Synthesis of block copolymers by atom transfer radical polymerization of *tert*-butyl acrylate with poly(oxyethylene) macroinitiators

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SUMMARY: Poly(oxyethylene)s terminated at both ends with 2-bromopropionate end-groups were prepared and characterized by means of MALDI TOF mass spectrometry. It was shown, that atom transfer radical polymerization (ATRP) of methyl methacrylate with a poly(oxyethylene) macroinitiator in bulk proceeds with low initiation efficiency while polymerization of *tert*-butyl acrylate proceeds with practically quantitative initiation, leading to ABA block copolymers. Originally formed *tert*-butyl acrylate blocks contain terminal bromine, as expected for the ATRP mechanism. MALDI TOF analysis indicates, however, that in the later stages of polymerization side reactions lead to elimination of terminal bromine.

Introduction

Recent developments in the area of controlled radical polymerization processes opened new synthetic possibilities for the synthesis of well defined polymers from monomers polymerizing by radical mechanism[1–6]. In many systems sequential polymerization could be successfully conducted, leading to well defined block copolymers, including block copolymers comprising blocks formed by different polymerization mechanisms[7].

Due to the versatility of ionic ring-opening polymerization, allowing the preparation of polymers with different structures of the main chain, the combination of controlled ionic ring-opening and controlled radical polymerizations is of special interest for the synthesis of novel block copolymers. Both nitroxide mediated[8–10] and atom transfer radical polymerizations[11, 12] were applied to prepare block copolymers from radically polymerizable monomers and macroinitiators, obtained by ionic ring-opening polymerization.

Atom transfer radical polymerization (ATRP) is a convenient method for the preparation of block copolymers, because the 2-bromopropionate group, which is an efficient initiator of ATRP polymerization, can easily be introduced as the end-group to different polymers obtained by ionic mechanism, either by direct termination of living ionic active species or by esterification of hydroxy terminated polymers (e.g. poly(oxyethylene) diols). The first approach has been recently used to prepare block copolymers of poly(tetrahydrofuran) with styrene[12] while block copolymers of poly(oxyethylene) with styrene were obtained by the second approach[11].

The aim of the present work was the synthesis of ABA block copolymers in which block B is poly(oxyethylene) (POE) and block A is poly(*tert*-butyl acrylate) containing

ester groups, which may be hydrolysed relatively easily, leading eventually to double hydrophilic block copolymers, which show interesting cation binding properties[13]. POE macroinitiators were prepared and characterized and ATRP polymerization of *tert*-butyl acrylate initiated by POE macroinitiators was investigated in both in model and real systems.

Experimental part

Ethyl 2-bromopropionate (Aldrich) and pentamethyldiethylenetriamine (PMDETA) (Aldrich) were purified by distillation (*b. p.* = 156–160 °C and 198 °C, respectively), CuBr (Aldrich) was purified according to the procedure described in the literature[14].

Poly(oxyethylene) macroinitiators were obtained from commercially available (Aldrich) poly(oxyethylene) diols with $\bar{M}_n$ = 1 500, 6 000 or 20 000 and 2-bromopropionyl bromide (Aldrich) according to the following procedure:

9.89 g (1.65 mmol) of poly(oxyethylene) diol with $\bar{M}_n$ = 6 000 (or equivalent amounts of poly(oxyethylene) diols with $\bar{M}_n$ = 1 500 or 20 000) was dissolved in 25 mL of acetonitrile. 0.97 g (17 mmol) of solid CaO was added and 1.81 g (7.9 mmol) of 2-bromopropionyl bromide was introduced dropwise at room temperature to the stirred suspension. After 48 h, 15 mL of CH₂Cl₂ was added, the solution was filtered and washed three times with 50 mL of water. The product was isolated by evaporation of solvents on the rotary evaporator and finally dried on a vacuum line at 70°. To achieve complete functionalization, the described procedure was repeated three times. The products were analysed by GPC, ¹H NMR and MALDI TOF mass spectrometry.

