the polymerization of MMA initiated with Na ester enolate in the presence of *t*-BuONa, the active centres are sufficiently stabilized. This feature is well applicable to synthesis of methacrylate block copolymers and, therefore, diblock poly(BuMA-*b*-MMA) was prepared in this way [133]. BuMA was polymerized first by the complex EIB-Li/*t*-BuONa with mole ratio 1:6 in toluene at room temperature for 4 min. Then, a solution of MMA was added and left to polymerize for



Fig. 30. MWD curves of poly(St-*b*-BuMA) (B) and corresponding poly(St) (A); first run, Table 23. (Reproduced with the kind permission of Polymer 1993;34:2875.)

one hour, again at room temperature. The block character of the product was verified by extractions with selective solvents, by NMR analysis and by dynamic mechanical measurements. *tert*-Alkoxide-assisted polymerization can also be used for the synthesis of block copolymers with acrylate blocks (see below).

Living poly(St), prepared by BuLi is capable of initiating polymerization of *t*-BuA at -60° C in the presence of *t*-BuOLi producing poly(St-*b*-*t*-BuA) with a narrow MWD similarly to Teyssié's system with LiCl ligand — see Section 5.1. In the first experiments, the THF solution of *t*-BuOLi was added immediately before an addition of the acrylate [150] into the living poly(St) solution prepared in the first step. As it was published earlier that various BuLi/BuOLi mixed complexes can polymerize non-polar vinyl monomers [151,152], an attempt has been recently made to polymerize styrene with BuLi/*t*-BuOLi complex in THF at low temperatures [126] to prepare a macroinitiator for methacrylate block copolymerization. The process is rather fast and the formed pSt has MWD slightly broadened toward low-molecular-weight region (Fig. 30). This likely indicates lowering the initiation rate by the alkoxide, which is in accordance with literature [153]. This *t*-BuOLi-ligated pSt⁻Li initiates quantitative polymerization of methacrylate producing block copolymers with good parameters; the system does not

Table 23

Monor	Monomers		Homopolyme	Homopolymer		Block copolymer				
			SEC		SEC		NMR			
M_1	M_2	$M_1/M_2 ({ m m/m})$	$M_{\rm n} \times 10^{-3}$	$M_{ m w}/M_{ m n}$	$M_{\rm n} \times 10$	$M_{\rm w}/M_{\rm n}$	$m_1/m_2 ({ m m/m})$	$M_{\rm n} \times 10^{-3}$		
St ^a	BuMA	1:1	18.5	1.18	39.1	1.20	1.08:1	41.8		
St ^a	BuMA	1:1	17.9	1.20	36.5	1.23	0.96:1	43.3		
St ^b	BuMA	1:1	17.7	1.32	36.6	1.34	1.04:1	40.9		
\mathbf{St}_{d8}^{a}	MMA	6.5:1	65.7	1.12	73.5	1.12	6.6:1	74.5		
St ^a	t-BuA	10:1	9.7	1.25	11.3	1.25	_	_		

Block copolymers prepared with BuLi/t-BuOLi complex in THF. (Reproduced with the kind permission of Polym Prepr (Am Chem Soc, Div Polym Chem) 1997;38(1):446)

^a *t*-BuOLi added: before styrene.

^b *t*-BuOLi added: simultaneously with styrene.

[<i>M</i> ₁] (mmol)	[<i>M</i> ₂] (mmol)	Initiator (mmol)	Δt (min)	Homopolymer		Copolymer	
				$\overline{M_{\rm n}({\rm SEC})}$	$M_{\rm w}/M_{\rm n}$	$\overline{M_{\rm n}~({\rm SEC})}$	$M_{\rm w}/M_{\rm n}$
St	t-BuA	BuLi					
39	41	0.78^{a}	30	4300	1.23	10510	1.27
t-BuA	EtHA	tBIB-Li					
39	38	0.78 ^b	8	13620	1.06	30230	1.08
39	38	0.39 ^b	30	26170	1.06	63000 ^c	1.17
t-BuA	BuA	tBIB-Li					
40	35	1.21 ^a	7	8560	1.09	13850 ^d	1.25
40	41	0.81 ^e	20	14870	1.05	20300	1.37

Synthesis and characterization of acrylate block copolymers. (Reproduced with the kind permission of Macromolecules 1995;28:7662)

^a Mole ratio [Init]₀/[*t*-BuOLi]₀: 1/6.

^b Mole ratio [Init]₀/[*t*-BuOLi]₀: 1/3.

^c By ¹³C NMR: mole ratio *t*-BuA/EtHA = 0.76; $M_n(NMR) = 75600$.

^d From ¹³C NMR: mole ratio *t*-BuA/BuA = 1.1; $M_n(NMR) = 16$ 300.

^e Mole ratio [Init]₀/[*t*-BuOLi]₀: 1/10.

require usual modification of the highly nucleophilic pSt⁻Li by DPE [154]. The alkoxide can be added into the reaction mixture either in advance or dissolved in St, i.e. simultaneously with St as a first monomer. Some of the results are given in Table 23.

In the preparation of fully acrylate block copolymers, i.e. poly(t-BuA-b-EtHA) and poly(t-BuA-b-BuA), *t*-BuA was polymerized first with the *t*BIB-Li/*t*-BuOLi system at -60° C in the mixture toluene/ THF [155]. Then, the solution of the second acrylate was rapidly added and polymerized up to full conversion. The time interval between additions of the first and second monomer, Δt , was chosen as a function of the mole ratio [*t*-BuA]₀/[*t*BIB-Li]₀. Details on the copolymer synthesis and their characteristics are given in Table 24. The reaction conditions in the first copolymerization step, polarity of the solvent and composition of the initiating complex, must be chosen with respect to the second monomer

Solvent	$[s-BuLi]_0 \text{ mmol } l^{-1a}$	A^{a}	Temperature (°C)	$M_{ m w}/M_{ m n}$	f^{b}	
THF	6.6	0	-78	3.61	_	
THF	6.6	0.59	-78	1.52	0.67	
THF	6.6	1.97	-78	1.30	0.80	
THF	6.6	5.02	-78	1.20	0.77	
75/25°	3.8	1.30	-78	1.20	0.72	
75/25	3.8	1.22	-30	1.30	0.71	
75/25	3.8	1.22	0	1.63	0.61	

Polymerization of *t*-BuA with the *s*-BuLi/LiCl system capped with few units of α MeSt. (Reproduced with the kind permission of Macromolecules 1987;20:1442)

^a Mole ratio [LiCl]₀/[s-BuLi]₀.

^b Initiator efficiency from the ratio $M_{\rm n}({\rm calc})/M_{\rm n}({\rm SEC})$.

^c Toluene/THF (v/v).

Table 25

Polymerization of MMA at -78° C in THF in the presence of various Li salts ([MMA]₀ = 0.468 mol l⁻¹; time 100 s). (Reproduced with the kind permission of Macromolecules 1990;23:2618)

Run	Initiator	Salt	<i>X</i> _p (%)	SEC	f^{a}	
				$M_{\rm n} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$	
1 ^b	αMeStLi	_	99	41.0	1.20	0.67
2	αMeStLi	LiCl	99.5	32.5	1.09	0.85
3	αMeStLi	LiF	99	46.5	1.17	0.58
4	αMeStLi	LiBr	96	38.0	1.16	0.69
5	αMeStLi	$LiBPh_4$	68	25.5	1.24	0.74
6 ^c	DPHLi		100	16.0	1.13	0.94
7	DPHLi	LiBPh₄	100	18.0	1.12	0.86
8 ^d	DPMPLi	LiCl	93	22.0	1.09	0.93

^a Efficiency of the initiator.

^b Run 1–5: $[\alpha MeStLi]_0 = 1.7 \text{ mmol } l^{-1}; [salt]_0 = 1.8 \text{ mmol } l^{-1}.$ ^c Run 6,7: $[DPHLi]_0 = [salt]_0 = 3.0 \text{ mmol } l^{-1}.$ ^d $[DPMPLi]_0 = 2.2 \text{ mmol } l^{-1}; [LiCl]_0 = 2.4 \text{ mmol } l^{-1}.$

and the poly(t-BuA) remains active for a sufficiently long time. Under these conditions, the extent of self-termination in the second step of synthesis is virtually negligible and the block length can be controlled stoichiometrically. If extracted with hexane, poly(t-BuA-b-EtHA) is almost completely soluble, which can be regarded as a proof of its block character [156].

5. Other types of stabilizing additives (ligands) and their effect on (meth)acrylate polymerization

5.1. Alkali metal halides

5.1.1. Homopolymers and functionalized polymers

The use of alkali metal halides in the anionic polymerization of (meth)acrylates was reported by Teyssié's group in Liége 1987 [112]. LiCl was used as a ligand in the polymerization of t-BuA at temperatures from -78 to 0°C, initiated by sec-BuLi, which was capped with several units of α MeSt forming α MeStLi. LiCl in the system affords the formation of a polymer with a narrow MWD, keeping the initiator efficiency high—see Table 25. The effect of different lithium salts as ligands of complex initiators was studied in more detail in the polymerization of MMA [157]; the results summarized in Table 26 document that in fact only LiCl has a favourable effect on the anionic polymerization of MMA. The addition of other salts leads to the same results as the process without additive. The effect of LiCl is remarkable only if a less sterically hindered initiator (α MeStLi) is used. In combination with highly hindered initiators, (DPHLi, DPMLi, or DPMPLi), the added salts in fact do not influence the course of MMA polymerization because it proceeds quantitatively with a high initiator efficiency producing PMMA with a narrow MWD without LiCl as well.

