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POLYMERIC DESIGN BY MACROMONOMER TECHNIQUE

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1. INTRODUCTION

'Macromonomer' or 'macromer' is an abbreviation for macromolecular monomer and hence it is a monomer and a polymer at the same time, with a molecular weight of, say, 10^3–10^4. It usually contains a polymerizable group on one chain end, so that it can either homopolymerize to give a regular comb polymer or copolymerize with a conventional monomer to give a graft copolymer, as illustrated in Fig. 1. Thus the macromonomer

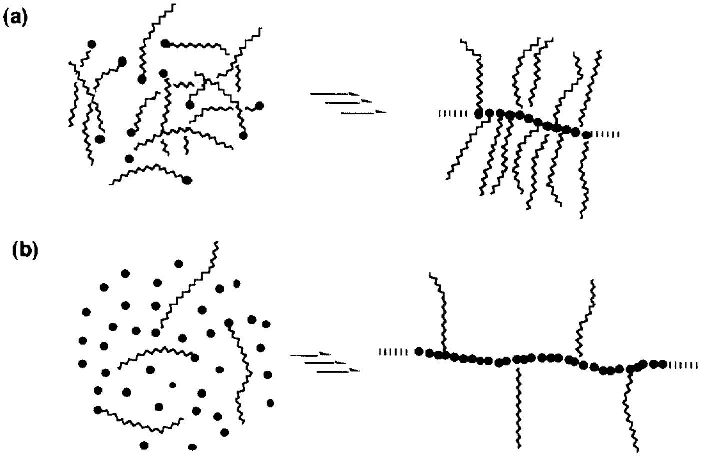
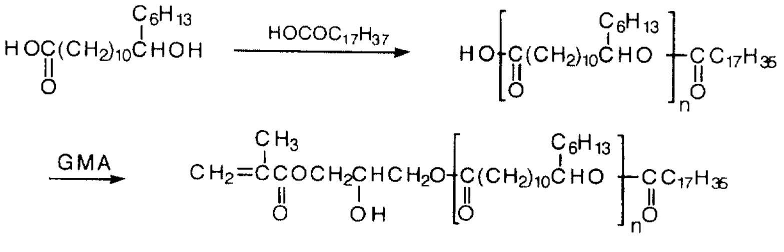


Fig. 1. Basic scheme of the macromonomer technique. (a) Homopolymerization to a comb copolymer. (b) Copolymerization with a comonomer to a graft copolymer.

technique can be regarded to give access to well-defined branched polymers, at least in the sense that the chain length (degree of polymerization) of the macromonomer, as the branch or the side chain, is usually predetermined and that the chain length and the composition of the backbone or the main chain may also be controlled in principle by the subsequent polymerization or the copolymerization step. With much progress in the syntheses of end-functional polymers, we can even say that almost all types of conceivable macromonomers are available or at least can be prepared so that we can envisage enormous varieties of branched polymers with different architectures, combinations and compositions.

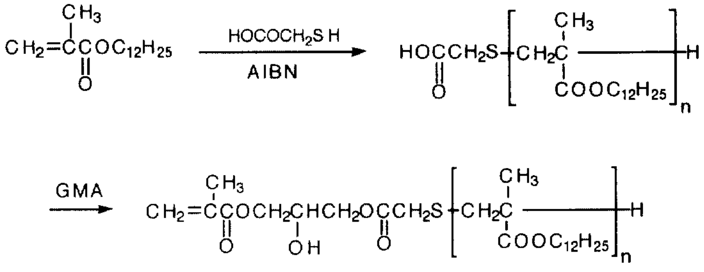
Historically speaking, two significant events should be mentioned. The first 'macromonomer' was introduced by researchers at ICI for the development of well-known, high solids, nonaqueous dispersions (NAD).[1,2] They prepared organo-soluble macromonomers, **1** or **2**, either by polycondensation of 12-hydroxystearic acid in the presence of stearic acid or by radical polymerization of lauryl methacrylate in the presence of thioglycolic acid, followed by the reaction of the carboxyl end groups with glycidyl methacrylate (GMA) as follows:



$$HO\underset{\underset{O}{\|}}{C}(CH_2)_{10}\overset{\overset{C_6H_{13}}{|}}{C}HOH \xrightarrow{HOCOC_{17}H_{37}} HO\left[\underset{\underset{O}{\|}}{C}(CH_2)_{10}\overset{\overset{C_6H_{13}}{|}}{C}HO\right]_n\underset{\underset{O}{\|}}{C}C_{17}H_{35}$$

$$\xrightarrow{GMA} CH_2{=}\overset{\overset{CH_3}{|}}{C}\underset{\underset{O}{\|}}{C}OCH_2\underset{\underset{OH}{|}}{C}HCH_2O\left[\underset{\underset{O}{\|}}{C}(CH_2)_{10}\overset{\overset{C_6H_{13}}{|}}{C}HO\right]_n\underset{\underset{O}{\|}}{C}C_{17}H_{35} \qquad (1)$$

(1)



(2)

(2)

These macromonomers were copolymerized in organic media with a large amount of conventional monomers such as methyl methacrylate to afford submicron-sized dispersions. Effective steric stabilization was brought about by the very soluble macromonomer chains incorporated as the surface grafts, which protected against coagulation of the otherwise unstable microspheres.

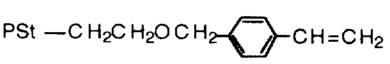
Secondly, the term 'macromer' was introduced as a trade name by Milkovich of CPC International for macromonomers prepared by the end-capping of well-established living anionic polymers prepared from monomers such as styrene and isoprene.[3-6] Typical end groups introduced included:

$PSt{-}CH_2CH{=}CH_2$

(3)

$PSt{-}CH_2CH_2OCH{=}CH_2$

(4)



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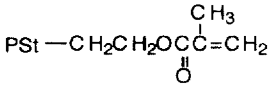
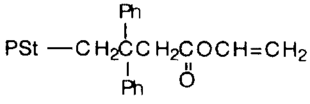


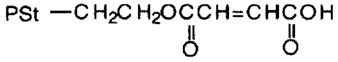
$PSt{-}CH_2CH_2OC(=O)C(CH_3){=}CH_2$

(6)



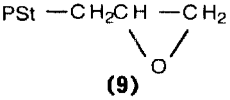
$PSt{-}CH_2C(Ph)_2CH_2C(=O)OCH{=}CH_2$

(7)



$PSt{-}CH_2CH_2OC(=O)CH{=}CHC(=O)OH$

(8)



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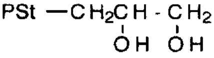


$PSt{-}CH_2CH(OH){-}CH_2(OH)$

(10)

where PSt stands for polystyrene but it can also be polyisoprene (PIp) or their block copolymer, PSt-*b*-PIp. They were prepared from polystyryl or polyisoprenyl living anions by reactions with allyl chloride (for **3**), 2-chloroethyl vinyl ether (for **4**), ethylene oxide followed by *p*-vinylbenzylchloride (for **5**), ethylene oxide followed by methacryloyl chloride (for **6**), 1,1-diphenylethylene followed by vinyl chloroacetate (for **7**), ethylene oxide followed by maleic anhydride (for **8**), epichlorohydrin (for **9**), and by the hydrolysis of **9** (for **10**). Ethylene oxide and 1,1-diphenylethylene were used to reduce the reactivity of the living ends to avoid possible side reactions with carbonyl groups or double bonds of the end-capping reagents. These 'macromers' were claimed to be useful precursors to well-defined graft copolymers for high impact plastics and for thermoplastic elastomers.

The two approaches mentioned have been the bases for subsequent progress which has made the macromonomer technique a widely applicable method for the design of a variety of multiphase, branched polymers. The method may be expected to further increase in importance with a clearer understanding and improvement in macromonomer reactivity during polymerization and copolymerization, together with unique developments in macromonomer applications. The present article will discuss the general syntheses of macromonomers, their characteristic polymerization and copolymerization behaviors, and the polymeric architectures offered by the technique along with some characteristic properties of branched polymers that have been prepared by this process.

2. GENERAL SYNTHETIC METHODS FOR MACROMONOMERS

Basically, four methods are available for introducing a polymerizable functional group into a polymer chain end:

(a) End-capping (termination) of a living polymer by x-**F**;

$$\mathrm{P}_n^* + x - \mathbf{F} \longrightarrow \mathrm{P}_n - \mathbf{F} \tag{3}$$

(b) Initiation of living polymerization by **F**-I

$$\mathbf{F} - \mathrm{I} + n\mathrm{M} \longrightarrow \mathbf{F} - \mathrm{I} - \mathrm{P}_n^* \longrightarrow \mathbf{F} - \mathrm{I} - \mathrm{P}_n \tag{4}$$

(c) Transformation of end-functional group

$$\mathrm{P}_n - y + x - \mathbf{F} \longrightarrow \mathrm{P}_n - \mathbf{F} \tag{5}$$

(d) Polyaddition

$$\mathbf{F} - \mathrm{P} - x \longrightarrow \mathbf{F} - \mathrm{P}_n - x \tag{6}$$

$$\mathbf{F} - \mathrm{P} - \mathbf{F} + x - \mathrm{Q} - x \longrightarrow \mathbf{F} - [\mathrm{PQ}]_n - x \tag{7}$$

where **F** stands for a polymerizable group, I is an initiator fragment, * is an active (living) chain end, x and y are appropriate functional groups, M is a monomer, P and Q are repeating monomer units, and n is the number of monomers polymerized per chain or number average degree of polymerization.

Along with current progress in living polymerizations including anionic,[7,8] cationic,[9] coordinate–anionic[10,11] and even radical mechanisms,[12–17] we can now expect a wide variety of polymer systems to be well controlled in structure, particularly in chain length and a narrow distribution. In an ideally living polymerization system with a rapid initiation compared to propagation and no termination or chain transfer, the average chain length, n in the above scheme, can be controlled just by the molar ratio of the polymerized monomer to the initiator in feed. Thus,

$$DP_\mathrm{n} = n = [\mathrm{M}]_0/[\mathrm{I}]_0 \tag{8}$$

after complete conversion. A narrow Poisson-type distribution is theoretically expected with an approximation by $DP_\mathrm{w}/DP_\mathrm{n} = 1 + 1/n$, where DP_n and DP_w are number- and weight-average degrees of polymerization, respectively. End-group functionalization can also be easily accomplished because all the chains in the system have active chain ends to react with an appropriate end-capping (terminating) reagent. Alternatively, a functional end group can be introduced in the initition step either directly as an initiator fragment or in a masked form, provided that it is unreactive during the subsequent polymerization. A number of well-defined macromonomers have thus been successfully prepared via the termination and the initiation for living polymerization (methods a and b above, respectively), as will be shown in detail in Section 5.