Monomers and solvents were purified by distillation.

Polymerizations were carried out using typical procedure for ATRP polymerization, as described in the literature[15]. CuBr was used as catalyst and multidentate aliphatic amine

(pentamethyldiethylenetriamine (PMDETA)) as complexing agent[15]. Polymerizations were carried out in ampoules, which after several freeze-thaw cycles were sealed in vacuum. Polymers were isolated by evaporation of volatiles and analysed without reprecipitation.

^{1}H NMR spectra were recorded with Bruker MSL 300 MHz spectrometer, in CDCl$_3$ solvent.

MALDI TOF mass spectra were recorded with Voyager Elite MALDI TOF mass spectrometer, using dihydroxybenzoic acid as a matrix.

GPC measurements were performed using LKB 2150 HPLC pump and a set of TSK-GEL G2000 HXL and G4000 HXL columns with CH$_2$Cl$_2$ as eluent. Polystyrene calibration was used to calculate the $\bar{M}_n$ values.
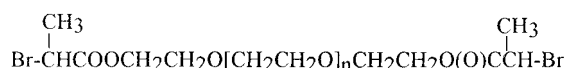
Results and discussion

Characterization of poly(oxyethylene) macroinitiators

Poly(oxyethylene)s terminated at both ends with 2-bromopropionate groups were obtained from poly(oxyethylene) (POE) diols and 2-bromopropionyl bromide as described in the Experimental part. Reaction proceeded exclusively at the chain ends, without affecting the backbone, as evidenced by GPC analysis. Number average molecular weights, determined by GPC, increased slightly (e.g. from $\bar{M}_n = 5860$ for POE diol to $\bar{M}_n = 6870$ for POE macroinitiator) after esterification due to the incorporation of relatively large end-groups, while the $\bar{M}_w/\bar{M}_n$ ratio remained unchanged ($\bar{M}_w/\bar{M}_n = 1.095$ and

1.10, respectively). Fig. 1 shows the MALDI TOF spectrum of the product with $\bar{M}_n = 6870$ (according to GPC).

Two series of signals are present in the spectra; within each series signals are separated by 44 molecular weight units, which corresponds to the molecular weight of the oxyethylene repeating unit. The minor series is shifted towards higher molecular weights by 16 molecular weight units from the major series; both series have the same molecular weight distribution. This leads to the conclusion, that only one homologous series is present in the analysed sample, giving signals of species cationated with Na$^+$ (major series) and K$^+$ (minor series), as frequently observed in MALDI TOF spectra. The observed molecular weights correspond to the expected structure with two 2-bromopropionate ester end-groups:

Scheme 1:

$$\underset{\text{Br-CHCOOCH}_2\text{CH}_2\text{O}[\text{CH}_2\text{CH}_2\text{O}]_n\text{CH}_2\text{CH}_2\text{O(O)CCH-Br}}{\overset{\text{CH}_3\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{CH}_3}{\mid\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\mid}}$$

Thus, for the oligomer with $DP_n = 151$, the calculated molecular weight is equal to 6962.98 (+Na$^+$) and 6978.98 (+K$^+$) while the values observed for major and minor series are equal to 6963.4 and 6979.3, respectively.