The method ensures virtually living polymerization of the mentioned monomers so that it can be used for synthesis of number of tailored polymers based on MMA or t-BuA. When initiated with an appropriately sterically hindered monofunctional initiators or by bifunctional initiator TPDLB, t-BuA can be

Terminating agent	$M_{\rm n} \times 10^{-3}$			$M_{ m w}/M_{ m n}$	F^{a}	
	Theor ^b	SEC	NMR			
Benz aldehyde	1.40	1.45	1.44	1.10	0.93	
dtto	1.80	2.10	2.30	1.14	0.91	
Anthracene-9-carbaldehyde	3.0	3.7	4.3	1.10	0.86	

Synthesis of ω -hydroxy-terminated poly(t-BuA)s. (Reproduced with the kind permission of Macromolecules 1992;25:5578)

^a Functionality of the polymer.

Table 27

^b Calculated from the ratio [*t*-BuA]₀/[Initiator]₀.

polymerized to products with molecular weights as high as 10^5 , keeping MWD relatively narrow [158]. The mole ratio of [LiCl]/[initiator], however, has to be distinctly higher than 1–10 usually used by Teyssié. For the controlled synthesis of polymers with a molecular weight over 10^5 , the mole ratio [monomer]/[LiCl] was kept equal to 44 and the initiator concentration was chosen according to the required molecular weight. Nevertheless, high-molecular-weight polymers (200 000 and more) have M_n values lower than calculated, their polydispersities being broadened up to M_w/M_n above 2 as a consequence of unavoidable chain transfer and possible termination by residual protic impurities. In fact, the last fact indicates the limitation of the inert atmosphere technique.

By the end-capping reaction of the living poly(*t*-BuA) with an appropriate unsaturated electrophile, macromonomers can be purposefully prepared [159]. Examples involve 4-vinylbenzyl poly(*t*-BuA) synthesized by quenching of the living polymer with 4-bromomethylstyrene and ω -methacryloyloxy-poly(*t*-BuA), resulting from the reaction of the living poly(*t*-BuA) with 3-(chlorodimethylsilyl)propyl methacrylate. The number of vinyl bonds per chain was checked by UV spectroscopy. Similar results were obtained, when living poly(*t*-BuA) was quenched with 4-vinylbenzoyl chloride or 4-(chlorodimethylsilyl) styrene, or 4-(chloro dimethylsilyl)- α -methylstyrene at -78° C in THF [160]. The content of vinyl bonds per chain is above 90% in all experiments as determined from ¹H NMR spectra. Direct acylation of living poly(*t*-BuA) with methacryloyl chloride gave a polymer with a remarkably broadened MWD and with a low content of methacrylic unsaturation. The most likely reason is a competing nucleophilic attack of the vinyl double bond in methacryloyl chloride by the enolate living chain-end.

Hydroxy-functionalized poly(*t*-BuA)s (mono- or telechelics) were prepared with very good results [160] by the addition of the living chain-end onto the carbonyl group of benzaldehyde or anthracene-9-carbaldehyde. These aromatic compounds were chosen as they can be simply detected by UV spectroscopy, by SEC with UV detection or by ¹H NMR spectroscopy. The living poly(*t*-BuA) was treated with a small excess of an aldehyde at low temperature for 1 h and then isolated; the results of these syntheses are summarized in Table 27.

Using the same principle, Gnanou [161] prepared ω -mono- or α,ω -difunctionalized diblock copolymers poly(MMA-*b*-*t*-BuA) and poly(St-*b*-*t*-BuA) or triblocks based on the same monomers with poly(St) or PMMA as a central block. Living polymers prepared with monofunctional initiators form in a reaction with terephtalaldehyde products with two central hydroxy groups and the molecular weight twice higher than that of the precursor. However, those, prepared by bifunctional initiators, form in the same reaction "polycondensates" having molecular weights several times higher than of that the original polymer and bearing more than two hydroxy groups.

Synthesis and parameters of poly(*t*-BuA-*b*-MMA) block copolymers in THF at -78° C, mole ratio ([LiCl]₀/[Initiator]₀ = 10). (Reproduced with the kind permission of Macromolecules 1991;24:4997)

Initiator		M_1	M_1		Homopolymer		Copolymer	
Туре	mmol	Туре	Mol		$M_{\rm n} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$	$M_{\rm n} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$
αMeStLi ^a	0.20	MMA	0.047	0.070	33.0	1.20	76.0 ^b	2.30
αMeStLi ^c	0.20	MMA	0.047	0.070	25.5	1.15	79.0 ^d	1.25
αMeStLi ^e	0.20	MMA	0.047	0.070	23.5	1.15	83.0 ^d	1.15
αMeStLi	3.60	MMA	0.800	2.145	24.0	1.05	125.0	1.10
DPMLi	0.25	MMA	0.020	0.038	8.5	1.05	30.5	1.05
DPMK	0.15	MMA	0.047	0.070	34.0	1.05	113.0	1.15
αMeStLi ^a	0.45	t-BuA	0.040	0.050	27.0	1.65	51.0	1.55
αMeStLi	0.45	t-BuA	0.040	0.050	12.0	1.14	24.0	1.20
αMeStLi	1.06	t-BuA	0.195	0.150	25.5	1.10	42.0	1.10
DPMLi	0.20	t-BuA	0.034	0.080	23.0	1.05	67.0	1.05
DPMNa	0.20	t-BuA	0.035	0.080	24.5	1.05	68.0	1.05
DPMK	0.20	t-BuA	0.040	0.080	27.0	1.07	74.5	1.10

^a Polymerization in the absence of LiCl.

^b Bimodal MWD.

^c [LiCl]₀/[Initiator]₀ = 1.

^d Hint of bimodality.

 $^{\circ}$ [LiCl]₀/[Initiator]₀ = 5.

Functionalization of the living poly(*t*-BuA) with an excess of carbon dioxide is also mentioned together with a few data characterizing the product. As the *t*-BuA polymerization was initiated with a combination Li naphtylide/LiCl, the final product is α,ω -dicarboxy functionalized polymer [161].

ω-Hydroxylated polymers are also good precursors for the preparation of acrylate macromonomers using in principle the same reaction with methacryloyl chloride as was earlier used for ω-methacryloyloxy terminated poly(St) macromonomers by Asami [162] or even earlier by Schulz [163]. In this case, poly(*t*-BuA) capped with benzaldehyde was, before protonation, treated with methacryloyl chloride producing in this way ω-methacryloyloxy terminated poly(tBuA) macromonomer. Using a terminating agent with styrene unsaturation, such as 4-vinylbenzoyl chloride or 4-(chlorodimethylsilyl)-α-methylstyrene, poly(*t*-BuA) macromonomers with styrene double bonds were prepared.

5.1.2. Block and random copolymerization

The method of LiCl-ligated polymerization gives good results also in the synthesis of block copolymers, with the condition that the acrylic block is poly(*t*-BuA). Using living poly(St) with Li counterion assisted with a five-fold excess of LiCl, in THF at -78° C, diblock copolymer poly(St-*b*-*t*-BuA) can be prepared in a wide range of composition, virtually without contamination by the corresponding homopolymers [164]. The MWD of the final product is in fact the same as that of the first block and its M_n follows theoretical predictions. Without LiCl, the formed block copolymer has a MWD distinctly broadened and its SEC trace exhibits a tail toward higher molecular weights. If the first step was initiated by Li naphtylide under the same experimental conditions as in the former case, triblock copolymers poly(*t*-BuA-*b*-St-*b*-*t*-BuA) were prepared in good yields and with good properties. Both these



Fig. 31. SEC eluograms of PMMA homopolymer (a); p(MMA-*b*-GMA) diblock (b); and p(MMA-*b*-GMA-*b*-MMA) triblock (c) prepared in three-step copolymerization with DPMPLi/LiCl complex 1/5 (m/m) in THF at -60° C. (Reproduced with the kind permission of Macromolecules 1995;28:1758.)

copolymers are good precursors for the synthesis of the amphiphilic block copolymers containing, after hydrolysis of the *tert*-butoxy-groups, hydrophilic blocks of poly(acrylic acid).

Di- and tri-block copolymers composed of PMMA and poly(t-BuA) blocks were prepared virtually in the same way [165]. However, if the MMA is polymerized first, the block copolymer is always contamined by the PMMA homopolymer, the amount of which decreases with an increasing ratio $[\text{LiCl}]_{0}$ [initiator]₀. Nevertheless, the MWD of the block copolymer remains narrow with M_w/M_n 1.10–1.15, whereas the M_w/M_n ratio of the poly(MMA) precursor is 1.05. This fact indicates partial deactivation of the living PMMA before or upon addition of the second monomer. Further increases in the mole ratio $[LiCl]_0/[initiator]_0$ have no benefitial effect. In the reverse system, when living poly(t-BuA) precursor was prepared first, no residual homopolymer was observed and the MWD of the final product remains virtually unchanged. Some of these results are summarized in Table 28. This is in accordance with the fact, that living PMMA lacking a favourable effect of bulky tert-butoxy groups along the polymer chain autoterminates more easily than living poly(t-BuA), the tendency of which to a back-biting reaction is extremely low as well as in the polymerization of t-BuMA [166]. In the same way, a diblock poly(MMA*b*-4-vinylpyridine) was successfully synthesized [167] with a system DPMPLi/LiCl = 1/4 in THF at -70° C. In contrast to the MMA/t-BuA diblock, this final product does not contain detectable amounts of homopolymers exhibiting two T_g values, obtained from DSC measurements which correspond well with the $T_{\rm g}$ s of the homopolymers.