End-functional polymers have also been readily available either by conventional radical polymerizations or by stepwise (polycondensation or polyaddition) polymerizations. Thus the radical polymerization of a monomer, M, in the presence of an appropriate mercapto transfer agent, HS-*y* may afford an oligomer having the *y*-S-end group:

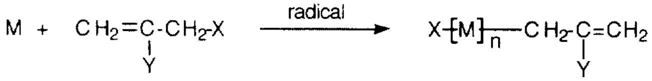
$$\mathrm{M} \xrightarrow[\text{radical}]{\mathrm{HS}-y} y-\mathrm{S}-[\mathrm{M}]_n-\mathrm{H} \tag{9}$$

with an instantaneous number-average degree of polymerization as follows:

$$n=[\mathrm{M}]/(C_s[\mathrm{HS}-y]) \tag{10}$$

where C_s is the chain transfer constant. The distribution in the degree of polymerization (*DP*), *n*, or in molecular weight should be of the most probable type with $DP_w/DP_n = 2$. The polymerization of methacrylates in the presence of thioglycolic acid, as in reaction (2), is typical with C_s around 0.3–0.5, producing essentially pure carboxyl-terminated polymethacrylates provided that *n* is not too high (e.g. less than 50).[18–20]

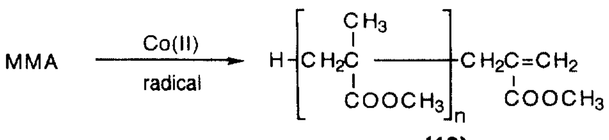
Table 1 lists related examples of radical chain-transfer controlled polymerizations to prepare end-functionalized polymers. Symmetrical disulfide transfer agents give rise to polymers functionalized on both ends that are of potential use for telechelic macromonomers applicable for network design. Difunctional thiol compounds such as thiomalic acid and thioglycerol are used to prepare polymethacrylates or polyacrylates carrying the difunctional (dicarboxyl and diol) groups at one end, which are useful as macromonomers for stepwise polymerizations.[36–39] Some allylic compounds effectively undergo chain transfer via radical addition–fragmentation mechanisms to afford macromonomers with allylic terminal groups in one-step:[40–43]



$$\mathrm{M} + \mathrm{CH_2{=}C(Y){-}CH_2{-}X} \xrightarrow{\text{radical}} \mathrm{X{-}[M]_n{-}CH_2{-}C(Y){=}CH_2}$$

(11)

Also to be noted is an effective hydrogen chain transfer catalysis with a Co(II) complex in the radical polymerization of MMA to give a PMMA macromonomer with a 2-methoxy-carbonylallyl chain end:[44,45]



$$\mathrm{MMA} \xrightarrow[\text{radical}]{\text{Co(II)}} \mathrm{H{-}[CH_2C(CH_3)(COOCH_3)]_n{-}CH_2C(COOCH_3){=}CH_2}$$

(12)

Introduction of a functional end group has also been achieved in the initiation step of radical polymerization by the use of an appropriate azo initiator coupled with an allyl compound as a degradative chain-transfer agent:[46–49]

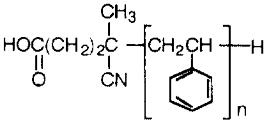
$$\mathrm{M} \xrightarrow[\text{allyl compound}]{\mathrm{F{-}R{-}N{=}N{-}R{-}F}} \mathrm{F{-}R{-}[M]_n{-}H} \tag{13}$$

Table 1. End-functionalized polymers by radical chain-transfer polymerization*

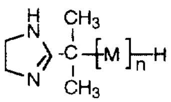
Monomer	Transfer agent	Polymer	C_s	Reference
RMA	$HSCH_2COOH$	$HOCOCH_2S{-}[RMA]_n{-}H$	0.3–0.5	18–20
RMA	$HSCH_2CH_2OH$	$HOCH_2CH_2S{-}[RMA]_n{-}H$	0.6–0.9	21
MMA	$HSCH_2CH_2NH_2$	$H_2NCH_2CH_2S{-}[MMA]_n{-}H$	0.16	18
LA	$HSCH_2CH_2OH$	$HOCH_2CH_2S{-}[LA]_n{-}H$	0.9	22
HEMA	$HSCH_2CH_2NH_2$	$H_2NCH_2CH_2S{-}[HEMA]_n{-}H$	0.06	23
St	ICH_2COOH	$HOCOCH_2{-}[St]_n{-}I$	0.4–0.6	24
St	$OCNC_6H_4SSC_6H_4NCO$	$OCNC_6H_4S{-}[St]_n{-}SC_6H_4NCO$	—	25
St	$H_2NC_6H_4SSC_6H_4NH_2$	$H_2NC_6H_4S{-}[St]_n{-}SC_6H_4NH_2$	0.24	26,27
St	$HSCOCH_3$	$CH_3COS{-}[St]_n{-}H$	—	28
*t*BA	$H_2NC_6H_4SSC_6H_4NH_2$	$H_2NC_6H_4S{-}[tBA]_n{-}SC_6H_4NH_2$	0.23	29
VPyr	$HSCH_2CH_2COOH$	$HOCOCH_2CH_2S{-}[VPyr]_n{-}H$	—	30
AAm	$HSCH_2CH_2COOH$	$HOCOCH_2CH_2S{-}[AAm]_n{-}H$	—	30
VAc	$HSCH_2CH_2OH$	$HOCH_2CH_2S{-}[VAc]_n{-}H$	260	31
VAc	$HSCOCH_3$	$CH_3COS{-}[VAc]_n{-}H$	—	32
VAc	$HSiMe_2Cl$	$ClSiMe_2[VAc]_n{-}H$	0.067	33
VC	$HSCH_2COOH$	$HOCOCH_2S{-}[RMA]_n{-}H$	1	34,35
VC	$HSCH_2CH_2OH$	$HOCH_2CH_2S{-}[RMA]_n{-}H$	1	34,35
MMA	$HSCH_2CH(OH)CH_2OH$	$HOCH_2CH(OH)CH_2S{-}[MMA]_n{-}H$	0.6–0.9	36
MMA	$HSCH(COOH)CH_2COOH$	$HOCOCH_2CH(COOH)S{-}[MMA]_n{-}H$	0.3–0.4	37–39
RA	$HSCH(COOH)CH_2COOH$	$HOCOCH_2CH(COOH)S{-}[RA]_n{-}H$	0.3–0.7	39
MMA	$CH_2{=}C(Y)CH_2StBu$	$tBuS{-}[MMA]_n{-}CH_2C(Y){=}CH_2$	0.7–1.3	40
St	$CH_2{=}C(Y)CH_2StBu$	$tBuS{-}[St]_n{-}CH_2C(Y){=}CH_2$	0.8–1.9	40
MMA	$CH_2{=}C(COOMe)CH_2Br$	$Br{-}[MMA]_n{-}CH_2C(COOMe){=}CH_2$	0.9	41
MMA	$CH_2{=}CHCH{=}CHCH_2StBu$	$tBuS{-}[MMA]_n{-}CH_2CH{=}CHCH{=}CH_2$	—	42
MAA	$CH_2{=}C(Ph)CH_2StBu$	$tBuS{-}[MAA]_n{-}CH_2C(Ph){=}CH_2$	0.3–0.5	43

*RMA, alkyl methacrylates; MMA, methyl methacrylate; LA, lauryl acrylate; HEMA, 2-hydroxyethyl methacrylate; St, styrene; *t*BA, *tert*-butyl acrylate; VPyr, N-vinylpyrrolidone; AAm, acrylamide; VAc, vinyl acetate; VC, vinyl chloride; RA, butyl and 2-ethylhexyl acrylates; MAA, methacrylic acid; Y, $-CO_2Et$, $-Ph$, $-CN$.

For example, 4,4′-azobis(4-cyanovaleric acid) and 2,2′-azobis(N,N′-dimethylene-isobutyramidine) were used to polymerize styrene and vinyl acetate in the presence of diethyl allylmalonate to afford **13** and **14**, respectively.



(13)[46]



(14) (M = St, VAc)[47-49]

Symmetrically functionalized azo initiators are well known to afford symmetrical telechelic polymers by radical polymerization provided with that recombination or coupling is the termination mechanism as for case of styrene polymerization,[50,51] although some ambiguity does remain.[52,53]

$$\mathrm{M} \xrightarrow{\mathrm{F-R-N=N-R-F}} \mathbf{F}-\mathrm{R}-[\mathrm{M}]_m-[\mathrm{M}]_n-\mathrm{R}-\mathbf{F} \tag{14}$$

The stepwise polymerization of bifunctional monomers through chain-extending, condensation or addition reactions is also a convenient method to obtain end-functional polymers.[54-56] Let x and y represent functional groups that undergo a 1:1 reaction each other either by condensation or by addition like carboxyl and hydroxy, carboxyl and amino, hydroxy and isocyanate, and so on. Then the stepwise polymerization may be expressed by:

$$x-\mathrm{A}-y \rightarrow x-[\mathrm{A}]_n-y \tag{15}$$

and

$$x-\mathrm{A}-x+y-\mathrm{B}-y \rightarrow y-\mathrm{B}-[\mathrm{A}-\mathrm{B}]_m-y \tag{16}$$

where A and B are the respective monomer residues, and [A] and [A – B] are the corresponding repeating monomer units. Thus in reaction (15), the monomer x-A-y polymerizes to give invariably a heterotelechelic (x- and y-ended) polymer with a number average degree of polymerization (DP_n) given by:

$$DP_\mathrm{n}=n=1/(1-p) \tag{17}$$

where p is the extent of reaction of x or y. In reaction (16), the monomer x-A-x plus y-B-y usually polymerizes to a mixture of telechelic polymers with either x or y as the end groups. In the case of excess y-B-y and after complete reaction of the A monomer, a telechelic (y-ended) polymer will result with a DP_n given by:

$$DP_\mathrm{n}=2m+1=(1+r)/(1-r) \tag{18}$$

with r being a molar ratio of A to B in the feed, $r=[\mathrm{A}]_0/[\mathrm{B}]_0$. In any case the DP distribution should be approximated by a most probable type with $DP_\mathrm{w}/DP_\mathrm{n}=2$.

On addition of a monofunctional compound to either the reaction system (15) or (16), we can have monofunctional-ended polymers after complete conversion as follows:

$$x-\mathrm{A}-y \xrightarrow{\mathrm{A}'-y} \mathrm{A}'-[\mathrm{A}]_n-y \tag{19}$$

$$DP_\mathrm{n}=n=[\mathrm{A}]_0/[\mathrm{A}']_0 \tag{20}$$

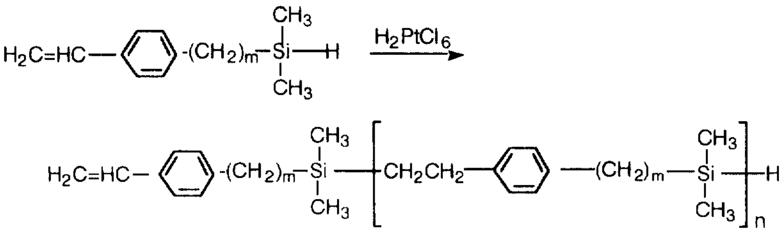
or

$$x-\mathrm{A}-x+y-\mathrm{B}-y \xrightarrow{\mathrm{B}'-y} \mathrm{B}'-[\mathrm{A}-\mathrm{B}]_m-y \tag{21}$$

$$DP_\mathrm{n}=2m=2[\mathrm{A}]_0/[\mathrm{B}']_0 \tag{22}$$

with an equimolar feed composition assumed ($r = 1$). A typical example of the reaction (19) with eqn (20) is the carboxyl-ended prepolymer to derive the macromonomer, **1**, prepared by polycondensation of 12-hydroxystearic acid in the presence of small amount (*ca.* 15%) of stearic acid, as shown first in the reaction (1).

Polyaddition involving vinyl groups as **F** in reactions (6) and (7) is one of the convenient methods to prepare macromonomers directly. One example is hydrosilylation polymerization to give a silicon-containing macromonomer, **15**, as follows:[57]



(15) (m = 0, 1, 4)

Many other examples are given in Section 5. DP_n and distribution values basically follow the same relationships as for the polycondensation described above.

3. POLYMERIZATION AND COPOLYMERIZATION BEHAVIOR CHARACTERISTIC OF MACROMONOMERS

Why is a macromonomer different in its polymerization or copolymerization reactivity from a corresponding conventional monomer? This has been a continuing question of both practical and academic importance. Although a conclusive discussion is not possible at present, this chapter is intended to briefly summarize recent understandings about the above question, i.e. the so-called polymer effect of macromonomers on their polymerization and copolymerization behaviors.

Macromonomers often homopolymerize with some difficulty because of their high molecular weights as compared to lower molecular weight monomers. This is certainly true if a comparison is made on the basis of the same weight concentrations of monomers, which means much lower molar concentrations of macromonomers and therefore polymerizing end groups in the system. Initiators' absolute concentrations are also accordingly low on the same molar basis relative to the monomers. Recent kinetic and ESR investigations on radical polymerizations of macromonomers by Tsukahara[58] and Hatada *et al.*[59] have revealed that propagation is somewhat unfavored but that termination is much more hindered so that the overall polymerization rates for macromonomers (on the molar basis), are comparable to or even higer than those for corresponding conventional monomers.