The results of MALDI TOF analysis show, that applied experimental procedure leads to complete functionalization of POE and resulting difunctional macroinitiator is essentially free from POE diol and/or monoester.
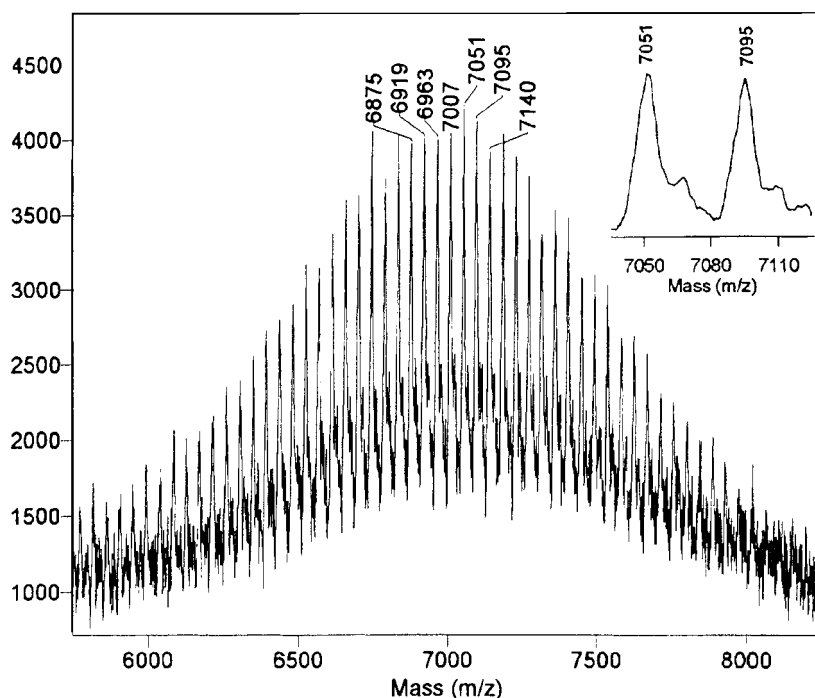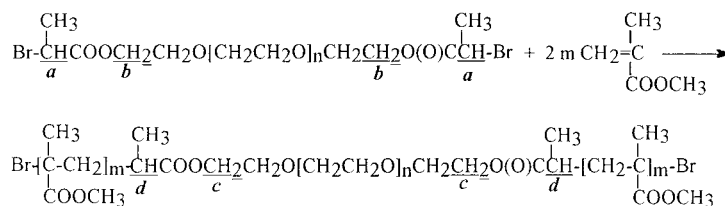

Fig. 1. MALDI TOF mass spectra of poly(oxyethylene) macroinitiator prepared from poly(oxyethylene) diol with $\bar{M}_n = 6000$. In the upper right corner, the expanded fragment of the spectrum is shown

Scheme 2:

$$Br\text{-}\underset{a}{\underline{C}H}COO\underset{b}{\underline{CH_2}}CH_2O[CH_2CH_2O]_nCH_2\underset{b}{\underline{CH_2}}O(O)C\underset{a}{\underline{C}H}\text{-}Br \;+\; 2\,m\,CH_2\!=\!\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \longrightarrow$$

$$Br\text{-}[\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2]_m\text{-}\underset{c}{\underline{C}H}COO\underset{d}{\underline{CH_2}}CH_2O[CH_2CH_2O]_nCH_2\underset{d}{\underline{CH_2}}O(O)C\underset{c}{\underline{C}H}\text{-}[CH_2\text{-}\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}]_m\text{-}Br$$

Efficiency of initiation of atom transfer radical polymerization (ATRP) by POE macroinitiators

For the synthesis of block copolymers free of homopolymer fraction, it is essential, that initiation by the macroinitiator is quantitative. POE macroinitiators used in this work were fitted with end-group resembling closely the typical initiator of ATRP, namely ethyl 2-bromopropionate. The initiating groups connected as end-group to the polymer chain may be, however, less easily accessible to the monomer molecules than the same groups in low molecular weight initiators and the efficiency of initiation by macroinitiators may depend on the conformation of the macroinitiator chains in solution. This was indeed shown for a model system, in which ATRP polymerization of methyl methacrylate (MMA) was conducted with POE macroinitiators in bulk or in different solvents.

The initiation efficiency in this system can be followed by ^{1}H NMR. Groups denoted as *a* and *b* in POE macroinitiators are transformed upon initiation into groups denoted as *c* and *d* at the junction points of two blocks in the block copolymer (cf. Scheme 2).