With a similar system, DPMPLi/LiCl 1/5 in THF at temperature between -40 and -60° C, pGMA was successfully prepared with the epoxy groups remaining untouched. Using a living PMMA as the macroinitiator, diblock p(MMA-*b*-GMA) was formed containing, again in contrast to the MMA/*t*-BuA block copolymerization [165], no residual PMMA and having a narrow MWD [168]. An attempt to prepare the p(MMA-*b*-GMA-*b*-MMA) triblock in a three-step process led to the product contaminated with a small amount of p(MMA-*b*-GMA) diblock from the second reaction step (see Fig. 31). The

Alkyl	pBut block		Poly(alkylMA	Copolymer		
	$M_{\rm n} \times 10^{-3}$ (calc)	$M_{\rm n} \times 10^{-3}$ (SEC)	$M_{\rm w}/M_{\rm n}$	$M_{\rm n} \times 10^{-3}$	Content (%) ^a	$M_{\rm w}/M_{\rm n}$
Et	50	59	1.10	2 × 13	31 (35)	1.10
t-Bu	62	70	1.10	2×14	29 (31)	1.10
Me	70	80	1.10	2×25	38 (40)	1.10
i-Bu	50	55	1.10	2×20	42 (44)	1.10

Triblock copolymers with central poly(But) block and alkyl methacrylate outer blocks. (Reproduced with the kind permission of Macromolecules 1996;29:8362)

^a By ¹H NMR, theoretical values are in parentheses.

triblock p(GMA-*b*-MMA-*b*-GMA) without detectable residual PMMA homopolymer and with a narrow MWD [169] was obtained by the system composed of a bifunctional initiator TPDLB and a five-fold excess of LiCl in THF at -60° C.

If, however, simple *s*-BuLi is used instead of DPHLi or DPMLi, polymerization of MMA, GMA and DMAEMA does not proceed satisfactorily even in the presence of ten-fold excess of LiCl [170] at -78° C. Only *t*-BuMA polymerizes in a living manner under these conditions and its growing enolate chain-end remains active for a long time.

The addition of LiCl also improves the MWD of poly(methacrylate-*b*-But-*b*-methacrylate) triblocks prepared by hydrocarbon-soluble bifunctional initiators based on a diadduct of *sec-* or *tert*-BuLi onto 1,3-diisopropenylbenzene (LiDIBLi), which was developed earlier [171,172]. To attain a complete bifunctional activity of the LiDIBLi, polymerization of But has to be performed in a mixed solvent cyclohexane/diethyl ether (100/5 v/v) which, however, increases the content of 1,2-placement in pBut. The formed bifunctional living pBut is then end-capped with DPE to avoid side reactions in the second step and the polymerization mixture is diluted with THF wherein a calculated amount of LiCl is dissolved. Thus, methacrylate polymerization proceeds at -78° C in a solvent with moderate polarity

Table 30

Random anionic copolymerization of MMA/t-BuA mixtures (in THF at -78° C; mole ratio [LiCl]₀/[α MeStLi]₀ = 10; 60 min). (Reproduced with the kind permission of Macromolecules 1990;23:4024)

Run	t-BuA in feed (mol%)	<i>X</i> _p (%)	SEC		t-BuA in copolymer (mol%)	
			$M_{\rm n} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$		
1 ^a	0	100.0	32.6	1.08	0	
2	8	6.9	2.97	2.20	73.5	
3	16	7.5	2.93	2.00	73.7	
4 ^b	16	6.8	2.91	2.50	87.1	
5	44	17.5	23.5	2.10	92.0	
6	76	71.0	27.0	2.00	98.2	
7	88	86.0	32.0	2.10	99.0	
8	100	100	31.9	1.07	100	

^a Neat MMA.

^b Polymerization without LiCl.



Scheme 35.

in the presence of a five-fold excess of LiCl over the growing centres [173]. In this way, a number of ABA type triblocks with a central pBut block and outer blocks formed by various methacrylate esters were prepared [174,175]; examples are given in Table 29. Nevertheless, it should be noted here that similar copolymers with only slightly broadened MWD values can also be synthesized using a LiCl-free process [172,176].

In random copolymerizations of MMA/*t*-BuA mixtures, the differrent tendencies of these two monomers to self-termination can be clearly seen [177]. Initiated with α MStLi in the presence of a ten-fold excess of LiCl, the mixtures give products with high contents of *t*-BuA, whatever was the composition of the initial monomer mixture. If the content of *t*-BuA in the feed is lower than ca. 50% (m/m), only oligomers are formed with broad MWD values, and in poor yields, see Table 30. The likely explanation for this phenomenon is based on a back-biting reaction of the living polymer chain ended by *t*-BuA unit with an antepenultimate MMA unit of the same chain according to Scheme 35. This is corroborated by the formation of violet complex of enolized oxo ester with FeCl₃ and by appearance of a peak at 12.75 ppm in ¹H NMR spectrum, which is typical of the enol proton. The findings suggest two important conclusions. First, for a low extent of self-termination in the anionic polymerization of (meth)acrylates, steric hindrance and inductive effects of a bulky *tert*-butoxy-group along the chain are key factors [102– 104,135]. Second, the lowering of the self-termination rate by LiCl is rather moderate, this fact being

Table 31

Solvent	Y ^a		Triads (%)	
		Iso	Hetero	Syndio
THF	1/0	1	21	78
	1/2	1	21	78
	1/10	1	20	79
Toluene/THF ^b	1/0	17	25	58
	1/1	6	25	69
	1/2	4	24	73
	1/5	3	25	72

Effect of LiCl on a microstructure of PMMA pr	pared with DPMLi in	n different media at	- 78°C. (Reproduced	l with the kind
permission of Macromolecules 1993;26:5984)				

^a Mole ratio DPMLi/LiCl.

^b 9:1 (v/v).

Influence of LICI on MWD and microstructure of poly(t-BuMA	A) prepared with α MeStLi in THF at -78° C. (Reproduced with
the kind permission of Macromolecules 1994;27:1076)	

Y ^a	$M_{\rm w}/M_{\rm n}$		Triads (%)	
		Iso	Hetero	Syndio
1/0	1.36	8.7	49.6	41.7
1/1	1.20	8.4	46.4	45.2
1/2	1.15	8.5	47.3	44.2
1/3	1.05	26.7	53.4	19.9
1/5	1.05	27.1	52.3	20.6
1/10	1.10	27.4	51.9	20.7

supported also by the results of kinetic and mechanistic studies of *t*-BuA oligomerization and polymerization [101,110]. Thus, the stabilizing effect of LiCl is not high enough to attain controlled anionic polymerization of acrylates with less- or non-branched alkoxy groups (EtHA, BuA) [178].

5.1.3. Microstructure of polymers, effect of LiCl

LiCl also affects the microstructure of the formed PMMAs in a mixture toluene/THF 9:1, but not in neat THF [179]. It can be seen from Table 31, that the LiCl addition governs the PMMA microstructure in an opposite direction than that of t-BuOLi. In the mixed solvent, LiCl changes the microstructure of the formed polymer closer to a tacticity of PMMA prepared in THF under the same conditions, i.e. the number of syndiotactic triads increases with increasing LiCl concentration up to the mole ratio [LiCl]/[initiator] = 2. A favourable effect of LiCl on the kinetics of MMA and t-BuA polymerizations and MWDs of the formed polymers becomes constant at a ratio [LiCl]/[initiator] of 4 and higher. It follows from spectral studies that in THF, LiCl forms complexes with MIB-Li with molar ratios between 1:1 and 3:1 (cf. Section 2.4.2). Thus, in the mixed solvent without LiCl, the self-aggregated initiator (or growing chains) are in equilibrium with non-aggregated ones [84] so that both the meso and racemo arrangements are basically possible. LiCl, forming complexes with the non-aggregated centres, increases the population of the ligated "free" (non-aggregated) centres which are responsible for a syndiotactic addition of the monomer. This is corroborated by the fact that with increasing concentration of DPHLi initiator in a mixed solvent (toluene/THF 9:1), the content of isotactic microstructure in the formed polymer also increases due to an increasing content of self-aggregated growing chains. Thus, the polymerization can be most probably controlled by at least two types of active species (multiplicity of active species, "multistate" mechanism [85,111]) with different degrees of association and complexation, having different stereospecific efficiencies, especially in a solvent of moderate polarity (see Scheme 30). Consequently, LiCl, as well as the other ligands-among others-affects these equilibria. In addition, E/Z isomerism most probably plays an important role in the stereochemistry of the growing polymer [180] so that, at least in some cases, both of the effects are combined.

A significant effect of various aggregation and complexation phenomena can be well seen in the polymerization of *t*-BuMA proceeding virtually without condensation side reactions even at ambient temperatures, in the presence of any of common alkali metal counterions [181]. At -78° C, Varshney et al [182] obtained, using α MeStLi in THF, p*t*-BuMA with a broadened MWD, containing non-negligible



Fig. 32. Effect of ligand concentration on the MWD of pt-BuMA prepared by DPHLi in a toluene/THF mixture 9/1 at -78° C. (Reproduced with the kind permission of Macromol Rapid Commun 1994;15:517.)

amounts of oligomers; the MWD of the product became narrower if LiCl was added into the system up to the [LiCl]/[α MeStLi] ratio of 2 (see Table 32). Further increases in the salt concentration had no beneficial effect on the MWD; however, the polymerization rate decreases with increasing the [LiCl]/ [α MeStLi] ratio. It must be stressed here that in another work [183], the formation of unimodal pt-BuMAs in the presence of Li counterion in THF as well as in neat toluene was described. Polymerization with Li counterion in a mixed solvent toluene/THF of various compositions gives polymers with broad, bimodal MWDs. The addition of a ligand, LiCl, MEEOLi, (see below) or cryptand K211 makes MWDs of the prepared polymers narrower but to a different extent. (Fig. 32).

Regarding the microstructure of pt-BuMA, prevailingly syndiotactic product is formed [182] in THF with the Li counterion. If the mole ratio [LiCl]/[initiator] is 3 or higher, the content of syndiotactic triads

Anionic polymerization of EtHA initiated with the DPHLi/MEEOLi system at -78° C. (Reproduced with the kind permission of Macromolecules 1994;27:4890)

$[EtHA]_0 \ (mol \ l^{-1})$	$[DPHLi]_0 \pmod{l^{-1}}$	Y^{a}	Z^{b}	Z^{b} X_{p} (%)	$M_{\rm n} \times 10^{-3}$ (theor)	SEC	
						$M_{\rm n} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$
0.465	0.01	0	9/1	45	4.0	2.0	3.20
0.465	0.01	2	9/1	90	7.9	24.0	1.70
0.528	0.01	10	9/1	100	10.0	11.0	1.05
0.233	0.0012	10	9/1	98	32.5	36.0	1.10
0.233	0.0012	10	19/1	100	32.5	36.0	1.09
0.212	0.01	10	7/3	99	4.0	4.5	1.15
0.212	0.01	10	6/4	98	4.0	4.7	1.30
0.466	0.005	10	0/10	100	17.6	21.5	2.55

^a Mole ratio [MEEOLi]₀/[DPHLi]₀.