Based on radical polymerization kinetics, the rate of propagation, R_p, which is essentially equal to overall rate of polymerization, and the rate of termination, R_t, are expressed by:

$$R_p = -d[M]/dt = k_p[P\cdot][M] \tag{24}$$

$$R_t = -d[P\cdot]/dt = k_t[P\cdot]^2 \tag{25}$$

where k_p and k_t are the rate constants for propagation and termination, respectively, and $[P\cdot]$ and $[M]$ are the overall propagating radical and monomer concentrations, respectively.

Together with the steady-state assumption,

$$R_i = 2k_d f[\mathrm{I}] = R_t \tag{26}$$

we have the well-known rate equation:

$$R_p = k_p \left(\frac{2k_d f}{k_t} \right)^{1/2} [\mathrm{I}]^{1/2}[\mathrm{M}] \tag{27}$$

where R_i is rate of initiation, k_d and f are rate constants of initiator decomposition and initiation efficiency, respectively, and [I] is initiator concentration. Also we have for the kinetic chain length, ν:

$$\nu = R_p / R_t = \frac{k_p[\mathrm{M}]}{(2k_d f k_t)^{1/2}[\mathrm{I}]^{1/2}} = \frac{(1+\mathrm{x})}{2} DP_n^\circ \tag{28}$$

where DP_n° is the instantaneous number-average degree of polymerization assuming no chain transfer and x is the fraction of disproportionation in termination.

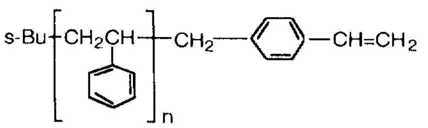
The determination of steady-state concentrations of propagating radicals by ESR together with the rate of polymerization allowed an estimation of k_p from eqn (24), while k_t was evaluated either from eqn (28) with measured DP_n assuming no chain transfer[58] or directly from eqn (25) by following the decay of the radicals after turning off the irradiated polymerization.[59] As shown in Table 2, the k_p values thus estimated for *p*-vinylbenzyl- or methacrylate-terminated polystyrene, **16** and **17**,[58] and *p*-vinylbenzyl-terminated poly(methyl methacrylate (PMMA, highly isotactic or syndiotactic) macromonomers, **18**,[59] were found to be smaller than those for the corresponding conventional monomers such as styrene and MMA by factors of 1/3 to 1/50, while the k_t values were much more reduced by factors of 10^{-3}–10^{-5}, leading to comparable, or even higher, overall rates of polymerization, R_p, for the macromonomers, by virtue of eqn (27), in spite of the accompanied reduction in f (1/3 to 1/4). We may suppose that a macromonomer, already a polymer by itself, will make a viscous system from the beginning and it will polymerize to a highly branched starlike polymer with an active radical occluded in its core. This situation will reduce f and k_p by some factor but

Table 2. Propagation and termination rate constants of some macromonomers in radical polymerization as compared with conventional monomers

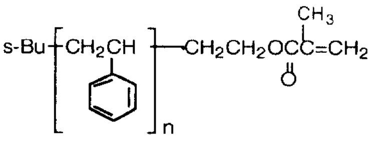
Monomer	*MW* (g/mol)	Solvent	Temp (°C)	k_p (l/mol·s)	k_t (10^3 l/mol·s)	Reference
PSt-VB (**16**)	4980	Benzene	60	4	1.3, 2.6*	58
PSt-MA (**17**)	4400	Benzene	60	18	8.4, 16.8*	58
PMMA-VB (**18**)						
isotactic	2900	Toluene	60	50	140*	59
syndiotactic	2720	Toluene	60	4.7	1.3*	59
PEO-VB (**19**, $m = 1$)	2260	Benzene	20	40	1.8	66
		Water	20	1100	5.4	66
Styrene	104	—	60	176	$7.2 \cdot 10^4$	67
		—	20	60	$3.5 \cdot 10^4$	67
MMA	100	—	60	515	$2.6 \cdot 10^4$	67

*The values are doubled from those in references [58] and [59], where a convention of $2k_t$ instead of k_t in eqs (25)–(28) was used in evaluation of k_t. The two k_t values listed for **16** and **17** correspond to an assumption of coupling (left) and disproportionation (right) for termination.

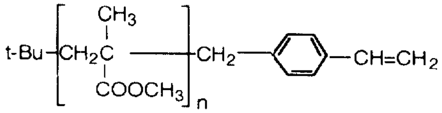
much more drastically reduce k_t, just as has been observed. Thus the diffusion-controlled termination between highly branched polymacromonomer radicals appears to be severely limited, making them relatively long-lived as compared to the linear polymer radicals formed from corresponding conventional monomers.



(16)



(17)

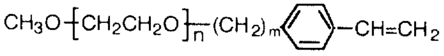


(18) *(highly isot. or syndiot.)*

Since diffusion-controlled termination should be more drastically hindered in a more viscous or more highly branched system, k_t will tend to decrease with macromonomer concentration, [M], as confirmed by Tsukahara *et al.*[60] Thus a 'gel effect' is present at the beginning in a solution polymerization of a macromonomer. This means from eqn (27) that the exponent of [M] dependence of R_p or DP_n should be higher than the conventional unity, as was experimentally observed.[61]

Also to be noted in Table 2 is a significant effect of PMMA stereoregularity on the propagation and termination rates, suggesting that differences in the solution properties of these species may affect their reactivities. Isotactic PMMA was found to have higher segment-mobility as compared to the syndiotactic one. The higher reactivity of isotactic PMMA was also observed in the copolymerization with styrene.[59]

One more feature to be added is a macromonomer's self-aggregation or self-organization in a polymerization system. Poly(ethylene oxide) (PEO) macromonomers carrying *p*-styrylalkyl end groups, **19**, are amphiphilic, giving micelles in water with the hydrophobic polymerizing groups locally organized into the cores so that they polymerize almost a hundred times more rapidly than those in benzene.[62–65] Recent ESR studies[66] showed that k_p and k_t in benzene followed a very similar tendency as descrived above, while k_p in water was about 30 times higher than that in benzene, strongly supporting the enhanced polymerization as a result of self-organization of the macromonomer in water (Table 2). Various factors affecting the kinetics of polymerization of macromonomers have been discussed recently.[68]



(19) (m = 1, 4, 7)

Copolymerization involving macromonomers is very important for designing well-defined graft copolymers.[69–72] Consider a copolymerization between a conventional monomer, A, and a macromonomer, B, to get a graft copolymer with A as a backbone or trunk and B as a side chain or branch, i.e. poly(A-*g*-B). Then we have from a conventional Mayo–Lewis composition equation that

$$y = \frac{-\mathrm{d}[\mathrm{A}]}{-\mathrm{d}[\mathrm{B}]} = \frac{1 + r_{\mathrm{A}}[\mathrm{A}]/[\mathrm{B}]}{1 + r_{\mathrm{B}}[\mathrm{B}]/[\mathrm{A}]} \tag{29}$$

where r_A and r_B are the respective monomer reactivity ratios. The molar ratio y corresponds to the average number of trunk monomer units inserted between the two nearest branches in an instantaneously formed graft copolymer chain. The average number of branches per chain is given by $l/(y + 1)$ with l being the number-average degree of polymerization of the trunk. The weight ratio of trunk/brunch can be given by y/k with k as the ratio of the molecular weights of the branch (macromonomer) to the trunk monomer.

Since $k \gg 1$ in the present case and we are usually concerned with graft copolymers with y/k near unity, we have a general condition that $[\mathrm{A}]/[\mathrm{B}] \gg 1$ and $y \gg 1$, so that eqn (29) can be reduced to Jaacks' equation:[3,73,74]

$$y = \mathrm{d}[\mathrm{A}]/\mathrm{d}[\mathrm{B}] = r_{\mathrm{A}}[\mathrm{A}]/[\mathrm{B}] \tag{30}$$

which means that the copolymer composition here is essentially determined by the relative rates of the two propagation reactions expressed by eqns (33) and (34) below. Therefore the trunk/branch composition is essentially controlled by the monomer composition and the monomer reactivity ratio of the trunk monomer. In other words, the other monomer reactivity ratio, r_B, is essentially insignificant[69] in the condition of $[\mathrm{A}]/[\mathrm{B}] \gg 1$. Integration of eqn (30) gives:[75]

$$\ln(1-\theta_{\mathrm{A}})/\ln(1-\theta_{\mathrm{B}}) = r_{\mathrm{A}} \tag{31}$$

or[76,77]

$$1-\theta = \left(\frac{f_{\mathrm{A}}}{f_{\mathrm{A}}^{o}}\right)^{\frac{1}{r_{\mathrm{A}}-1}} \left(\frac{f_{\mathrm{B}}}{f_{\mathrm{B}}^{o}}\right)^{\frac{r_{\mathrm{A}}}{1-r_{\mathrm{A}}}} \tag{32}$$

where θ_A, θ_B, and θ are the fractional conversions of A, B, and total monomers, respectively, and the fs are the corresponding residual monomer fractions, with f^os being those in initial feed. Eqn (32) holds by using the units of θs, fs and f^os in either mole or weight fractions throughout.

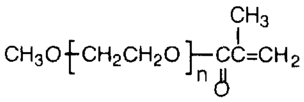
A number of copolymerizations involving macromonomers have been reported with the corresponding monomer reactivity ratios mostly determined by use of the approximate composition equation.[70,71] A macromonomer's relative reactivity in copolymerization with a common comonomer, A, can be assessed by $1/r_A = k_{AB}/k_{AA}$, i.e. the rate constant of the monomer B relative to that of the monomer A in propagation reactions toward a common A-ended polymer radical, which can be represented by poly-A radical in the present approximation:[69]

$$-[\mathrm{A}]_y\cdot + \mathrm{A} \xrightarrow{k_{\mathrm{AA}}} -[\mathrm{A}]_y - \mathrm{A}\cdot \tag{33}$$

$$-[\mathrm{A}]_y\cdot + \mathrm{B} \xrightarrow{k_{\mathrm{AB}}} -[\mathrm{A}]_y - \mathrm{B}\cdot \tag{34}$$

where the average number, y, of the A-successive units in the polymer radical can be approximated by that in eqn (30).

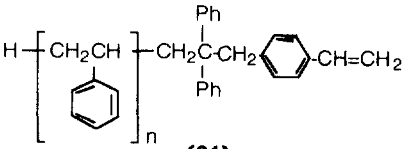
In summarizing a number of monomer reactivity ratios reported so far,[70,71] it appears in many cases of solution systems that the reactivities of macromonomers in copolymerization with a conventional monomer are largely determined by the nature of their polymerizing end-groups, i.e. essentially by their chemical reactivities. In some not so rare cases, however, macromonomer reactivity was found to be reduced by the nature of their polymer chains. For an example, *p*-vinylbenzyl- or methacrylate-ended poly(ethylene oxide) (PEO) macromonomerss (as B), **19** ($m = 1$) or **20**, were found to copolymerize with styrene (as A) with increasing difficulty, down to about half in $1/r_A$, with increasing chain length of the PEO.[78] Since we are concerned with polymer–polymer reactions, as in eqn (34), the results suggest that any thermodynamically repulsive interaction, which usually works between different, incompatible polymer chains (PEO and polystyrene chains here), may apparently retard the approach and hence the reaction between their end groups, (polystyryl radical and *p*-vinylbenzyl or methacrylate group here). Such an incompatibility effect was discussed in terms of the degree of interpenetration and the interaction parameters between unlike polymers to support the reduction in macromonomers' copolymerization reactivity as observed.[70,79]



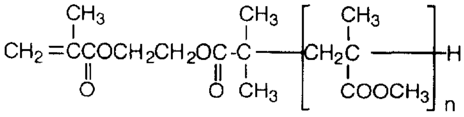
$CH_3O\left[CH_2CH_2O\right]_n\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}{=}CH_2$

(20)

In an unambigously compatible copolymerization system, some critical notions have been reported about macromonomer reactivity. Gnanou and Lutz[80] anionically copolymerized *p*-vinylbenzyl-ended polystyrene macromonomers, **21**, with styrene or *p*-methylstyrene and concluded that only the end-group's chemical reactivity was important in determining the macromonomers' copolymerizability, without any kinetic excluded-volume effect. Radke and Müller[81] used methacrylate-ended PMMA macromonomers, **22**, in radical copolymerization with MMA to point out retarding effects of solution vicosity or of branching in polymer radicals on the macromonomer's access to the propagation site.