The signals of the protons of the groups *d* overlap with the signals of the POE backbone, but the signals of the protons of the groups *a*, *b* and *c* are well resolved and can be observed separately. Thus, the progress of initiation may be followed by observing the disappearance of signal *a* and transformation of signal *b* into signal *c*. Fig. 2 shows the relevant regions of the ^{1}H NMR spectra of the reaction mixtures of ATRP polymerization of MMA with POE macroinitiators in bulk and three different solvents.

In all cases the spectra were recorded after sufficiently long reaction times to ensure comparable and high conversions of MMA (exceeding 80 mol-%) irrespective of
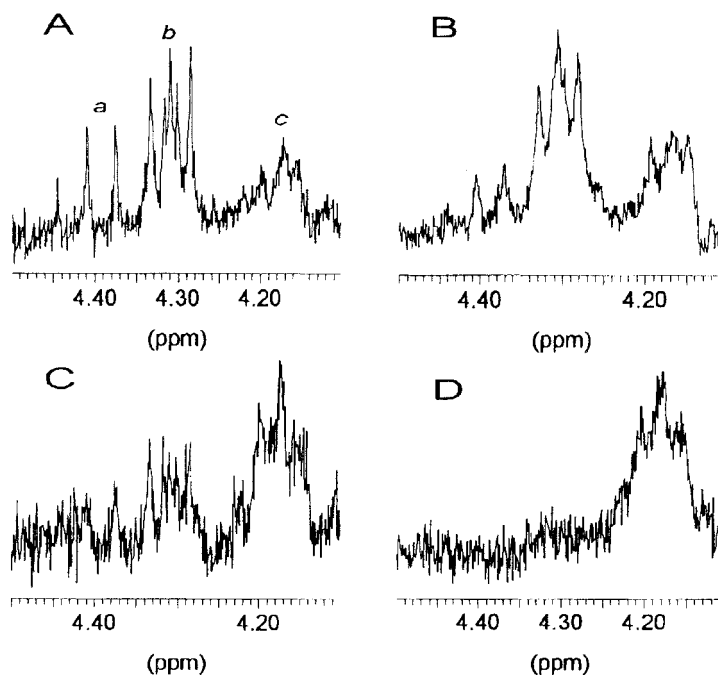

Fig. 2. The expanded fragments of ^{1}H NMR spectra of methyl methacrylate (MMA) polymerizing with poly(oxyethylene) macroinitiator at 80° for 2 h. [MMA]/[CH$_3$CHBrCOO⁻] = 100, [CH$_3$CHBrCOO⁻]/[CuBr]/[PMDETA] = 1/2/4. (A) In bulk. Conversion of the initiating groups determined from the spectra ≅25%; (B) in toluene. Conversion of the initiating groups determined from the spectra ≅35%; (C) in 1,4-dioxane. Conversion of the initiating groups determined from the spectra ≅70%; (D) in glyme. Conversion of the initiating groups determined from the spectra ≅100%. The assignments of the signals a, b and c as in Scheme 2

possible differences in polymerization rates. Although due to the low concentration of initiating groups the quality of the spectra is rather poor, it is evident, that at comparable MMA conversion, the degree of conversion of initiating groups in POE macroinitiators is very much different. In bulk and in toluene solution the initiation efficiency is poor, it is moderate in 1,4-dioxane solution and only in glyme (dimethyl ether of ethylene glycol, which is a good solvent for POE) the initiation is nearly quantitative. These results clearly show, that reaction conditions elaborated for homopolymerization with low molecular weight initiators are not necessarily suitable for the preparation of block copolymers with macroinitiators, because the accessibility of initiating groups, connected as end-groups to the polymer chain, may depend quite strongly on the properties of the solvent. This may be especially pronounced, when, as in the studied case, the properties of both blocks differ considerably.

This limitation may be of no critical importance when a relatively low molecular weight (oligomeric) macroinitiator is used, but it may become increasingly important with increasing molecular weight of the macroinitiator.