^b Volume ratio toluene/THF.

in the polymer sharply decreases and an isotactic arrangement is enhanced by a factor of about 3 (Table 32).

5.2. Bidentate lithium alkoxides

5.2.1. Homopolymerization of acrylates

Bidentate lithium alkoxides (dual σ -µ ligands) of the general formula CH₃(O-CH₂-CH₂)_nOLi, form strong complexes with a living chain-end (see Section 2.4.2), restricting the tendency for the back-biting reaction even in the polymerization of EtHA and BuA [184]. The best results offers the alkoxide with two ethoxy groups in the molecule (n = 2; MEEOLi); however, the polymerization has to be performed at very low temperatures, i.e. from -78 to -100°C and in a reaction medium with moderate polarity. The same effect of solvent was already found [139,143] in the *t*-BuOLi assisted polymerization of acrylic esters—see Section 4. Some of the results of the "dual-ligated" EtHA polymerizations under variable conditions are shown in Table 33. At -100°C, the two-dose sequential polymerization of EtHA stabilized with MEEOLi produces a polymer without a detectable amount of the first-dose product, whereas at -78°C, a non-negligible part of the active centers from the first-dose polymerization is lost in the interval between the both monomer doses [185]. This means that even at such a low temperature, the

CH ₃ O-(CH ₂ CH ₂ O) ₂ Li	MEEOLi
CH3O – CH2– CH2 O — Li	MEOLi
СН3О-(^{СН} 2 — СНО)2 — Li СН3	MPPOLi
(CH ₃) ₂ N-(-CH ₂ -CH ₂ O) ₂ -Li	NEEOLi

Scheme 36.

Table 34

Polymerization of primary alkyl acrylates in the presence of various bidentate alkoxides (in toluene/THF mixture 9/1 (v/v), mole ratio Initiator/Ligand = 1/10 (m/m)). (Reproduced with the kind permission of JPS, Polym Chem Ed 1997;35:361)

Alkyl Initiator		Ligand	Temperature (°C)	$X_{\rm p}(\%)$	$M_{\rm n} \times 10^{-3}$ (calc)	SEC	
						$M_{\rm n} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$
Bu	DPMLi	NEEOLi	-78	46	8.6	23.0	1.65 ^a
Bu	DPMLi	MPPOLi	-78	25	4.3	13.0	2.00^{a}
Bu	DPHLi	MPPOLi	-78	25	4.4	9.0	2.35
Bu	DPMLi	MEOLi	-78	80	7.0	22.0	3.3
Bu	DPMLi	MEEOLi	-78	100	24.7	34.0	1.30
Bu	DPHLi	MEEOLi	-78	80	_	10.0	1.85
Nonyl	DPMLi	MEEOLi	-78	98	_	14.0	1.20
Et	DPMLi	MEEOLi	-78	100	12.5	19.0	1.30
Et	DPMLi	MEEOLi	-100	99	12.5	17.0	1.80
Me	DPMLi	MEEOLi	-78	100	10.9	13.0	1.50
Me	DPMLi	MEEOLi	-100	98	10.9	13.0	1.60

^a Polymodal MWD.

self-termination reaction in the polymerization process cannot be avoided completely. Moreover, to reach a well-controlled process, MEEOLi has to be combined with sterically hindered initiators. If the polymerization is initiated by a simple alkylmetal (*s*-BuLi), a polymer with a broad MWD is formed, the initiator efficiency is low, and, surprisingly, the process stops at low limiting conversions even in the presence of a ten-fold excess of MEEOLi. Lithium diisopropyl amide or EIB-Li give, however, good results in the presence of MEEOLi, so that the high nucleophilicity of the *s*-BuLi is probably also responsible for the unfavourable results. Similar indications followed already from a comparison of the EtHA polymerization initiated with BuLi or *t*BIB-Li in the presence of *t*-BuOLi under comparable conditions [137,139] (see above).

Various types of bidentate alkoxides (see Scheme 36) were tested as ligands in BuA polymerization at low temperature [186]. Again, MEEOLi only, in combination with a sterically hindered initiator, in particular DPMLi, has the expected and beneficial effect on the polymerization, enabling the formation of pBuA with a narrow MWD in a quantitative yield (Table 34). The DPMLi ligated with MEEOLi was also used in polymerizations of EtA and MeA at -78 and/or -100°C leading to polymers with slightly broadened MWDs. This indicates an increasing tendency of acrylates for side reactions with decreasing length and, in particular, branching of their alkoxy groups which was already stated in earlier works [102–104,142–147]. The extent of self-termination increases with increasing starting monomer concentration and this phenomenon, observed also in MMA polymerization with Na counterion [187]as well as in the polymerization of BuA initiated with the *t*BIB-Li/*t*-BuOLi system [144], has not been satisfactorily explained.

5.2.2. Block and random copolymerization

This type of the "dual-ligated" additives, in a ten-fold excess over the initiator, was successfully used in synthesis of di- and tri-block copolymers composed of MMA and EtHA blocks [188]. The results and reaction conditions are shown in Table 35. If living PMMA is prepared as a first block at -78° C, the final copolymer poly(MMA-*b*-EtHA) has a narrow MWD and does not contain detectable amount of the

MEEOLi-assisted synthesis of poly(MMA-*b*-EtHA) diblock copolymers (initiated with the complex DPMPLi/MEEOLi 1/10 (mol/mol) in a toluene/THF mixture 75/25 (v/v); total monomer conversion 95–100%). (Reproduced with the kind permission of Macromolecules 1994;27:4908)

Monomer		$\operatorname{Poly}(M_1)$			Copolymer			
M_1 (mmol)	M_2 (mmol)	Temperature (°C)	$M_{\rm n} \times 10^{-3}$ (theor)	$M_{\rm n} \times 10^{-3}$ (SEC)	$M_{\rm w}/M_{\rm n}$	$\overline{M_{\rm n} \times 10^{-3}}$ (theor)	$M_{\rm n} \times 10^{-3}$ (SEC)	$M_{\rm w}/M_{\rm n}$
MMA	EtHA							
20	27	-78	5.5	6.0	1.03	19.6	19.2	1.09
30	15	-78	7.0	7.2	1.06	12.5	13.6	1.09
40	10	-78	31.0	33.0	1.08	45.2	46.4	1.09
EtHA	MMA							
13	37	-78	5.1	5.6	1.09	15.0	81.1	1.04^{a}
20	60	-78	8.0	8.1	1.09	24.0	43.3	1.09 ^a
13	110	-100	4.4	4.9	1.10	29.0	31.4	1.10
17	55	-100	5.3	5.3	1.06	17.0	19.1	1.10
27	21	-100	9.4	10.0	1.05	15.0	16.0	1.06

^a Bimodal MWD, in the calculation only the block copolymer peak was considered.

Microstructure of PMMA prepared by DPMLi in various media at -78° C; effect of MEEOLi. (Reproduced with the kind permission of Macromolecules 1994;27:4902)

Solvent	Y^{a}		Triads (%)	
		Iso	Hetero	Syndio
THF	1/0	1	21	78
	1/2	1	16	83
	1/10	1	16	83
Toluene ^b	1/0	88	9	3
	1/2	10	21	69
	1/3	1	18	81
	1/10	1	16	83
tol/THF ^c	1/0	17	25	58
	1/2	5	21	74
	1/3	1	16	83
	1/10	1	16	83

^a Mole ratio [Initiator]/[MEEOLi].

^b Initiated with DPHLi.

^c Toluene/THF 9/1 (v/v).

PMMA. If, however, the polymerization of MMA is initiated with the living poly(EtHA) block under the same conditions, the resulting block copolymer is contaminated with a certain amount of poly(EtHA). To avoid this, the synthesis has to be performed at -100° C, similarly to the two-dose homopolymerization of EtHA mentioned above. The favourable effect of a low reaction temperature could be expected, in particular, if the temperature dependence of the self-termination rate, discussed in Section 4, is considered [142,144] (see Table 18). As for the triblocks, TPDLB was used as an initiator in the presence of ten-fold exces of MEEOLi in a toluene/THF mixture 75/25 (v/v). The copolymers with central PMMA blocks were succesfully prepared, having narrow MWDs and no residual homopolymer in contrast to the opposite arrangement. Even at -100° C, the copolymer poly(MMA-*b*-EtHA-*b*-MMA) has a polymodal MWD while the central block exhibits good and expected characteristics. It is interesting that this triblock copolymer is formed well by a three-step sequentional polymerization initiated with DPMLi using an excess of MEEOLi in a toluene/THF mixture 75/25 at -100° C. The reasons for the behaviour of the former copolymerization are not clear yet.

Strong complexation of (meth)acrylate growing chain-ends with MEEOLi is also evident from its effect on the microstructure of the formed PMMA [134]. Data on tacticities of PMMAs, prepared with DPMLi in various solvents in the presence or absence of MEEOLi, are given in Table 36. Virtually no effect is seen in neat THF, whereas in toluene or a mixture toluene/THF 9/1 (v/v), a three-fold excess of MEEOLi over the initiator changes the tacticity of the formed polymer dramatically. The content of syndiotactic triads sharply increases at the expense of the isotactic ones, so that, under these conditions, the microstructure of PMMA is virtually the same as that of PMMA prepared in a neat THF without any additive. In this sense, the effect of MEEOLi is similar to that of cryptand K211, mentioned in the foregoing section. Thus, in agreement with the results of NMR studies of ester enolate/MEEOLi complexes [90], it can be assumed that even in non-polar solvents, MEEOLi forms strongly ligated

Y ^a	Yield (%)	M_n (SEC)	$M_{\rm w}/M_{\rm n}$ (SEC)	$Z\left(\% ight)^{\mathrm{b}}$
1/0	18	23 400	2.50	92.0
1/1	80	77 900	1.50	54.0
1/2	86	42.6	1.30	45.0
1/5	85	18.5	1.20	44.0
1/10	100	21.7	1.15	42.0

Table 37

Effect of MEEOLi on the anionic copolymerization of MMA/t-BuA mixture initiated with DPMLi in THF at -78° C (MMA/t-BuA mole ratio 58/42). (Reproduced with the kind permission of Macromolecules 1994;27:4635)

^a Mole ratio DPMLi/MEEOLi.