(21)



$CH_2{=}\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\|}}{C}}COCH_2CH_2O\underset{\underset{O}{\|}}{C}\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{—}\left[CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{COOCH_3}{|}}{C}}\right]_n\text{—}H$

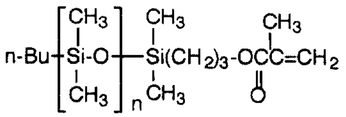
(22)

We have carried out radical copolymerizations between two kinds of macromonomers in an expectation that polymer chain effects, if any, will be more developed in this system. In fact, PEO macromonomers with *p*-vinylbenzyl and methacrylate end groups, **19** ($m = 1$) and **20**, copolymerized azeotropically ($r_A{\sim}r_B{\sim}1$)[82] in contrast with a well-known alternating tendency of their low molecular weight monomers like styrene and MMA ($r_A{\sim}r_B{\sim}0.5$).[67]

Thus the same PEO chains appear to make the intrinsic reactivity difference of their end groups almost insignificant. On the other hand, different polymer chains such as polystyrene versus PEO[82] or polyisoprene[83,84] with the same polymerizing end group appeared to show different reactivities, probably due to some incompatibility or conformational effects.

In heterogeneous systems, including apparently homogeneous but microscopically heterogeneous systems such as in micellar copolymerizations, relative monomer concentrations around the actual reaction sites have to be considered. Thus the monomer reactivity ratios estimated from eqn (29) or eqn (30) with overall monomer and copolymer compositions must be apparent ones including the relative monomer partition.[85–87] For example, a copolymerization between the PEO macromonomers, **19** ($m = 1$) and **20**, which exhibited azeotropic behavior in benzene, as described above, was conducted in a micellar system in water.[82] Indeed, **19** with the *p*-vinylbenzyl-end group ($m = 1$) was found to be much more reactive than **20** with the methacrylate end, probably due to a higher incorporation of the more hydrophobic, former monomer into micelles. Emulsion and dispersion copolymerizations involving macromonomers are of increasing concern in view of the preparation of well-defined microsheres in a soap-free system, as will be discussed in Section 4. The related monomer reactivities, however, appear to have been little understood so far.

A further problem to be discussed is the composition distribution of graft copolymers obtained by the macromonomer method. Due to the high molecular weights of the macromonomers as the branches, the composition distribution has been shown theoretically[76,77,88,89] to be statistically broader as compared to a corresponding, conventional, linear copolymer. This has been experimentally confirmed by Stejskal[77] and Teramachi *et al.*[90–92] with poly(dimethylsiloxane), **23**, and polystyrene macromonomers, **16** or **17**, respectively, copolymerized with MMA. The chemical composition distribution was found to broaden with increasing molecular weight and with decreasing frequency of the macromonomers, as expected.

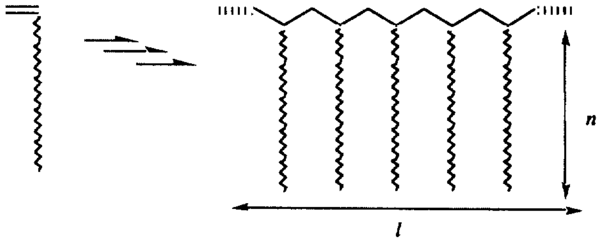


$$n\text{-Bu}\left[\text{Si}(\text{CH}_3)_2\text{-O}\right]_n\text{-Si}(\text{CH}_3)_2(\text{CH}_2)_3\text{-OC}(=\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$$

(23)

4. POLYMER ARCHITECTURES DESIGNED BY MACROMONOMER TECHNIQUES

Macromonomers have been applied in various ways to design branched polymers, offering useful models for the investigation of branched systems in general. Homopolymerization formally affords a regular comb polymer since the known branches are regularly spaced along the backbone, i.e. on every other carbon for a vinyl-type polymerization:



(35)

where l and n stand for the DP_ns of a trunk and a branch, or the number and length of branches, respectively.

Actual polymacromonomers, however, will take on star- or brush-like conformations in solution or in solid state, as illustrated in Fig. 2a,b. In fact, polymers from polystyrene, **17**[93] and PEO macromonomers, **19** (m = 1)[94] have been shown to have very compact forms in solution as compared to their linear counterparts of the same molecular weights. Very low values near zero were found for the exponent, a, for the molecular weight dependence of the intrinsic viscosity in the Mark–Houwink–Sakurada equation, $[\eta] = KM_w^a$, suggesting a rigid spherelike conformation for a polymacromonomer with a limited number (l) of sufficiently long (n) branches or arms. Studies by MALLS of the polymacromonomer solutions from **17**[95,96] or **19** (m = 1)[97] and by DLS and sedimentation of those from **17**[98] indicated a rod-like or cylinder-like structure. A number of densely tethered, long branches apparently force the backbone chains to be much less flexible with a relatively long persistence length, giving an anisotropic structure as a whole. Indeed a liquid crystalline phase was found to form in a film of the polymacromonomer from **17**, even though no mesogenic groups were included in the structure.[99]

The lengths of branches and trunks in a comb polymer, n and l in eqn (35), can be controlled during the preparation and polymerization, respectively, of the macromonomer of interest. An advantage here is the use of a known macromonomer as a branch. Thus n and its distribution can be predicted or controlled by the method of preparation, as discussed in Section 2, and can be at least independently characterized by a suitable method such as GPC. Also l and its distribution can be in principle similarly controlled by the method of polymerization of the macromonomer, as discussed in Section 3 for radical polymerization. Living polymerizations, if successfully applied to macromonomers, will undoubtedly promise a comb polymer of a truly well-defined structure, together with a very sharp distribution, both in the trunk and branch. In practice, however, very few studies have been completely successful, probably because of difficulty in the complete removal of impurities from the macromonomers. To be noted among such attempts, Hatada *et al.*[100] reported stereospecific anionic polymerization of highly stereoregular PMMA macromonomers, and Lutz *et al.*[101]

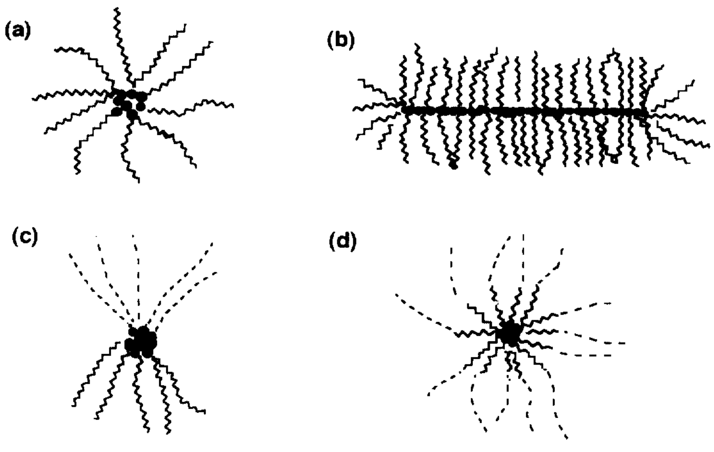
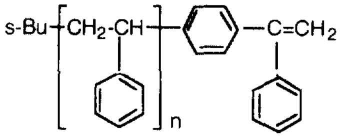


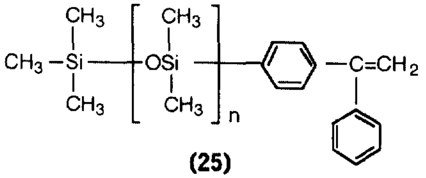
Fig. 2. Schematic picture of polymacromonomers with various architectures: (a) star-like, (b) rod-like, (c) A_nB_n star, (d) $(AB)_n$ star.

reported anionic polymerization of polystyrene macromonomers with some hindered propagation. A comb polymer with a completely uniform structure, isolated by means of SFC from oligo(PMMA macromonomers), will be the most promising model for studying structure–property relationships for branched or star polymers.[102]

Some star-like polymers with relatively limited numbers of arms have been designed by taking advantage of the macromonomer technique. A 1,1-diphenylethylene-terminated macromonomer cannot homopolymerize so it is useful for introducing a single arm at an intended position. For example, Quirk *et al.* prepared the polystyrene macromonomer, **24**, and synthesized a three-armed star polystyrene by inserting the macromonomer during anionic polymerization of styrene.[103] Fujimoto *et al.*[104] reacted polystyryl living anions with a poly(dimethylsiloxane) macromonomer, **25**, followed by polymerization of *tert*-butyl acrylate to prepare a corresponding three-armed star polymer, carrying three different arms.

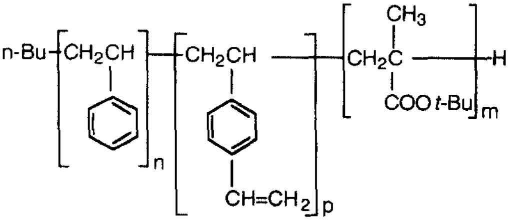


(24)

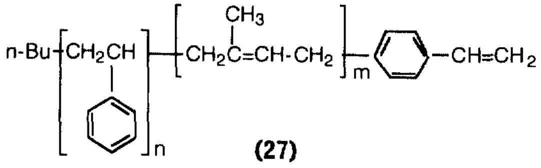


(25)

Ishizu *et al.*[105] polymerized diblock macromonomers such as **26**[106] and **27**,[107] which have polymerizing groups at the central and the end positions, respectively, and obtained star polymers of A_nB_n and $(AB)_n$ types (Fig. 2c,d), where A and B stand for different polymer chains. It appeared that microphase-separation of the unlike block segments in these macromonomers caused the polymerizing groups to locally concentrate into the interphase and the core regions, thus enhancing their polymerizations.



(26) (p = 2.5)



(27)

A further interesting architecture designed by the macromonomer technique is a combination of linear and star polymers, looking like a palm-tree or a dumbbell, as was attempted by Takaki *et al.* who polymerized **16** with one-end or two-end living polyisoprene anions.[108] A palm-tree like polymer was also reported by Ishizu *et al.* by copolymerizing 4-vinylpyridine with a polystyrene macromonomer carrying several allyl groups, on the end which was prepared by decomposition under supersonic irradiation of polystyrene in the presence of diallylmalonic acid.[109]

Needless to say, one of the most important architectures which can be designed by the macromonomer technique is, and has been, graft copolymers. We have indeed so many kinds of macromonomers, as will be summarized in Chapter 5, and we have even far more kinds of monomers available to be copolymerized as the trunk components. Therefore, at least in principle, we can suppose almost unlimited numbers of combinations to obtain graft copolymers. However, proper care must be taken account for apparent monomer reactivities which may be essentially the same as, or significantly different from, those of the corresponding conventional or low-molecular-weight monomer pairs, as was dicussed in Chapter 3. In any case, such wide applicability has so far made this technique a very attractive one.