Synthesis of block copolymers by ATRP polymerization of tert-butyl acrylate with POE macroinitiators

ATRP polymerization of *tert*-butyl acrylate (tBA) with POE macroinitiators, was carried out at typical polymerization conditions with CuBr/PMDETA as catalytic system[15]. On the basis of the results of the model system, glyme was used initially as a solvent. The system, however, was heterogeneous, and the resulting polymers showed broad molecular weight distribution. The reaction seemed to proceed cleanly in bulk, thus, the efficiency of initiation in the system POE macroinitiator – bulk tBA was checked by ^{1}H NMR, as desribed earlier in this paper. Fig 3.1 shows the relevant regions of the spectra of the POE macroinitiator and reaction mixture at high (>80 mol-%) conversion of tBA. The results show, that in contrast to the bulk MMA-POE macroinitiator system (cf. Fig. 2), the efficiency of initiation in the case of the bulk tBA-POE macroinitiator system is nearly quantitative, which reflects different properties of both monomers as solvents for POE.

Fig 3.2 shows the GPC curves for POE macroinitiator and block copolymer. The product shows monomodal molecular weight distribution. By comparing the elution volumes it may be concluded, that macroinitiator has been practically completely consumed. The results of the experiments are collected in Tab. 1.

The results of Tab. 1 show, that ABA block copolymers (A = poly-tBA, B = poly-EO) with well defined structure, desired lengths of both blocks and relatively narrow molecular weight distribution are formed at the applied conditions.

Analysis of the structure of the products of ATRP polymerization by MALDI TOF mass spectrometry

The unequivocal confirmation of the structure of the polymers may by obtained by MALDI TOF mass spectrometry. This method provides information not on the aver-
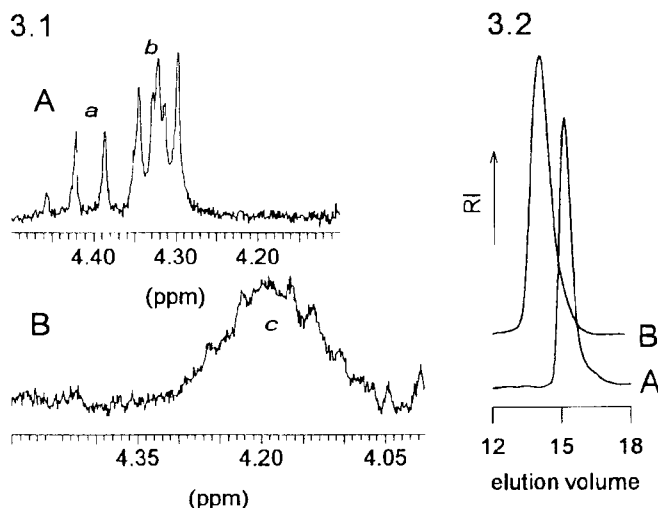

Fig. 3.1. The expanded fragments of the ^{1}H NMR spectra of poly(oxyethylene) macroinitiator (upper spectrum – A) and *tert*-butyl acrylate (tBA) polymerizing with poly(oxyethylene) macroinitiator at 80° for 4 h (lower spectrum – B). The assignments of the signals as in Fig. 2.

3.2. GPC chromatograms of poly(oxyethylene) macroinitiator (lower curve – A) and block copolymer – product of polymerization of *tert*-butyl acrylate with poly(oxyethylene) macroinitiator (upper curve – B)