^b Molar content of *t*-BuA in copolymer.

non-aggregated active species of polymerization, which are supposed to be the origin for syndiotactic placement.

MEEOLi also ensures the living character of MMA/t-BuA random copolymerization, in which the stabilizing effect of LiCl was not high enough [177] — see Section 5.1.2. The results of copolymerizations of MMA/t-BuA mixture (58/42, m/m) initiated by DPMLi in THF at -78° C in the presence of various amounts of MEEOLi [189] are given in Table 37. With a ten-fold excess of the ligand, the system produces random MMA/t-BuA copolymers quantitatively. Using a comonomer feed of various compositions, various copolymers can be successfully prepared, exhibiting single various $T_{\rm g}$ values between those of the corresponding homopolymers, in dependence on the composition of the feed. The calculated monomer reactivity ratios; $r_{\rm MMA} = 0.29$ and $r_{t-\rm BuA} = 6.92$ document a distinctly higher reactivity of the acrylate than that of MMA. Similar results were obtained in the copolymerization of the same monomer pair initiated with DPMNa [190] in the presence of a strongly chelating crown-ether DB-18-CE-6.

Thus, chelating ligands promote the living character of a low-temperature (co)polymerization of (meth)acrylates affording the possibility to prepare homopolymers, block and random copolymers [191].

5.3. Alkylaluminiums

5.3.1. Homopolymerization of methacrylates

The favourable effects of simple alkylaluminiums (e.g. Et_3Al) on low-temperature MMA anionic polymerizations was already described by Hatada [10,11,13–16]. It has been recently shown by Ballard et al. [192] that tetraorganylaluminates containing structurally more complex alkylaluminiums with bulky aryloxy substituents (see Scheme 37) and *t*-BuLi, polymerize MMA in toluene in a living manner at room or even at slightly elevated temperatures. This "screened anionic polymerization" is initiated by



Scheme 37.

Run	Al/Li (mol)	$A (mol)^a$	<i>X</i> _p (%)	SEC			
				$M_{\rm n} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$		
1	0.43	179	46	17.1	1.28		
2	0.75	200	75	19.9	1.12		
3	1.07	179	99	29.6	1.18		
4	1.40	186	99	29.4	1.10		
5	2.00	200	99	30.3	1.15		
6	3.00	200	99	28.4	1.09		

Polymerization of MMA initiated with the complex *t*-BuLi/(2,6-di-*tert*-butyl-4-methylphenoxy) diisobutylaluminium (in toluene at 0° C). (Reproduced with the kind permission of Macromolecules 1992;25:5907)

^a Mole ratio [MMA]₀/[t-BuLi]₀.

Table 38

the bimetallic complex lithium tetraalkylaluminate of the general formula $Li^{+}[AlR_{4}]^{-}$. In the polymerization process, Li cation is coordinated with AlR₃, forming a bulky counter-ion which protects the living chain-end against side reactions. The concentration of the alkylaluminium has to be at least the same as that of alkyllithium; an excess of the AlR₃ compound is recomended for practical reasons (purification of the reaction system in situ). NMR studies of the system showed that the *t*-Bu carbanion is a true initiating species; no part of the aluminium compound was found in the polymer. In Table 38, some of the results of MMA polymerization are shown, documenting the effect of the Al/Li mole ratio on the polymerization process. An extremely high stability of the active centres has been demonstrated in a series of experiments in which four equal doses of MMA were successively added to the reaction mixture. The time interval was always 60 min after completion of the reaction taking ca. 5 min per dose, so that the total reaction time was 260 min. The molecular weight of the final product was four times higher than that of the polymer formed from the first monomer dose and its MWD was virtually the same. This was advantageously used for the synthesis of block copolymers composed of various methacrylic esters [193,194]. On average, the initiating efficiency of t-BuLi is ca. 60-70% as estimated from the M_n values. The authors assumed that this was due to the existence of two types of the initiating complex. The first type contains both the components in the ratio Al/Li 1:1 and all t-BuLi is utilized in an initiation reaction, whereas the second one is composed of two molecules of the Al compound and two



Scheme 38.

Table 39

Effect of butyllithium structure and premixing of the reaction components on the MMA polymerization with $RLi/(i-Bu)_3Al$ (1:2) in toluene at 0°C. (Reproduced with the kind permission of Polym Prepr (Am Chem Soc, Div Polym Chem) 1994;35(2):599)

RLi	Components premixed	Conversion (%)	$M_{ m n}$	$M_{\rm w}/M_{\rm n}$
t-BuLi	(i-Bu) ₃ Al/RLi	100	23 700	1.10
	(i-Bu) ₃ Al/MMA	99	28 000	1.18
s-BuLi	(i-Bu) ₃ Al/RLi	100	37 500	2.00
	(i-Bu) ₃ Al/MMA	100	18 200	1.13
BuLi	(i-Bu) ₃ Al/RLi	84	97 100	2.02
Bulli	(i-Bu) ₃ Al/MMA	75	39 300	1.22

molecules of *t*-BuLi and the authors assume that, in the latter case, only one *t*-BuLi molecule can add onto MMA (Scheme 38). If less sterically hindered alkylaluminiums are used, e.g. *i*-Bu₃Al or Et₃Al, the initiating efficiency of the initiator decreases to 50% most likely because of higher aggregation states of these simple tetraorganylaluminates. This is corroborated by the formation of a certain amount of gel [194] in the systems containing simple alkylaluminiums which was not found in polymerizations performed in the presence of bulky organylaluminiums or in those, initiated with the system DPHLi/ Et₃Al at 0°C in the presence of pyridine [195]. The idea of the generation of true active species is demonstrated in Scheme 38. The structure of the alkyllithium as well as the order of mixing of the reactants play an important role [196,197] so that the systems composed of *n*-, *s*-, or *t*-BuLi and *i*-Bu₃Al behave, as to the MWDs of products and attainable monomer conversion, somewhat differently—see Table 39.

5.3.2. Mechanistic studies

It has been shown in Müller's studies [198,199] that bimetallic "ate" complex with the Al/Li mole ratio 1:1 can be regarded as a model for the growing centre in the initial stage of polymerization. This was corroborated by a ¹³C NMR study [199] of the model compound EIB-Li in the presence of AlR₃. The complex, formed according to Scheme 39, has the signal of the carbonyl group shifted upfield and that of the α -carbon atom downfield (see Fig. 33) in a way similar to the analogous signals of silyl enolate MTS (initiator in GTP, cf. Section 1.2). The excess of aluminium alkyl (if used) can coordinate with the carbonyl group of the monomer or polymer. However, it was observed in further studies [200], that this coordination does not accelerate the polymerization process which is in contrast to the dramatic



 $[EIB - AlR_3]$ ⁻Li⁺ "ate" complex

Scheme 39.


Fig. 33. Effect of AlR₃ on the chemical shifts of EIB-Li in the ¹³C NMR spectra in toluene at temperatures below 0°C. (Reproduced with the kind permission of Macromol Rapid Commun 1995;16:399.)

acceleration of the MMA polymerization initiated with metalloporphyrin initiators after the addition of bulky alkyl(diphenoxy)aluminiums as was described by Inoue and Aida [51] (cf. Section 1.2). If an additional dose of AlR₃ was added into the polymerizing mixture (MMA + R'Li + simple AlR₃), the reaction rate even decreased. The lowering of the polymerization rate by AlR₃ addition is demonstrated in Fig. 34 where a significant curvature of the plots in the presence of an alkylaluminium at low conversions as well as linear second parts of the plots (after the kink) are clearly seen. A very similar shape of the plots was obtained in polymerizations with various starting concentrations of monomer or initiator [200] (Fig. 35). As the second parts of all these plots are linear, at least in the measured conversion range, self-termination can hardly be assumed to be a reason for the lowering of the reaction rate. Moreover, it may indicate that the active centres are of one type, either completely aggregated or non-aggregated. The kink on the time-conversion plots clearly relates to a certain monomer conversion (critical monomer conversion, $X_{p,crit}$, see Figs. 34 and 35) in dependence on the starting conditions [200,201], namely on the mole ratio $[MMA]_0/[P^*]_0$. Thus, it is reasonably assumed that the kink position depends on a critical degree of polymerization, $P_{n,crit}$, which was found to range between 2 and 8, rather closer to 2. The first possible explanation is on the basis of a probable coordination of a chain aluminate end-group with a penultimate ester carbonyl according to Scheme 40. According to this consideration,



Fig. 34. Semilogarithmic conversion plots of the MMA polymerizations in toluene at -78° C with Et₃Al/*t*-BuLi at various Al/Li mole ratios. [MMA]₀ = 0.23 mol 1⁻¹; [*t*-BuLi]₀ = 4.5.10 mol 1⁻¹. Al/Li = (1) 0; (2) 1.6; (3) 3.4; (4) 6.0. (Reproduced with the kind permission of Macromol Rapid Commun 1995;16:399.)