One of the most fascinating applications of macromonomers is for emulsion and dispersion systems, as was the first report for nonaqueous dispersions (NAD) by the ICI group described earlier in the Introduction. Among a variety of methods for preparing polymeric microspheres, the macromonomer technique is unique and simple in that the macromonomers themselves act as emulsifiers or dispersants without the need for conventional surfactants. The resulting emulsions or dispersions are sterically stabilized against flocculation.[110-115] Furthermore, the microspheres, more or less monodisperse in size around submicrons to microns, are obtained conveniently in a single step. As a counterpart of NAD, a number of emulsion or dispersion systems in water or in alcoholic media (which are of increasing interest for environmentally friendly systems) have been developed using hydrophilic macromonomers.[115] Some examples are PEO macromonomers, **19**, for emulsion or dispersion copolymerizations of styrene[116] and *n*-butyl methacrylate,[117] polyoxazoline block macromonomers, **28**[118] and **29**,[119] for emulsion copolymerizations with styrene and vinyl acetate, respectively, and poly(N-vinylpyrrolidone), **30**,[120] for dispersion copolymerizations with styrene and MMA.

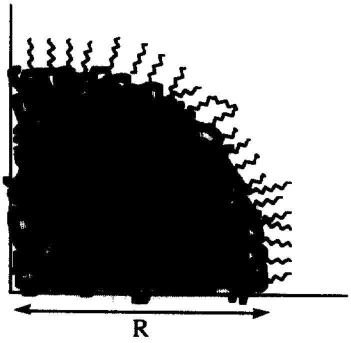
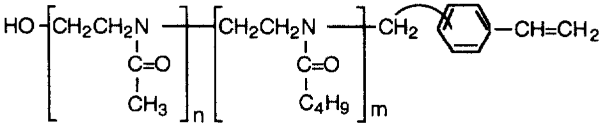
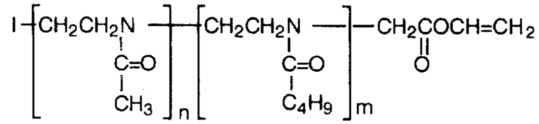


Fig. 3. Schematic picture (quarter section) of a microsphere in an emulsion or dispersion system obtained by the macromonomer technique.

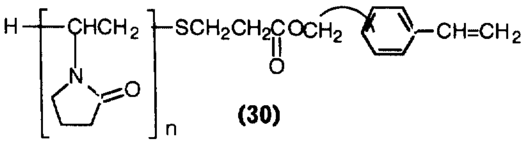


(28)



$$\mathrm{I{-}[CH_2CH_2N(C{=}O)CH_3]_n{-}[CH_2CH_2N(C{=}O)C_4H_9]_m{-}CH_2COCH{=}CH_2}$$

(29)



(30)

Schematically, a microsphere thus obtained by copolymerization with a small amount of macromonomer will have a core–shell structure as given in Fig. 3, with the core occupied by the insoluble substrate polymer chains and the shell by the soluble graft-copolymerized macromonomer chains. The trunk chains of the graft copolymers, which must be insoluble in the medium, serve as anchors going into the core. The average particle size of microspheres can be determined by the core–shell composition, as follows:

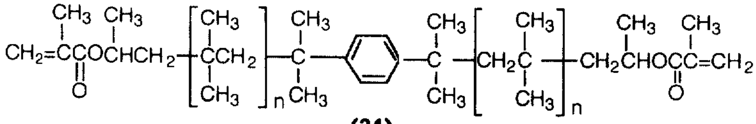
$$R=\frac{3M_{\mathrm{D}}W_o\theta}{\rho N_{\mathrm{A}}W_{\mathrm{D}o}\theta_D S} \tag{36}$$

where R is the radius of the particle core, which consists of homopolymers from the substrate monomer plus trunk chains of the graft copolymers, W_o is weight of the substrate monomer in the feed, $W_{\mathrm{D}o}$ is weight of the macromonomer in the feed, θ is conversion of the substrate monomer, θ_{D} is conversion of the macromonomer, M_{D} is molecular weight of the macromonomer, ρ is density of the polymers in the particle core, N_{A} is Avogadro's number and S is the cross-sectional area per copolymerized macromonomer chain on the particle core surface (core–shell interface). Coupled with the multibin kinetics simulation for initial diffusion-controlled coalescence between microparticles, developed by Paine,[121] we obtained a following equation as the final expression:[116,117,122]

$$R=\theta^{\frac{1}{3}}\left(\frac{3W_o}{\rho N_{\mathrm{A}}}\right)^{\frac{2}{3}}\left(\frac{M_{\mathrm{D}}r_{\mathrm{A}}}{W_{\mathrm{D}o}S_{\mathrm{crit}}}\right)^{\frac{1}{2}}\left(\frac{0.386k_2}{4\pi k_{\mathrm{p}}}\right)^{\frac{1}{6}}\left(\frac{k_{\mathrm{t}}}{2k_{\mathrm{d}}f[\mathrm{I}]_{\mathrm{o}}}\right)^{\frac{1}{12}} \tag{37}$$

where S_{crit} is S at the critical point when the formation of sterically stabilized particles is established, k_2 is the rate constant of coalescence of similar-sized microparticles, which was assumed to be 10^9 l/mol·s, r_{A} is the monomer reactivity ratio of the substrate monomer before the critical point, and the other notations (k_{p}, k_{d}, f, $[\mathrm{I}]_{\mathrm{o}}$) have the same meanings as in Section 3. S_{crit} corresponds to a highest possible occupancy of a lowest possible number of macromonomer chains grafted onto the surface and no coalescence of such particles occur thereafter. Eqn (37) was found to successfully explain the experiments with reasonable parameters of S_{crit}/r_A for dispersion copolymerizations of styrene and *n*-butyl methacrylate in a methanol–water mixture.[116,117]

Finally, telechelic or multifunctional macromonomers, carrying two or more polymerizing groups on both ends or along the chain, respectively, are no doubt of potential use in designing polymer networks in general,[123] although there have not been many papers reported. A promising example is polyisobutylene macromonomer, **31**, by Kennedy *et al.*, which was copolymerized with hydrophilic comonomers such as 2-hydroxyethyl methacrylate and N,N-dimethylacrylamide to afford amphiphilic networks with excellent biocompatibility and biostability.[124,125]



(31)

5. MACROMONOMERS AS CLASSIFIED BY MONOMER TYPES

This section summarizes various macromonomers in addition to those cited above. One can refer to particular macromonomers that may be useful for constructing a desired architecture of branched or grafted polymers. They are classified and listed according to monomer types for those prepared via addition and ring-opening polymerizations, followed by those prepared via polycodensation and polyaddition. For simplicity, examples will provide only the structure of the polymerizing end group coupled with the abbreviated name of the polymer chain which constitutes the macromonomer.

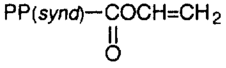
5.1. *Polyolefins*

Polyethylene is a common polymer with a simple structure but it is still one which gives difficulty when designing an end group. A promising approach is the polymerization of ethylene with butyllithium activated by tetramethylethylenediamine,[126–128] to afford a living polyethylene–lithium (PE–Li) with a molecular weight less than 1000, and end-functionalization to give carboxyl (PE-CO_2H), hydroxyl (PE–OH), and so on.

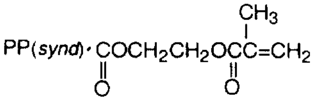
Living polypropylene (PP, syndiotactic), prepared with V(*acac*)$_3$-$AlEt_2Cl$, was reacted with butadiene to give a 1-butenyl-ended macromonomer, **32**.[129] Transformations to end groups such as vinyl ester, **33** and methacrylate, **34**, have also been reported.[11] Metallocene-catalysed polymerization provides polyolefins with olefin end groups such as **35–38**. Thermolysis of polypropylene also provided isopropenyl group, like **35**.[130] **36** and **37** were copolymerized with ethylene and methyl acrylate, respectively, to give the corresponding graft copolymers.

$\mathrm{PP}(\mathit{synd})\text{—}\mathrm{CH_2CH_2CH{=}CH_2}$

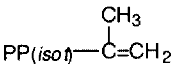
(32)


$\mathrm{PP}(\mathit{synd})\text{—}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OCH{=}CH_2}$

(33)


$\mathrm{PP}(\mathit{synd})\cdot\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OCH_2CH_2O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{{=}CH_2}$

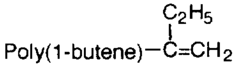
(34)


$\mathrm{PP}(\mathit{isot})\text{—}\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{{=}CH_2}$

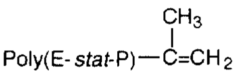
(35)[131]

$\mathrm{PP}(\mathit{atac})\text{—}\mathrm{CH_2CH{=}CH_2}$

(36)[132]

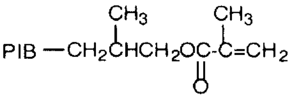

$\mathrm{Poly(1\text{-}butene)}\text{—}\overset{\overset{\mathrm{C_2H_5}}{|}}{\mathrm{C}}\mathrm{{=}CH_2}$

(37)[133]

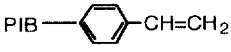

$\mathrm{Poly(E\text{-}}\mathit{stat}\mathrm{\text{-}P)}\text{—}\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{{=}CH_2}$

(38)[134]

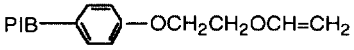
Many polyisobutylene (PIB) macromonomers have been prepared via cationic inifer and living polymerizations of isobutylene by Kennedy's group.[9,135] Examples are as follows:


$\mathrm{PIB}\text{—}\mathrm{CH_2}\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{HCH_2O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\text{-}\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{{=}CH_2}$

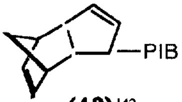
(39)[136-138]



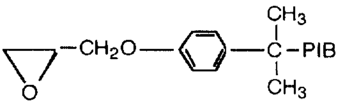
(40)[139,140]



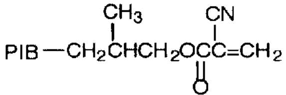
(41)[141]



(42)[142]



(43)[143]


$\mathrm{PIB}\text{—}\mathrm{CH_2}\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{HCH_2O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\overset{\overset{\mathrm{CN}}{|}}{\mathrm{C}}\mathrm{{=}CH_2}$

(44)[144]

They were copolymerized with appropriate conventional monomers to prepare graft copolymers with soft PIB chains as the branches, with some copolymerization reactivities evaluated. The corresponding telechelic macromonomers have also been prepared and copolymerized to design network polymers (see **31** for an example).[125,144] Methacrylate-ended PIB, **39**, was subjected to stereospecific anionic homopolymerizations to give comb polymers with isotactic and syndiotactic backbone chains.[145]

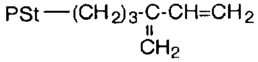
5.2. *Polystyrenes*

A number of polystyrene (PSt) macromonomers have been prepared via radical, anionic and cationic polymerizations, and have served as hard and hydrophobic branch components of graft copolymers. The first application by Milkovich of living anionic polymerization for macromonomer syntheses such as **3–10** was described in the Introduction. *p*-Styryl-ended

PSt macromonomers without ether linkages, **16**, could be directly prepared from the living polymer by reaction with *p*-vinylbenzyl chloride (VBC).[146] Similar macromonomers have been also obtained by initiating styrene polymerization with *p*-vinylbenzyllithium[147] and *p*-vinylbenzyl Grignard reagent.[148] Methacrylate-ended macromonomers, **6** or **17**, were already described. 4-Pentenyllithium is a useful initiator to give 1-olefin-ended PSt macromonomers, **45**.[149] Other examples of interest prepared via anionic polymerization are shown in the formulae, **46–51**:

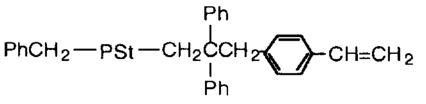
$CH_2{=}CH(CH_2)_3{-}PSt$

(45)[149]

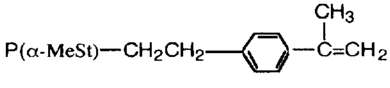


$$PSt{-}(CH_2)_3{-}\underset{\underset{CH_2}{\|}}{C}{-}CH{=}CH_2$$

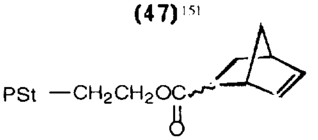
(46)[150]



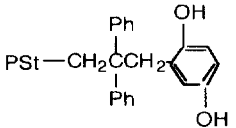
(47)[151]



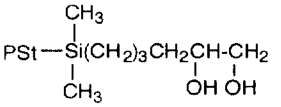
(48)[152]



(49)[153]



(50)[154,155]



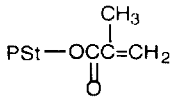
$$PSt{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}(CH_2)_3CH_2\underset{\underset{OH}{|}}{CH}{-}\underset{\underset{OH}{|}}{CH_2}$$

(51)[156]

Poly(α-methylstyrene) macromonomer, **48**, prepared by reaction of the anionic living polymer with *p*-isopropenylphenethyl chloride, has been subjected to living anionic systems to study kinetic and equilibrium characteristics of the macromonomer.[157] Macromonomer **49**[153] was used in olefin methathesis copolymerization with norbornene to give polynorbornene-*g*-PSt. Macromonomers **50** and **51** were used in polycondensations with bisphenol A plus triphosgene and polyadditions with diisocyanate to afford PSt-grafted polycarbonates and polyurethanes, respectively.