Tab. 1.   Calculated and found $\bar{M}_n$ values for block copolymers prepared by ATRP polymerization of *tert*-butyl acrylate with poly(oxyethylene) macroinitiators. Polymerization in bulk at $80°$ for 4 h. [CH₃CHBrCOO⁻]/[CuBr]/[PMDETA] = 1/1/4

| POE macroinitiator | | Block copolymer | | |
$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ calculated	$\bar{M}_n$ found, GPC	$\bar{M}_w/\bar{M}_n$
2370	1.10	5100	4970	1.24
6870	1.10	14000	14100	1.35

aged structure of the products present in the analysed sample but on the structure of individual macromolecules. MALDI TOF mass spectra of block copolymers are difficult to analyse, due to the overlapping of two molecular weight distributions (one resulting from the polydispersity of the POE blocks and the other from the polydispersity of the P-tBA block) which leads to a complex spectrum in which unequivocal assignments are questionable. For this reason, the MALDI TOF spectra of tBA homopolymers, prepared with ethyl 2-bromopropionate as initiator (model of initiating groups in POE macroinitiators) were analysed.

Polymerization was carried out in bulk at 60 °C. Samples were withdrawn at different stages of polymeriza-

Tab. 2.   Polymerization of *tert*-butyl acrylate with ethyl 2-bromopropionate as initiator. Polymerization in bulk at 60°. Reaction conditions: [tBA] = 15.3 mmol, [CH₃CHBrCOOC₂H₅] = 1.00 mmol, [CuBr] = 1.05 mmol, [PMTEDA] = 2.09 mmol

No.	Time in min	tBA conv. in mol-%	$\bar{M}_n$ GPC[a]	$\bar{M}_w/\bar{M}_n$
1	15	36	1290	1.14
2	35	80	2320	1.15
3	60	96	2780	1.13
4	110	100	2690	1.14
5	200	100	2830	1.14

[a]   Determined with polystyrene calibration. The calculated $\bar{M}_n$ at complete tBA conversion is equal to $\bar{M}_n = 2150$.

tion; tBA conversion was determined from ¹H NMR and $\bar{M}_n$ of the polymer from GPC. The results are presented in Tab. 2.

The polymers isolated at different stages of polymerization were analysed by MALDI TOF mass spectrometry. Fig. 4 shows results obtained for samples 1, 2, 3 and 5.

In sample 1 essentially one homologous series of signals is observed: The signals are separated by 128 molecular weight units, which corresponds to the molecular weight of the tBA unit. The molecular weights observed
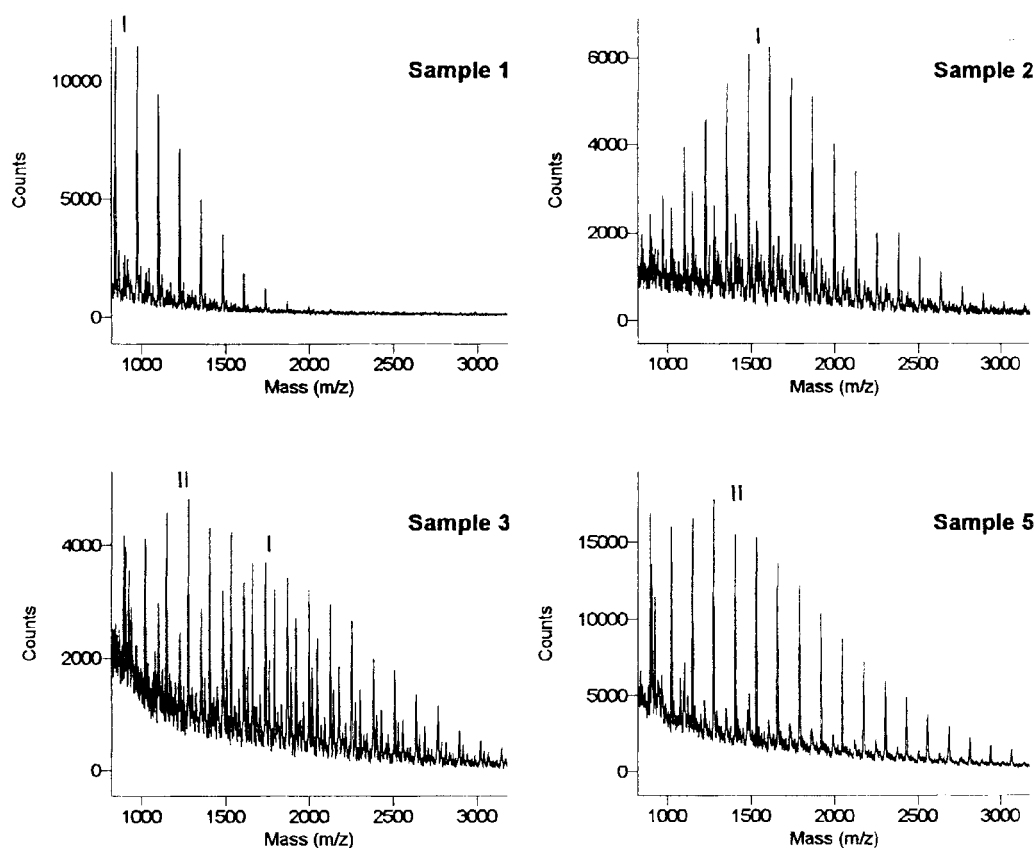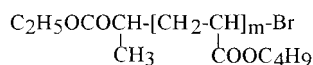