Fig. 35. Semilogarithmic conversion plots of MMA polymerizations initiated with *t*-BuLi/AlR₃ in toluene at -78° C. Variation of active centres concentration [P^{*}]₀, calculated from degrees of polymerization. [MMA]₀ = 0.23 mol 1⁻¹; [Et₃Al]₀ = 1.5.10 mol 1⁻¹; [P]₀ = (1)0.46; (2) 1.60; (3) 3.23; (4) 14.4 × 10 mol 1⁻¹. (Reproduced with the kind permission of Macromol Symp 1996;107:163.)

the "ate" complex is operative in the very first stage of the process, and, as soon as possible, probably in a stage of living dimer or trimer, it is changed to a penultimate coordination structure, which might be responsible for a sudden lowering of the polymerization rate. If so, bulkier alkylaluminiums should suppress coordination of the chains which should lead to an increase in $P_{n,crit}$ and, in a limiting case, the kink on the conversion plot should completely disappear. However, this was not verified with another study [202] in which kinked first-order time–conversion plots were found virtually in all experiments inspite of the presence of alkylaluminiums. Moreover, most of the plots exhibit a non-linear course in the second stage of polymerization, i.e. after the kink. Examples are shown in Fig. 36. This can hardly be explained by the penultimate coordination and back-biting self-termination reaction because of the absence of cyclic oxo esters in the product.

Another reason for the kink in the time–conversion plots, and, generally, the reason for a nonlinear shape of the plots, can be seen in the formation of a gel fraction during the course of polymerization [194,202–204] at temperatures $> -60^{\circ}$ C the amount of which, relative to a soluble fraction, increases with increasing monomer conversion. The gel was found to be soluble in toluene after termination with methanol or, if isolated without termination, in polar THF. Moreover, if a new dose of MMA is added to



"ate" complex

penultimate coordination

Scheme 40.

866



Fig. 36. Semilogarithmic conversion plots of the MMA polymerization with *t*-BuLi/R₃Al in toluene. [MMA]₀ = 0.23 mol 1^{-1} ; [*t*-BuLi]₀ = 4.5 × 10⁻³ mol 1^{-1} ; [R₃Al]₀ = 1.5 × 10⁻² mol 1^{-1} : (1) Et₃Al; (2) *i*-Bu₃Al; (3) (neopentyl)₃Al; (4) *t*-Bu₃Al. (Reproduced with the kind permission of Polymer J 1996;28:954.)

this "dissolved gel" in THF under inert conditions, the monomer is converted to polymer extending in this way the chains of a substantial part of the "gel"; thus the insoluble gel-fraction is formed by intermolecular coordination of living PMMA chains. SEC eluograms of the "dissolved gel" and the extended "block" copolymer are shown in Fig. 37 [203]. A tentative structure of this coordination network formed from two unimeric aluminate end-groups is given in Scheme 41; clearly, the dimeric end-groups can coordinate to tetrameric one in a similar way. It is interesting to note that if dissolved "gel" chains were quenched with benzoyl chloride, the total amount of chains is higher than that of benzoyl end-capped ones and no cyclic oxo esters were found in the polymer. This indicates the absence of the back-biting reaction in the gel fraction so that termination probably proceeds via a still unknown process including the formation of "dormant" species, the structure of which has also to be elucidated. Consequently, it is assumed that the process is controlled by two types of active species, soluble and



Fig. 37. SEC eluograms of a "block" copolymer (full line, $M_n = 1617$, $M_w/M_n = 1.8$) obtained by MMA polymerization initiated with a coordinated network (dashed line, $M_n = 1260$, $M_w/M_n = 1.3$) in THF at room temperature; MMA conversion 42%.



Scheme 41.

insoluble, with different kinetics of propagation and termination (Scheme 42). In addition, the type of substituent in R_3Al plays a role in the stereospecific efficiency of the process, because, e.g. Et_3Al or *i*-Bu₃Al-assisted polymerization gives syndiotactic product while *t*-Bu₃Al or (neopentyl)₃Al addition lead to atactic PMMA. If EtO₃Al is used instead of Et_3Al , probably no "ate" complex is formed and both the process and product with broad MWD are virtually the same as observed in aluminium-free anionic polymerization.

Although the MMA polymerization initiated by *t*-BuLi in the presence of bulky alkyl(phenoxy) aluminiums was shown to be at 0°C a perfectly living process [192], the polymerization assisted by simple R_3Al , where R = Et or *i*-Bu, exhibits a certain extent of side reactions in the initiation and propagation steps [204] even at $-78^{\circ}C$. *t*BIK is formed by 1,2-addition of *t*-BuLi onto MMA monomer (cf. Section 1.1) to a various extent at both 0 and $-78^{\circ}C$. Surprisingly, by Matrix-Assisted Laser Desorption Ionization Time-of-flight Mass Spectrometry (MALDI-TOF-MS), a higher content of *t*BIK was observed at the lower temperature [205]. The number of chains contaminated with *t*BIK decreases with an increasing molar ratio Al/Li, and, at the ratio equal to 2 or more, the content of *t*BIK in the polymer is virtually negligible. It was also found [204,206] that self-termination by the backbiting reaction (cf. Section 1.2) proceeds to a detectable extent only in the polymerization at 0°C; in polymers, prepared at $-78^{\circ}C$, no cyclic 2-oxo esters were detected.

The polymerization stabilized with alkylaluminiums is, due to a long lifetimes of the active species, convenient for the tailoring of poly(methacrylate)s, in particular, for the synthesis of block copolymers with various methacrylic esters.



Scheme 42.

6. Conclusion remarks

As tailored polymers with special and predetermined properties are becoming more and more important, methods of controlled polymerization are studied very intensively, in particular, in the field of polar vinyl monomers. Thus, a number of novel ways to tailor-made poly((meth)acrylate)s have been found recently, solving more or less the problems which complicate the process. However, owing to a wide spectrum of monomers with various chemical compositions and reactivities, virtually none of the mentioned polymerization methods is generally applicable, in particular, to the synthesis of block copolymers. Thus, for individual tailored products, a convenient method must be found and, in many cases, reaction conditions have to be optimized. This review, gives a brief summary of one of the many ways for controlling (meth)acrylate polymerization. It is based on classical anionic initiators modified with appropriate ligands, restricting the extent of undesired side reactions. The method is well compatible with the controlled polymerization of non-polar styrene and diene monomers and has its advantages and drawbacks. Nevertheless, it is one of the useful methods for controlling the polymerization process and can lead to tailored polymers.

Acknowledgements

The authors thank Professor Otto Vogl for his kind invitation to contribute this review to *Progress in Polymer Science*. Financial assistance from the Grant Agency of the Czech Republic and from the American-Czech Science and Technology Program are also greatly acknowledged.

References

- [1] Paul DR. In: Paul DR, Newman S, editors. Polymer blends. New York: Academic Press, 1978.
- [2] Tuzar Z, Kratochvíl P. In: Matijevic E, editor. Surface and colloid science, vol 15. New York: Plenum Press, 1993.
- [3] Szwarc M. In: Morton M, editor. Anionic polymerization: principles and practice. New York: Academic Press, 1983.
- [4] Young RN, Quirk RP, Fetters LJ. Adv Polym Sci 1984;56:1.
- [5] Quirk RP, Kuang JJ, Hasegawa H. J Appl Polym Sci, Appl Polym Symp 1994;53:15.
- [6] La Chimie des Acryliques, Techno-Nathan Nouvelle Librairie S.A., Paris, 1987.
- [7] Kawabata N, Tsuruta T. Makromol Chem 1965;86:231.
- [8] Wiles DM, Bywater S. J Phys Chem 1964;68:1983.
- [9] Müller AHE. In: Hogen-Esch TE, Smid J, editors. Recent advances in anionic polymerization. Amsterdam: Elsevier, 1987.
- [10] Hatada K, Kitayama T, Fimikawa K, Ohta K, Yuki H. Polym Bull 1978;1:103.
- [11] Kitayama T, Ute K, Hatada K. Polym J 1984;16:925.
- [12] Glusker DJ, Lysloff I, Stiles E. J Polym Sci 1961;49:315.
- [13] Hatada K, Ute K, Tanaka K, Okamoto Y, Kitayama K. Polym J 1986;18:1037.
- [14] Hatada K, Ute K, Kitayama T, Yamamoto M, Nishimura T, Kashiama M. Polym Bull 1989;21:489.
- [15] Kitayama T, Shimozaki T, Sakamoto T, Yamamoto M, Hatada K. Makromol Chem 1989;15(Suppl):167.
- [16] Hatada K, Kiayama T, Ute K, Nishiura T. Macromol Symp 1995;89:465.
- [17] Warzelhan V, Höcker H, Schulz GV. Makromol Chem 1978;179:2221.
- [18] Janata M, Lochmann L, Müller AHE. Makromol Chem 1990;191:2253.
- [19] Janata M, Lochmann L, Vlček P, Dybal J, Müller AHE. Makromol Chem 1992;193:101.
- [20] Webster OW, Farnham WB, Sogah DY. Eur Pat Appl 0068887, assigned to E.I. DuPont de Nemours & Co., 1983.
- [21] Schubert W, Sitz H, Bandermann F. Makromol Chem 1989;190:2193.
- [22] Catagil H, Jenkins AD. Eur Polym J 1991;27:651.
- [23] Dicker IB, Cohen GM, Farnham WB, Hertler WR, Laganis ED, Sogah DY. Macromolecules 1990;23:4034.