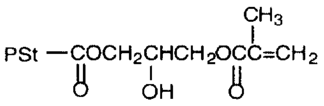
Recent development in cationic living polymerization of styrenes also made possible the introduction of end groups in initiation[158] and termination steps.[159] Examples are **3** and **52** carrying allyl and methacrylate end groups directly attached to PSt:

Radical polymerization of styrene by use of an appropriate transfer agent[24] (Table 1) or initiator[47] (see **13**) provides PSt with carboxy ends, which were in turn reacted with glycidyl methacrylate (GMA) to afford methacrylate-ended macromonomers, **53**. Transformation of the carboxyl by reaction with hexamethylenediamine to an amino group, followed by reaction with VBC, GMA and allyl glycidyl ether, introduced *p*-vinylbenzyl, methacrylate and allyl ether end groups, respectively.[46] Imidazoline rings introduced by the initiator method, **14**, were reacted with VBC or GMA to afford styryl or methacrylate end groups.[47] 2-Substituted allyl end groups can be directly introduced by addition–fragmentation chain transfer, as described for **11**.[40–42] 2-Phenylallyl-ended PSt macromonomers were also obtained by photolysis of polystyrene copolymerized with a small amount of methyl vinyl ketone.[160] Living radical polymerization by the iniferter method provided a PSt macromonomer, **54**.[161]



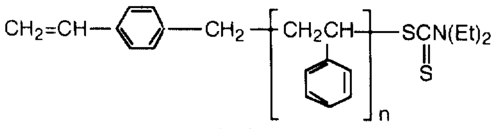
$\mathrm{PSt{-}O\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}{=}CH_2}$

(52)[158,159]



$\mathrm{PSt{-}\underset{\underset{O}{\|}}{C}OCH_2\underset{\underset{OH}{|}}{C}HCH_2O\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}{=}CH_2}$

(53)



(54)[161]

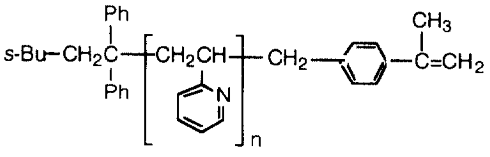
Much basic research has been made with PSt macromonomers, possibly as representatives of other macromonomers, to understand the macromonomers' reactivity in polymerization and copolymerization, and the physical properties of the resulting comb polymers and graft copolymers, as briefly discussed in Sections 3 and 4. Copolymerization reactivities, including those of other macromonomers, are well reviewed.[70,71] The properties and applications of the graft copolymers obtained have been reviewed in detail in a book edited by Yamashita.[162-164] Among a number of PSt graft copolymers reported, those with hydrophilic trunks obtained by copolymerization with 2-hydroxyethyl methacrylate (HEMA) or methacrylic acid (MAA) are amphiphilic, exhibiting interesting solution, solid and surface properties for applications including surface modification, contact lenses, adhesives, etc.

5.3. *Polydienes*

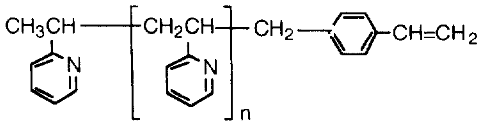
Termination methods of anionic polymerization are best suited to introduce a polymerizable end group into a polydiene of a fairly controlled microstructure. Polyisoprene (PIp) and polybutadiene macromonomers may be prepared by the same method as applied for polystyrene macromonomers. Thus PIp macromonomers with end groups such as those given for PSt in **3–10**[3-6] as well as PSt-PIp[105,107] and poly(α-methystyrene)-PIp[165] block macromonomers, as in **27**, have all been reported. They are of particular interest in providing soft, lyophilic, and reactive or cross-linkable domains in microphase-separated structures.

5.4. *Poly(vinylpyridines)*

Vinylpyridine polymers are of interest for their chelating abilities and for water-soluble, cationic polyelectrolytes after their quarternization. Anionic living polymerization of 2-vinylpyridine has been successfully applied to prepare macromonomers, just like those from styrene, as in the following examples: **55**. **56**



(55)[166]



(56)[167]

55 was prepared by polymerization initiated with an adduct of *sec*-butyllithium and 1,1-diphenylethylene (1,1-diphenyl-3-methylpentyllithium), followed by end-capping with *p*-isopropenylbenzyl bromide.[166] End-capping by ethylene oxide followed by methacryloyl chloride gave a macromonomer with a methacrylate end group like **6**. 1-(2-Pyridyl) ethyllithium, derived from 2-ethylpyridine with butyllithium, polymerized 2-vinylpyridine to afford **56** after end-capping with *p*-vinylbenzyl chloride.[167]

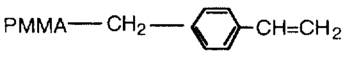
4-Vinylpyridine suffers from a problem of precipitation of its polymer during polymerization. A macromonomer with methacryloyl end groups was reported by direct end-capping with methacryloyl chloride, though characterized by a broad distribution.[168]

5.5. *Polyacrylates, polymethacrylates and their acid and amide derivatives*

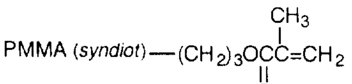
Great progress has been made for the controlled polymerization of acrylic and methacrylic monomers along with styrenes. In particular, anionic methods including group transfer polymerization (GTP) and ligated polymerization have made possible living polymerizations of these ester monomers without any appreciable side reactions on ester functions to afford polymers with well-controlled molecular weights and distributions.[169] A number of corresponding macromonomers have been prepared in anionic systems, as in the following examples for poly(methyl methacrylate) (PMMA):

$\text{PMMA}-\text{CH}_2\text{CH=CH}_2$

(57)[170]

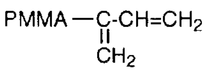


(58)[170-173]



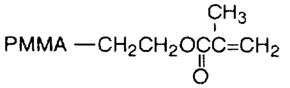
$\text{PMMA }(\textit{syndiot})-(\text{CH}_2)_3\text{O}\underset{\underset{\text{O}}{\|}}{\text{C}}\overset{\overset{\text{CH}_3}{|}}{\text{C}}=\text{CH}_2$

(59)[174]



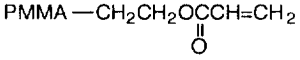
$\text{PMMA}-\underset{\underset{\text{CH}_2}{\|}}{\text{C}}-\text{CH=CH}_2$

(60)[175]



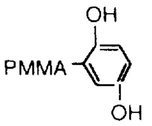
$\text{PMMA}-\text{CH}_2\text{CH}_2\text{O}\underset{\underset{\text{O}}{\|}}{\text{C}}\overset{\overset{\text{CH}_3}{|}}{\text{C}}=\text{CH}_2$

(61)[80,176,177]



$\text{PMMA}-\text{CH}_2\text{CH}_2\text{O}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{CH=CH}_2$

(62)[178]

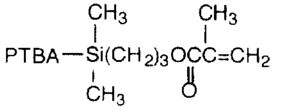


(63)[179]

Here anionic polymerization, initiated with a sterically hindered initiator such as 1,1-diphenylhexyllithium at a low temperature (– 78°C) and terminated with allyl bromide and *p*-vinylbenzyl bromide, produced **57** and **58**.[170] Highly isotactic and sydiotactic PMMA macromonomers with formulas **18** or **58** and **59**, were prepared via living polymerizations initiated with *t*-BuMgBr and *t*-BuLi/*n*-Bu$_3$Al in toluene at – 78°C, respectively.[171,174] Such stereoregulation is unique among the many macromonomers that have been prepared so far. They were also subjected to stereospecific polymerization[100] and copolymerization[180,181] to prepare a comb polymer and a graft copolymer with both trunks and branches of controlled chain-length and stereoregularity. 1,3-Butadienyl-, **60**, and (meth)acrylate-, **22**, **61**, **62** as well as *p*-vinylphenyloxycarbonyl- and hydroquinonyl-ends, **63**, were introduced by the corresponding initiators for GTP.[81,175–179] Anionic copolymerization of **61** with MMA produced homogeneous branched PMMA with controlled lengths in both trunks and branches.[176]

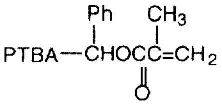
Similar methods leading to **58** were applied to prepare corresponding poly(*tert*-butyl methacrylate) macromonomers,[173,182] which are useful in providing poly(methacrylic acid) (PMAA) chains as the grafts by hydrolysis of the *tert*-butyl ester either in the form of the macromonomer or after copolymerization. Living anionic polymerization of protected monomers such as trimethylsilyl ether of 2-hydroxyethyl methacrylate (HEMA)[173,183] and isopropylidene-glyceryl methacrylate[173] also gives easy access to the corresponding hydrophilic macromonomers with *p*-vinylbenzyl or *p*-isopropenylbenzyl end groups.

tert-Butyl acrylate has been polymerized in the presence of lithium chloride and end-capped with *p*-vinylbenzyl bromide to afford a poly(*tert*-butyl acrylate) (PTBA) macromonomer like **58**.[184] Other end-capping agents such as methacryloyloxypropyl dimethylsilylchloride,[184] benzaldehyde followed by methacryloyl chloride, *p*-styryl dimethylsilylchloride and *p*-vinylbenzoyl chloride[185] afforded macromonomers that are useful precursors to poly(acrylic acid) (PAA) segments, as follows:



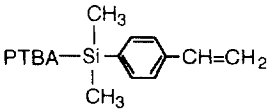
$$\mathrm{PTBA{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}(CH_2)_3O\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}{=}CH_2}$$

(64)[184]

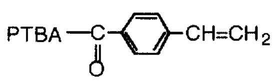


$$\mathrm{PTBA{-}\overset{\overset{Ph}{|}}{C}HO\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}{=}CH_2}$$

(65)[185]

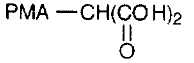


(66)[185]



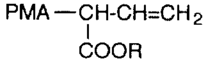
(67)[185]

Polyacrylate macromonomers including poly(methyl acrylate) (PMA) and poly(*n*-butyl acrylate) (PBA) have also been prepared by initiation with metal-free initiators or by GTP:



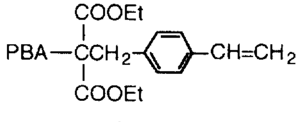
$$\mathrm{PMA{-}CH(\underset{\underset{O}{\|}}{C}OH)_2}$$

(68)[186]

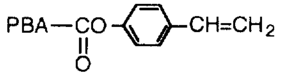


$$\mathrm{PMA{-}\underset{\underset{COOR}{|}}{C}H{-}CH{=}CH_2}$$

(69)[187]