Fig. 4.   MALDI TOF mass spectra of the products of the polymerization of t*ert*-butyl acrylate initiated with ethyl 2-bromopropionate, isolated at different reaction times. Numbers correspond to the numbers in Tab. 2

for the components of the series correspond to the formula:
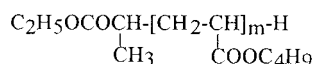
Scheme 3:

$$C_2H_5OCOCH\text{-}[CH_2\text{-}CH]_m\text{-}Br$$
$$\underset{CH_3}{\quad\quad\quad\;} \quad \underset{COOC_4H_9}{\quad\quad}$$

e.g. for $m = 10$ the calculated molecular weight is equal to 1485.72 (+Na$^+$) while the observed value is equal to 1484.96.

The analysis of the shape of the individual signals reveals, that the isotope distribution is characteristic of the species containing bromine; the observed distribution is compared with the calculated one in Fig. 5(A).

With progress of the reaction, the character of the MALDI TOF spectra changes. In sample 2 the signals of the main series (series I) are shifted towards higher molecular weight values due to the progress of polymerization but a new series (series II) appears for which the molecular weights correspond to the structure devoid of terminal bromine:

Scheme 4:

$$C_2H_5OCOCH\text{-}[CH_2\text{-}CH]_m\text{-}H$$
$$\underset{CH_3}{\quad\quad\quad\;} \quad \underset{COOC_4H_9}{\quad\quad}$$

e.g. for $m = 10$ the calculated molecular weight is equal to 1405.82 (+Na$^+$) while the observed value is equal to 1405.3.

The isotope distribution observed for individual peaks is different from that in series I. The comparison of the observed isotope distribution and the isotope distribution calculated for the structure shown in Scheme 4 is shown in Fig. 5(B), confirming clearly the absence of bromine in the polymers of series II.

After still longer reaction time the proportion of the signals of series II gradually increases and in sample 5 practically only the signals of series II are observed (cf. Fig. 4).

It should be noted, that conversion of tBA is high ($\cong 80$ mol-%) already in sample 2. Thus the changes observed in the later stages of polymerization are not due to the formation of a new population of macromolecules by a mechanism different from that operating at the earlier stages but rather to the transformation of macromolecules of series I into macromolecules of series II.