- [24] Witkowski R, Bandermann F. Makromol Chem 1989;190:2137.
- [25] Sogah DY, Hertler WR, Webster OW, Cohen GM. Macromolecules 1987;20:1473.
- [26] Masař B, Vlček P, Kříž J, Kovářová J. Macromol Chem Phys 1994;195:289.
- [27] Masař B, Vlček P. Macromol Chem Phys 1994;195:671.
- [28] Simms JA. Rubber Chem Technol 1991;641:139.
- [29] Brittain WJ. Rubber Chem Technol 1992;65:580.
- [30] Eastmond GC, Grigor J. Makromol Chem, Rapid Commun 1986;7:375.
- [31] Schubert W, Bandermann F. Makromol Chem 1989;190:2721.
- [32] Xu L, Lei W. Chin J Polym Sci 1989;7:299.
- [33] Dicker IB. Polym Prepr (Am Chem Soc, Div Polym Chem) 1988;29(2):114.
- [34] Zhuang R, Müller AHE. Workshop on anionic polymerization and related processes. Mainz, 1992, Abstracts p. 74.
- [35] Webster OW. J Macromol Sci, Pure Appl Chem A 1994;31:927.
- [36] Müller AHE. Macromolecules 1994;27:1685.
- [37] Webster OW, Hertler WR, Sogah DY, Farnham WB, RajanBabu TV. J Am Chem Soc 1983;105:5706.
- [38] Müller AHE. Makromol Chem, Macromol Symp 1990;32:87.
- [39] Quirk RP, Ren J, Bidinger G. Makromol Chem, Macromol Symp 1993;67:351.
- [40] Reetz MT, Ostarek R. J Chem Soc, Chem Commun 1988:213.
- [41] Reetz MT, Knauf T, Minet U, Bingel C. Angew Chem 1988;100:1422.
- [42] Sivaram S, Dhal PK, Kashikar SP, Khisti RS, Shinde BM, Baskaran D. Macromolecules 1991;24:1697.
- [43] Sivaram S, Khisti RP. Makromol Chem, Rapid Commun 1991;12:435.
- [44] Raj DJA, Vadgaonkar PP, Sivaram S. Macromolecules 1992;25:2774.
- [45] Bandermann F, Beckelmann D, Broska D, Fieberg A, Roloff T, Wolters D. Macromol Chem Phys 1995;196:2335.
- [46] Inoue S, Aida T. In: Kroschwitz JI, editor. Encyclopedia of polymer science and engineering, 2nd edn. New York: Wiley, 1990. p. 412.
- [47] Kuroki M, Aida T, Inoue S. J Am Chem Soc 1987;109:4737.
- [48] Adachi T, Sugimoto H, Aida T, Inoue S. Macromolecules 1993;26:1238.
- [49] Kuroki M, Watanabe T, Morita M, Hosokawa Y, Aida T, Inoue S. Polym Prepr Jpn 1991;40:220.
- [50] Sugimoto H, Kuroki M, Watanabe T, Kawamura C, Aida T, Inoue S. Macromolecules 1993;26:3403.
- [51] Aida T. Prog Polym Sci 1994;19:469.
- [52] Sugimoto H, Aida T, Inoue S. Macromolecules 1993;26:4751.
- [53] Kuroki M, Watanabe T, Aida T, Inoue S. J Am Chem Soc 1991;113:5903.
- [54] Hosokawa Y, Kuroki M, Aida T, Inoue S. Macromolecules 1991;24:824.
- [55] Yasuda H, Yamamoto H, Yokota K, Miyake S. J Am Chem Soc 1992;114:4908.
- [56] Yasuda H, Yamamoto H, Yamashita M, Yokota K, Nakamura A, Miyake S, Kai Y, Kanehisa N. Macromolecules 1993;26:7134.
- [57] Yasuda H, Ihara E, Morimoto M, Nodono M, Yoshioka S, Furo M. Macromol Symp 1995;95:203.
- [58] Boffa LS, Novak BM. Macromolecules 1994;27:6993.
- [59] Ihara E, Morimoto M, Yasuda H. Macromolecules 1995;28:7886.
- [60] Yamashita M, Takemoto Y, Ihara E, Yasuda H. Macromolecules 1996;29:1798.
- [61] Yasuda H, Ihara E. Macromol Chem Phys 1995;196:2417.
- [62] Yasuda H, Furo M, Yamamoto H. Macromolecules 1992;25:5115.
- [63] Lochmann L, Lím D. J Organomet Chem 1973;50:9.
- [64] Halaška V, Lochmann L. Collect Czech Chem Commun 1973;38:1780.
- [65] Halaška V, Lochmann L, Lím L. Collect Czech Chem Commun 1968;33:3245.
- [66] Lochmann L, Trekoval J. J Organomet Chem 1975;99:329.
- [67] Lochmann L, Trekoval J. Makromol Chem 1982;183:1361.
- [68] Cram DJ, Kopecky KR. J Am Chem Soc 1959;81:2748.
- [69] Braun D, Herner M, Johnsen U, Kern W. Makromol Chem 1962;51:15.
- [70] Glusker DL, Gallucio RA, Evans RA. J Am Chem Soc 1964;86:187.
- [71] Lochmann L, Pospíšil J, Vodňanský J, Lím D. Collect Czech Chem Commun 1965;30:2187.
- [72] Lochmann L, Doskočilová D, Trekoval J. Collect Czech Chem Commun 1977;42:1355.
- [73] Lochmann L, De RL, Janča J, Trekoval J. Collect Czech Chem Commun 1980;45:2761.

870

- [74] Lochmann L, De RL, Trekoval J. J Organomet Chem 1978;156:307.
- [75] Lochmann L, Trekoval J. Collect Czech Chem Commun 1988;53:76.
- [76] Vancea L, Bywater S. Macromolecules 1981;14:321.
- [77] Vancea L, Bywater S. Macromolecules 1981;14:1776.
- [78] Seebach D. Angew Chem 1988;100:1685.
- [79] Wang JS, Jérôme R, Warin R, Teyssié Ph. Macromolecules 1993;26:1402.
- [80] Kříž J, Dybal J, Vlček P, Janata M. Macromol Chem Phys 1994;195:3039.
- [81] Dybal J, Kříž J. Collect Czech Chem Commun 1994;59:1699.
- [82] Müller AHE, Lochmann L, Trekoval J. Makromol Chem 1987;187:1473.
- [83] Kunkel D, Müller AHE, Janata M, Lochmann L. Makromol Chem Macromol Symp 1992;60:315.
- [84] Müller AHE. In: Hogen-Esch TE, Smid J, editors. Recent advances in anionic polymerization. Amsterdam: Elsevier, 1987. p. 205.
- [85] Kunkel D. PhD Thesis, Johannes Gutenberg University, Mainz, 1991.
- [86] Wang JS, Warin R, Jérôme R, Teyssié Ph. Macromolecules 1993;26:6776.
- [87] Wang JS, Jérôme R, Warin R, Zhang H, Teyssié Ph. Macromolecules 1994;27:3376.
- [88] Zune C, Dubois Ph, Jérôme R, Kříž J, Dybal J, Lochmann L, Janata M, Vlček P. Macromolecules, submitted for publication.
- [89] Zune C, Dubois Ph, Jérôme R, Kříž J, Dybal J, Lochmann L, Janata M, Vlček P. Macromolecules, submitted for publication.
- [90] Wang JS, Jérôme R, Teyssié Ph. Macromolecules 1994;27:4896.
- [91] Kříž J, Dybal J, Janata M, Vlček P. Magn Res Chem 1994;32:S8.
- [92] Wang JS, Jérôme R, Warin R, Teyssié Ph. Macromolecules 1994;27:1691.
- [93] Kříž J, Dybal J, Janata M, Vlček P. Macromol Chem Phys 1995;196:3117.
- [94] Seebach D, Amstutz R, Laube T, Schweizer WB, Dunitz J. J Am Chem Soc 1985;107:5403.
- [95] Kříž J, Dybal J, Janata M, Lochmann L, Vlček P. Macromol Chem Phys 1995;196:3005.
- [96] Dybal J, Kříž J. Collect Czech Chem Commun 1995;60:1609.
- [97] Kříž J, Dybal J, Janata M, Lochmann L, Vlček P. Macromol Chem Phys 1996;197:1889.
- [98] Dybal J, Kříž J. Macromol Theory Simul 1997;6:437.
- [99] Lochmann L, Rodová M, Petránek J, Lím D. J Polym Sci, Polym Chem Ed 1974;12:2295.
- [100] Lochmann L, Trekoval J. Makromol Chem 1981;182:1951.
- [101] Lochmann L, Janata M, Machová L, Vlček P, Mitera J, Müller AHE. Polym Prepr (Am Chem Soc, Div Polym Chem) 1988;29(2):29.
- [102] Kitano T, Fujimoto T, Nagasawa M. Polym J 1997;9:153.
- [103] Busfield WK, Mathwen JM. Polymer 1973;14:137.
- [104] Garrett RS, Goode WE, Gratch S, Kincaid JF, Levesque CL, Spell A, Stroupe JD, Watanabe WH. J Am Chem Soc 1959;81:1007.
- [105] Adler HJ, Lochmann L, Pokorný S, Berger W, Trekoval J. Makromol Chem 1982;183:2901.
- [106] Lochmann L, Pokorný S, Adler HJ, Trekoval J, Berger W. Makromol Chem 1983;184:2021.
- [107] Lochmann L, Trekoval J, Müller AHE. Makromol Chem 1984;185:1819.
- [108] Lochmann L, Müller AHE. Makromol Chem 1990;191:1657.
- [109] Janata M, Lochmann L, Müller AHE. Makromol Chem 1993;194:625.
- [110] Janata M. PhD Thesis, Institute of Macromolecular Chemistry, Prague, 1989.
- [111] Coleman BD, Fox TG. J Chem Phys 1963;38:1065.
- [112] Fayt R, Forte R, Jacobs C, Jérôme R, Ouhadi T, Teyssié Ph, Varshney SK. Macromolecules 1987;20:1442.
- [113] Trekoval J, Lím D. J Polym Sci 1964;C-4:333.
- [114] Trekoval J. Collect Czech Chem Commun 1977;42:1529.
- [115] Wiles DM, Bywater S. Chem Ind 1963:1209.
- [116] Freireich S. Zilkha. J Macromol Sci, Chem A 1972;6:1383.
- [117] Tomoi M, Sekiya K, Kakiuchi H. Polym J (Tokyo) 1974;6:438.
- [118] Viguier M, Collet A, Schué F, Mula B. Br Polym J 1986;18:166.
- [119] Viguier M, Collet A, Schué F, Mula B. In: Hogen-Esch TE, Smid J, editors. Recent advances in anionic polymerization. Amsterdam: Elsevier, 1987. p. 249.