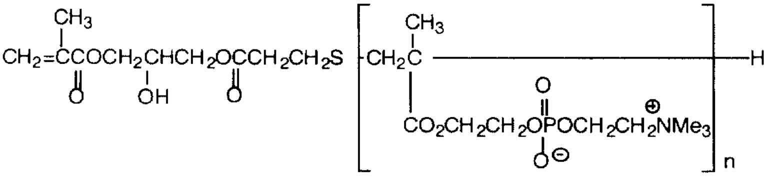


(70)[188]



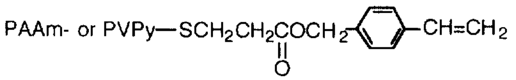
(71)[188]

Radical polymerization has also been conveniently applied to the syntheses of macromonomers from (meth)acrylates and related monomers. Functional groups introduced either by chain transfer or by initiation were transformed to appropriate polymerizable groups, as described in Section 1 and 2. A typical example is the methacrylate-ended poly(lauryl methacrylate) macromonomer, **2**, which was prepared by polymerization in the presence of thioglycolic acid as a transfer agent, followed by reaction with glycidyl methacrylate (GMA). The same method was applied to various methacrylate[2,19,189–194] and acrylate.[22] A further example for a phospholipid-containing methacrylate is shown as **72.**[195] Styryl end groups were introduced to PMMA by reaction of the imidazoline ring[190,191] or by the iniferter method,[196] similarly to PSt as in **14** or **54**. PMMA macromonomers with diol[36] or bis (carboxylic acid)-end groups[37–39] for application to polyaddition or polycondensation were described in Section 3 (Table 1). Also as discussed earlier, Co(II)-catalysed transfer in MMA polymerization directly affords an allyl-ended macromonomer, **12**,[44,45] which simulates exactly one of the products of termination by disproprtionation in MMA radical polymerization. Applications of PMMA- and related graft copolymers for surface modification have also been reviewed.[163]

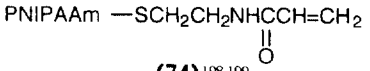


(72)[195]

Amide-containing macromonomers such as polyacrylamide (PAAm),[30] poly(N-vinylpyrrolidone) (PVPy)[30,197] and poly(N-isopropylacrylamide) (PIPAAm)[198,199] macromonomers, **73**, **74**, useful for providing water-soluble segments, were similarly prepared by chain-transfer-controlled radical polymerization coupled with end-group transformation. Poly(N-acryloylmorpholine) with an amino end group, **75**, prepared by chain-transfer polymerization, copolymerizes by polyaddition with bisacrylamide monomers to produce graft copolymers with a polyamideamine trunk.[200]

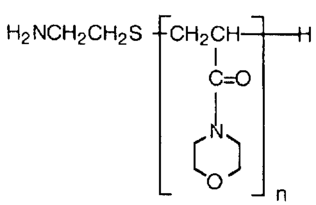


(73)[30,197]



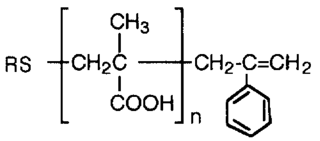
$$\text{PNIPAAm}-SCH_2CH_2NHC(=O)CH=CH_2$$

(74)[198,199]



(75)[200]

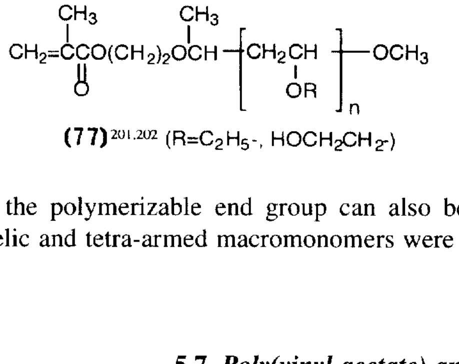
Polyacid (PMAA, PAA) macromonomers are easily derived from their corresponding *tert*-butyl esters, as described above, but also conveniently by a direct, one-step synthesis via a radical addition–fragmentation transfer process to 2-substitued allyl compounds, as discussed for **11**. A drawback is the poor polymerizability of the allyl functions. 2-Phenylallyl-ended PMAA macromonomers, **76**, however, were found in emulsion systems to copolymerize with styrene to give stable emulsions, probably as a result of enhanced local concentrations or organizations of the hydrophobic end group in water.[43]



(76)[43] (R=$HOCH_2CH_2$-, *t*-Bu-)

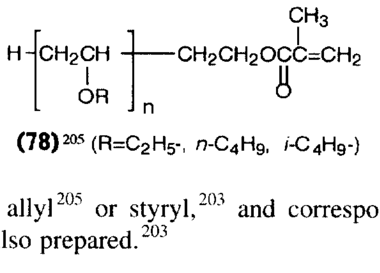
5.6. *Poly(vinyl ethers)*

Living cationic polymerization, developed by Higashimura *et al.*, has created a number of poly(vinyl ether)-based polymer architectures.[9] Macromonomers have been prepared either by initiation[201–203] or termination methods.[204,205] Examples follow:



$$CH_2{=}\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}}CO(CH_2)_2O\overset{\overset{CH_3}{|}}{C}H{-}\Big[CH_2\underset{\underset{OR}{|}}{C}H\Big]_n{-}OCH_3$$

(77)[201,202] (R=C_2H_5-, $HOCH_2CH_2$-)



$$H{-}\Big[CH_2\underset{\underset{OR}{|}}{C}H\Big]_n{-}CH_2CH_2O\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}{=}CH_2$$

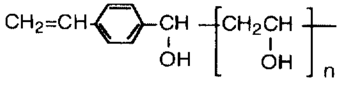
(78)[205] (R=C_2H_5-, *n*-C_4H_9, *i*-C_4H_9-)

where the polymerizable end group can also be allyl[205] or styryl,[203] and corresponding telechelic and tetra-armed macromonomers were also prepared.[203]

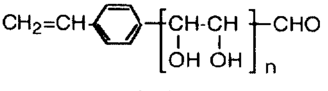
5.7. *Poly(vinyl acetate) and related polymers*

Poly(vinyl acetate) (PVAc) macromonomers were obtained by radical transfer polymerization in the presence of 2-mercaptoethanol[31] (Table 1), followed by reaction with methacryloyl chloride.[206] Imidazoline-terminated PVAc, **14**, was also reacted with *p*-vinylbenzyl chloride to afford the corresponding macromonomer.[49]

Poly(vinyl alcohol) (PVA) macromonomers, **79**, were successfully prepared by aldol-type GTP of *tert*-butyldimethylsilyl vinyl ether initiated with *p*-formylstyrene.[207–209] Similarly,



(79)[207-209]



(80)[210]

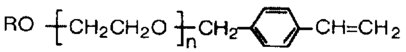
2-phenyl-1,3,2-dioxaborole polymerized to give a poly(vinylene glycol) macromonomer, **80**, after hydrolysis.[210]

5.8. *Halogenated vinyl polymers*

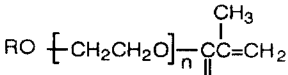
Syntheses of poly(vinyl chloride) and poly(vinylidene chloride) macromonomers with methacrylate or acrylate end groups by radical chain-transfer polymerization coupled with end group transformation have been reported.[34,35] Also perfluoroalkyl acrylate was polymerized in the presence of 2-mercaptoethanol, followed by reaction with methacryloyl chloride to afford the corresponding macromonomer.[211] Polymerization of vinylidene fluoride with di-*tert*-butylperoxide followed by reaction with methacryloyl chloride also provided a methacrylate-ended macromonomer.[212]

5.9. *Poly(alkylene oxides)*

Poly(ethylene oxide) (PEO) is one of the well-known, water-soluble, nonionic polymers, and its macromonomers have been a subject of considerable interest because of their interesting, amphiphilic properties as well as their many potential applications in various fields.[87] In general, PEO macromonomers with *p*-vinylbenzyl or methacrylate end groups, **81**, **82**, are prepared by anionic polymerization of ethylene oxide with the appropriate potassium alkoxide, followed by end-capping with *p*-vinylbenzyl chloride or methacryloyl chloride.[78,85,213] Alternatively, they are readily prepared from commercial poly(ethylene glycol) monoalkyl ethers by reaction with the same reagents in the presence of base or sodium hydride. Macromonomers **19** with m = 4 and 7 were prepared by reaction with corresponding *p*-styrylalkyl bromide.[64] Corresponding methacryloyloxyalkyl end groups are also available as in **83**.[214-216]

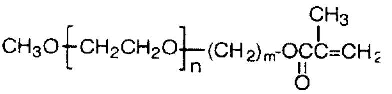


(81)



$RO\left[CH_2CH_2O\right]_n\underset{\overset{\|}{O}}{C}\overset{CH_3}{\overset{|}{C}}{=}CH_2$

(82)

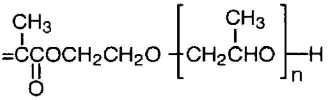


$CH_3O\left[CH_2CH_2O\right]_n(CH_2)_m{-}O\underset{\overset{\|}{O}}{C}\overset{CH_3}{\overset{|}{C}}{=}CH_2$

(83)[214-216] (m = 6, 10, 11)

Other examples include those with vinyl ether,[217-219] maleate or fumarate,[220] oxazoline,[221] allyl[222] and diol[223] as the polymerizable (α-) end groups, and those with hydroxyl,[63] carboxyl[224] and perfluoroalkyloxyterephthaloyl[225] as the ω-end.

Living or immortal polymerization of epoxides with an Al–porphilin complex including allyloxy, acryloyloxy, methacryloyloxyethyl (HEMA-), or *p*-vinylphenoxy groups allowed a direct method to corresponding macromonomers.[226] Cationic polymerization of ethylene oxide[227] or propylene oxide[228] with 2-hydroxyethyl methacrylate (HEMA) or acrylate in the presence of Lewis acids also directly afforded the corresponding macromonomers, for example, **84**.



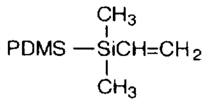
$CH_2{=}C(CH_3)COOCH_2CH_2O{-}[CH_2CH(CH_3)O]_n{-}H$

(84)[228]

The amphiphilic properties of the PEO macromonomers themselves[62-66,87] are of particular interest in view of their unique organizational effects on polymerization and copolymerization behaviors as well as their utility in emulsion and dispersion polymerization systems, as already dicussed in Section 3. Amphiphilic comb polymers and graft copolymers derived therefrom[87,229] are also of increasing concern in designing biocompatible and environmentally friendly polymeric materials.

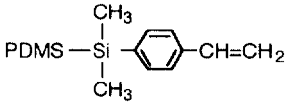
5.10. *Poly(dimethylsiloxane)*

Poly(dimethylsiloxane) (PDMS) macromonomers have also been extensively investigated because they provide soft, rubbery, hydrophobic segments for applications including surface modification[163] and oxygen-selective permeation.[72,230] PDMS macromonomers are most conveniently prepared by living anionic polymerization of hexamethylcyclotrisiloxane (D_3), followed by appropriate end-capping. Typical examples include **23** and the following:

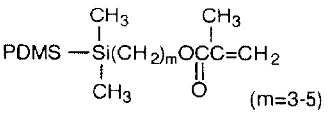


$PDMS{-}Si(CH_3)_2CH{=}CH_2$

(85)[231-233]

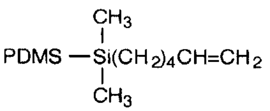


(86)[234,235]



$PDMS{-}Si(CH_3)_2(CH_2)_mOCOC(CH_3){=}CH_2$ (m=3-5)

(87)[176,236-240]



$PDMS{-}Si(CH_3)_2(CH_2)_4CH{=}CH_2$

(88)[241]

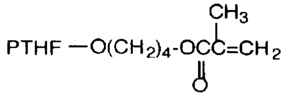
Telechelic macromonomers corresponding to **87** are also readily available.[242-244]

The PDMS macromonomers have been radical copolymerized with conventional monomers (**85** with vinyl acetate, **86** or **87** with MMA or styrene) allowing easy access to graft copolymers composed of speciality and commodity polymer segments endowed with interesting properties and applications. Anionic copolymerization of **23** with MMA[176,177] provided a graft copolymer with a narrow distribution in composition. **88** was copolymerized with 1-butene and SO_2 to give polysulfone-*g*-PDMS.[241]

PDMS macromonomers carrying bifunctional groups on one end, such as (3,5-diaminophenyl)ethyl,[245] (3,5-dicarboxyphenyl)propyl[246] and bis(4-aminophenyl)-methyl[247] have been prepared for use in polycondensation or polyaddition processes.