One possible explanation is a termination reaction i.e. recombination or disproportionation of two macroradicals. Recombination, however, would lead to macromolecules containing two propionate ester end-groups. No signals corresponding to such a series are observed in the MALDI TOF spectra. Disproportionation, on the other hand, would give a series corresponding to the structure shown in Scheme 4 but this series should be accompanied by another series, containing terminal unsaturation i.e. having molecular weight lower by two units. This should give a characteristic pattern in the mass spectra, which is not observed.
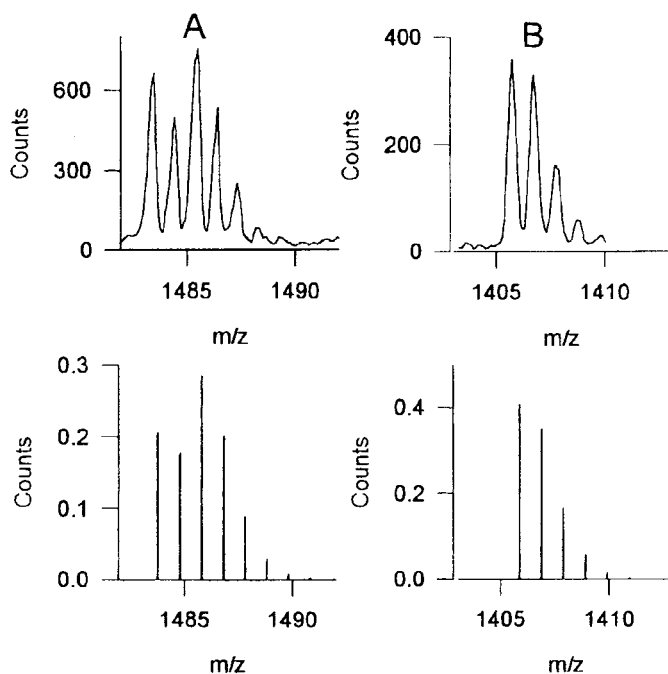

Fig. 5. Comparison of the calculated (lower spectra) and observed (upper spectra) isotope distributions for signals of the polymer with $DP_n = 10$: (A) belonging to series I (with terminal bromine, cf. structure (3)), (B) belonging to series II (without terminal bromine, cf. structure (4))

The analysis of the shape of the signal (cf. Fig. 5b) shows clearly, that only one series, with molecular weights corresponding exactly to the structure shown in Scheme 4 is observed. Thus, we conclude, that the reaction leading to elimination of the terminal bromine is not recombination or disproportionation but hydrogen abstraction from one of the components of the system to the macroradical, existing in equilibrium with the bromine terminated macromolecule even after complete consumption of the monomer. The possible participation of aliphatic amine (PMDETA), being the component of the catalytic system, can not be excluded, because it was shown, that such amines are hydrogen radical donors, at least in the redox initiated polymerization of acrylamide in aqueous media[16]. The nature of the side reaction is presently under investigation.

The similar effect was observed for ATRP polymerization of acrylonitrile. In this system, however, only small amounts of polymer devoid of the terminal bromine were observed after relatively long reaction times[17].

If the proposed explanation is correct, then the molecular weight distribution for both series should be nearly the same (upon losing bromine the molecular weight should decrease by about 80 molecular weight units). It appears from the mass spectra, that the maximum for series II is shifted considerably towards lower molecular weights. This, however, may be only an artefact due, for example, to the different abilities to undergo ionization for macromolecules belonging to both series, at the conditions of the MALDI TOF experiments. The results of GPC analysis (cf. Tab. 2) confirm unequivocally, that number average molecular weights increase slightly (due to the increasing monomer conversion) and not decrease as it could appear from the mass spectra.

We conclude, therefore, that at the applied conditions, polymerization of tBA initiated with POE macroinitiators proceeds in a controlled manner according to the ATRP mechanism, leading to block copolymers with expected molecular weights and relatively narrow molecular weight distribution. The resulting copolymers have originally bromine atoms at the chain end, as expected. The process is, however, not entirely free of side reactions leading to the elimination of terminal bromine. These side reactions are apparently slower than propagation, thus at the earlier stages, when the concentration of unreacted monomer is still relatively high, propagation dominates and contribution of side reactions is negligible. At the final stages of polymerization, when the concentration of the monomer is already low, the consequences of side reactions are becoming more pronounced and gradually all the macromolecules are transformed from their active (i. e. containing terminal bromine) form into inactive (without terminal bromine) form.

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