- [120] Trekoval J. J Polym Sci A-1 1971;9:2575.
- [121] Kolář A, Trekoval J, Vlček P. J Macromol Sci, Chem A 1978;12:757.
- [122] Trekoval J. PhD Thesis, Institute of Macromolecular Chemistry, Prague, 1970.
- [123] Trekoval P, Kratochvíl. J Polym Sci A-1 1971;10:1391.
- [124] Trekoval J, Vlček P. Chem Prům 1968;18:312.
- [125] Trekoval J. Collect Czech Chem Commun 1973;38:3769.
- [126] Vlček P, Otoupalová J, Kříž J, Composto RJ, Oslanec R. Polym Prepr (Am Chem Soc, Div Polym Chem) 1997;38(1):446.
- [127] Ishizone T, Hirao A, Nakahama S. Macromolecules 1989;22:2895.
- [128] Trekoval J, Vlček P, Lím D. Collect Czech Chem Commun 1971;36:3032.
- [129] Vlček P, Trekoval J. Makromol Chem 1975;176:2595.
- [130] Vlček P. PhD Thesis, Institute of Macromolecular Chemistry, Prague, 1975.
- [131] Lochmann L, Rodová M, Trekoval J. J Polym Sci, Polym Chem Ed 1974;12:2091.
- [132] Lochmann L. Unpublished results.
- [133] Lochmann L, Kolařík J, Doskočilová D, Vozka S, Trekoval J. J Polym Sci, Polym Chem Ed 1979;17:1727.
- [134] Wang JS, Jérôme R, Teyssié Ph. Macromolecules 1994;27:4902.
- [135] Overberger CG. Macromolecular syntheses, vol. 1. New York: Wiley, 1963.
- [136] Vlček P. J Polym Sci, Part A, Polym Chem 1990;28:2917.
- [137] Vlček P, Kříž J. J Polym Sci, Part A, Polym Chem 1992;30:1511.
- [138] Vlček P, Janata M, Otoupalová J. J Polym Sci, Part A, Polym Chem 1992;30:1519.
- [139] Vlček P, Lochmann L, Otoupalová J. Makromol Chem, Rapid Commun 1992;13:163.
- [140] Vlček P, Otoupalová J, Kříž J. Makromol Chem 1993;194:841.
- [141] Mrkvičková L, Daňhelka J, Vlček P. Polym Commun 1990;34:416.
- [142] Vlček P, Jakeš J, Otoupalová J. Collect Czech Chem Commun 1993;58:2565.
- [143] Dvořánek L, Vlček P. Polym Bull 1993;31:393.
- [144] Dvořánek L, Vlček P. Macromolecules 1994;27:4881.
- [145] Vlček P, Otoupalová J, Jakeš J. Polym Prepr (Am Chem Soc, Div Polym Chem) 1997;38(1):491.
- [146] Vlček P, Dvořánek L, Otoupalová J. Polym Prepr (Am Chem Soc, Div Polym Chem) 1994;35(2):601.
- [147] Vlček P, Dvořánek L, Otoupalová J. 208th ACS Meeting. Washington DC, Abstract POLY 1994;0502.
- [148] Vlček P, Dvořánek L, Otoupalová J, Lochmann L. Polym Bull 1995;34:1.
- [149] Jakeš J. Collect Czech Chem Commun 1993;58:2349.
- [150] Vlček P, Lochmann L. Makromol Chem, Macromol Symp 1993;67:111.
- [151] Guyot A, Vialle J. J Macromol Sci A 1970;4:79.
- [152] Cazzaniga L, Cohen RE. Macromolecules 1989;22:4125.
- [153] Ogle CA, Wang XL, Carlin CM, Strickler FH, Gordon III B. Submitted for publication.
- [154] Freyss D, Rempp P, Benôit H. Polym Lett 1964;2:217.
- [155] Vlček P, Dvořánek L, Janata M. Otoupalová. Macromol Symp 1995;95:27.
- [156] Vlček P, Otoupalová J, Sikora A, Kříž J. Macromolecules 1995;28:7262.
- [157] Varshney SK, Hautekeer JP, Fayt R, Jérôme R, Teyssié Ph. Macromolecules 1990;23:2618.
- [158] Klein JW, Gnanou Y, Rempp P. Polym Bull 1990;24:39.
- [159] Antolin K, Lamps JP, Rempp P, Gnanou Y. Polymer 1990;31:967.
- [160] Varshney SK, Bayard Ph, Jacobs C, Jérôme R, Fayt R, Teyssié Ph. Macromolecules 1992;25:5578.
- [161] Gnanou Y. Polymer 1994;35:4011.
- [162] Asami R, Takaki M, Moriyama T. Polym Bull 1986;16:125.
- [163] Schulz GO, Milkowitch R. J Appl Polym Sci 1982;27:4773.
- [164] Hautekeer JP, Varshney SK, Fayt R, Jacobs C, Jérôme R, Teyssié Ph. Macromolecules 1990;23:3893.
- [165] Varshney SK, Jacobs C, Hautekeer JP, Bayard Ph, Jérôme R, Fayt R, Teyssié Ph. Macromolecules 1991;24:4997.
- [166] Müller AHE. In: McGrath JE, editor. Anionic polymerization: kinetics, mechanism and synthesis, 166. ACS Symp, 1981. p. 441.
- [167] Nugay N, Hosotte C, Nugay T, Riess G. Eur Polym J 1994;30:1187.
- [168] Hild G, Lamps JP, Rempp P. Polymer 1993;34:2875.
- [169] Hild G, Lamps JP. Polymer 1995;36:4841.

872

- [170] Antoun S, Wang JS, Jérôme R, Teyssié Ph. Polymer 1996;37:5755.
- [171] Lutz P, Franta E, Rempp P. Polymer 1982;23:1953.
- [172] Ladd BJ, Hogen-Esch TE. Polym Prepr (Am Chem Soc, Div Polym Chem) 1989;30(1):261.
- [173] Yu JM, Dubois Ph, Teyssié Ph. Macromolecules 1996;29:6090.
- [174] Yu JM, Dubois Ph, Jérôme R. Macromolecules 1996;29:8362.
- [175] Yu JM, Dubois Ph, Jérôme R. Macromolecules 1996;29:7316.
- [176] Dubois Ph, Jérôme R, Teyssié Ph. J Polym Sci, Part A: Polym Chem 1996;34:2221.
- [177] Jacobs C, Varshney SK, Hautekeer JP, Fayt R, Jérôme R, Teyssié Ph. Macromolecules 1990;23:4024.
- [178] Vlček P. Upublished results.
- [179] Wang JS, Jérôme R, Warin R, Teyssié Ph. Macromolecules 1993;26:5984.
- [180] Baumgarten JL, Müller AHE, Hogen-Esch TE. Macromolecules 1991;24:353.
- [181] Müller AHE. Makromol Chem 1981;182:2863.
- [182] Varshney SK, Gao Z, Zhong XF, Eisenberg A. Macromolecules 1994;27:1076.
- [183] Wang JS, Zhong H, Jérôme R, Teyssié Ph. Macromolecules 1995;28:1758.
- [184] Bayard P, Jérôme R, Teyssié Ph, Varshney SK, Wang JS. Polym Bull 1994;32:381.
- [185] Wang JS, Bayard P, Jérôme R, Varshney SK, Teyssié Ph. Macromolecules 1994;27:4890.
- [186] Nugay N, Nugay T, Jérôme R, Teyssié Ph. J Polym Sci, Part A: Polym Chem 1997;35:361.
- [187] Gerner FJ, Höcker H, Müller AHE, Schulz GV. Eur Polym J 1984;20:349.
- [188] Wang JS, Jérôme R, Bayard P, Teyssié Ph. Macromolecules 1995;27:4908.
- [189] Wang JS, Jérôme R, Bayard P, Patin M, Teyssié Ph, Vuillemin B, Heim Ph. Macromolecules 1995;27:4635.
- [190] Wang JS, Jérôme R, Bayard P, Baylac L, Patin M, Teyssié Ph. Macromolecules 1994;27:4615.
- [191] Teyssié Ph, Bayard Ph, Jérôme R, Varshney SK, Wang JS. Macromol Symp 1995;98:171.
- [192] Ballard DHG, Bowles RJ, Haddleton DM, Richards SN, Sellens R, Twose DL. Macromolecules 1992;25:5907.
- [193] Haddleton DM, Muir AVG, O'Donnel JP, Twose DL. Polym Prepr (Am Chem Soc, Div Polym Chem) 1993;34(2):564.
- [194] Haddleton DM, Muir AVG, O'Donnel JP, Richards SN, Twose DL. Macromol Symp 1995;91:93.
- [195] Wang JS, Jérôme R, Teyssié Ph. Macromolecules 1995;28:2990.
- [196] Haddleton DM, Hunt KH. Polym Prepr (Am Chem Soc, Div Polym Chem) 1994;35(2):599.
- [197] Haddleton DM, Hunt KH, Crossman MC. Macromol Symp 1996;107:177.
- [198] Schlaad H, Müller AHE. Polym Prepr (Am Chem Soc, Div Polym Chem) 1994;35(2):597.
- [199] Schlaad H, Müller AHE, Kolshorn H. Macromol Rapid Commun 1994;15:517.
- [200] Schlaad H, Müller AHE. Macromol Rapid Commun 1995;16:399.
- [201] Schlaad H, Müller AHE. Macromol Symp 1995;95:13.
- [202] Schlaad H, Müller AHE. Macromol Symp 1996;107:13.
- [203] Schlaad H, Müller AHE. Polym J 1996;28:954.
- [204] Schlaad H, Müller AHE, Kolshorn H, Krüger RP. Polym Bull 1995;35:169.
- [205] Hunt KH, Crossman MC, Haddleton DM, Lloyd PM, Derrick PJ. Macromol Rapid Commun 1995;16:725.
- [206] Maloney DR, Hunt KH, Lloyd PM, Muir AVG, Richards SN, Derrick PJ, Haddleton DM. J Chem Soc, Chem Commun 1995:561.