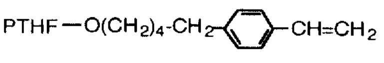
5.11. *Poly(tetrahydrofuran) and polyacetals*

Poly(tetrahydrofuran) or poly(oxytetramethylene) (PTHF) is also one of the macromonomers that have been extensively investigated from the beginning, together with polystyrene, PEO and PMMA.[213] Living cationic polymerization of tetrahydrofuran, which proceeds via a relatively stable oxonium ion as the propagating end, allowed ready introduction of polymerizable end groups either during the initiation or termination step. PTHF macromonomers derived have been copolymerized with various conventional monomers to give graft copolymers with flexible polyether chains as branches. Typical examples of the macromonomers obtained follow:

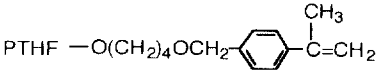


$\mathrm{PTHF{-}O(CH_2)_4{-}O\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}{=}CH_2}$

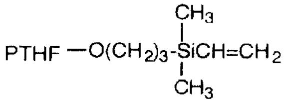
(89)[248-251]



(90)[251-254]



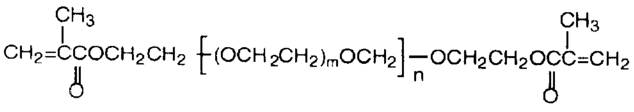
(91)[255]



$\mathrm{PTHF{-}O(CH_2)_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}CH{=}CH_2}$

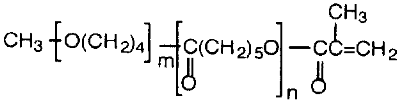
(92)[256]

1,3-Dioxolane[257] and 1,3,6-trioxocane[258] were cationically polymerized in the presence of 2-hydroxyethyl methacrylate to give the corresponding telechelic polyacetal macromonomers, **93** with *m* = 1 and 2, respectively, with methacrylate groups on both ends. Nomura and Endo prepared PTHF-poly(ε-caprolactone) block macromonomer, **94**, by transforming the PTHF living cation with SmI_2 to an alkoxide followed by anionic polymerization of the lactone and end-capping with methacryloyl chloride.[259]



$\mathrm{CH_2{=}\overset{\overset{CH_3}{|}}{C}\underset{\underset{O}{\|}}{C}OCH_2CH_2\left[(OCH_2CH_2)_mOCH_2\right]_n{-}OCH_2CH_2O\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}{=}CH_2}$

(93)[257,258] (m = 1, 2)



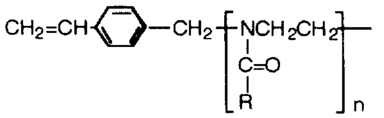
$\mathrm{CH_3\left[O(CH_2)_4\right]_m\left[\underset{\underset{O}{\|}}{C}(CH_2)_5O\right]_n{-}\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}{=}CH_2}$

(94)[259]

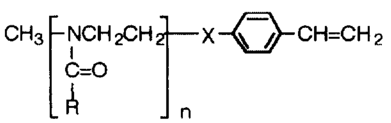
5.12. *Polyoxazolines and poly(ethylene imines)*

2-Alkyloxazolines polymerize by living cationic polymerization to provide the corresponding poly(N-acylethyleneimines), which can be water-soluble or insoluble depending on the alkyl group. Various macromonomers prepared include **95–98** other than **28** and **29** already described. A polyoxazoline macromonomer with a diol end group for polyaddition to oligoester–diisocyanate to form polyurethane grafts[267] and that with α-acrylate-ω-D-glucosamine end groups[268] were prepared. Water-soluble polyoxazoline macromonomers (R = Me) as well as their block macromonomers **28** and **29**[114] work effectively as reactive emulsifiers and dispersants.

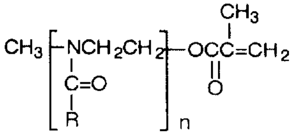
N-*tert*-Butylaziridine also undergoes living cationic polymerization to provide poly(N-*tert*-butylethyleneimine) macromonomers **99**, **100** after appropriate end-capping.[269,270]



(95)[260,261] (R = Me, Ph)

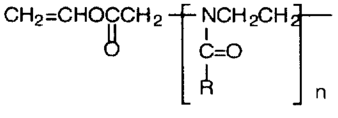


(96)[262] (R = Me, Et, Bu; X = O, S)



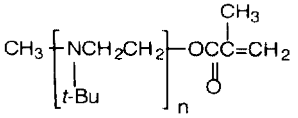
$CH_3\left[N(C(=O)R)CH_2CH_2\right]_n OC(=O)C(CH_3){=}CH_2$

(97)[263-265]



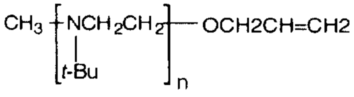
$CH_2{=}CHOC(=O)CH_2\left[N(C(=O)R)CH_2CH_2\right]_n$

(98)[266]



$CH_3\left[N(t\text{-}Bu)CH_2CH_2\right]_n OC(=O)C(CH_3){=}CH_2$

(99)[269]

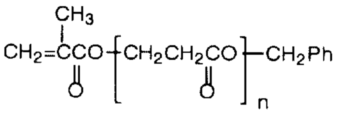


$CH_3\left[N(t\text{-}Bu)CH_2CH_2\right]_n OCH2CH{=}CH2$

(100)[270]

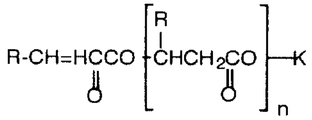
5.13. *Polylactones and polylactide*

Poly(β-propiolactone) macromonomers have been prepared by anionic polymerization with Al–porphilin complexes as were used for epoxides.[226] Potassium methacrylate polymerized β-propiolactone in the presence of dibenzo-18-crown-6 to give directly **101**.[271] Potassium hydride polymerized β-propio- and β-butyrolactone to give **102**.[272]



$CH_2{=}C(CH_3)C(=O)O\left[CH_2CH_2C(=O)O\right]_n CH_2Ph$

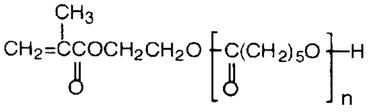
(101)[271]



$R\text{-}CH{=}HCC(=O)O\left[CH(R)CH_2C(=O)O\right]_n K$

(102)[272] (R = H, Me)

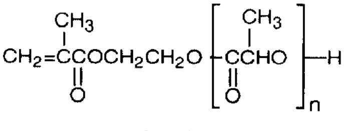
ϵ-Caprolactone (CL) can be best polymerized with Al-alkoxides without depolymerization. Thus allyl and methacrylate end groups were introduced by corresponding Al-alkoxides to afford polyester macromonomers.[273-275] An example is **103**:



$CH_2{=}C(CH_3)C(=O)OCH_2CH_2O\left[C(=O)(CH_2)_5O\right]_n H$

(103)[273,274]

A poly(adipic anhydride) macromonomer was similarly prepared.[276] A PTHF–PCL block macromonomer, **94**, was already described. Poly(D,L-lactide)[277] and poly(L-lactide) macromonomers,[278] **104**, as biodegradable systems, were similarly obtained by polymerization with methacryloyloxyethyl-AlEt$_2$:

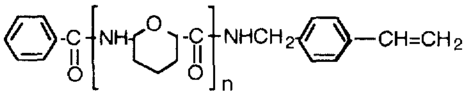


$CH_2{=}C(CH_3)C(=O)OCH_2CH_2O\left[C(=O)CH(CH_3)O\right]_n H$

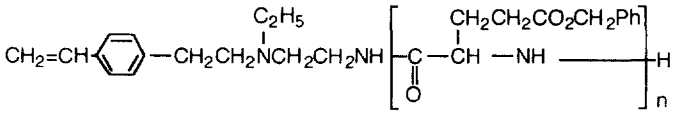
(104)[277,278]

5.14. *Polylactams and poly(amino acids)*

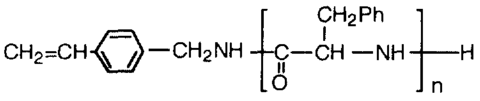
Ring-opening polymerization of lactams and α-amino acid N-carboxyanhydrides (NCAs) allows the preparation of corresponding polyamide or poly(α-amino acid) macromonomers, respectively, either by termination or initiation methods of living anionic polymerization. Examples follow:



(105)[279,280]



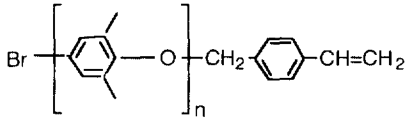
(106)[281]



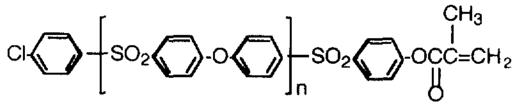
(107)[282]

5.15. *Macromonomers prepared by polycondensation*

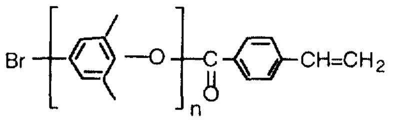
Since the first macromonomer from poly(12-hydroxystearic acid), **1**, was developed by the ICI group, there have not been many studies on macromonomers prepared via



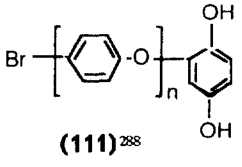
(108)[283,284]



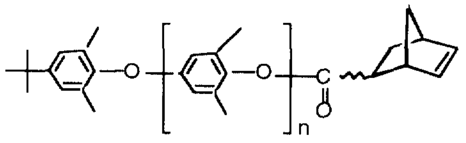
(109)[285]



(110)[286,287]



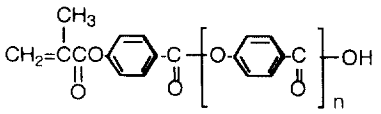
(111)[288]



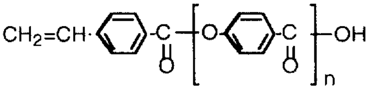
(112)[289]

polycondensation. Among others, the examples **108–112** prepared by polycondensation under basic conditions followed by appropriate end-group transformations are typical of providing rigid, rod-like, anisotropic segments as the graft components.

Polycondensation of *p*-hydroxybenzoic acid in the presence of *p*-carboxyphenyl methacrylate or *p*-carboxyphenylstyrene as a chain terminator produced methacrylate- or *p*-styryl-ended, soluble aromatic polyester macromonomers, **113** or **114**, respectively.[290] Similarly, a mixture of *p*- and *m*-aminobenzoic acid in the presence of methacrylic acid or *p*-carboxystyrene produced soluble, methacrylate- or *p*-styryl-ended polyaramide macromonomers.

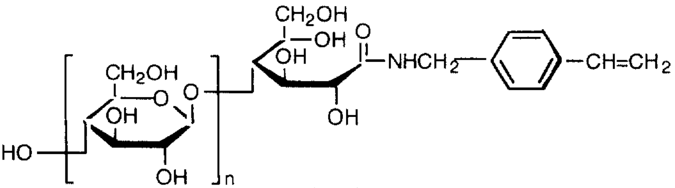


(113)[290]

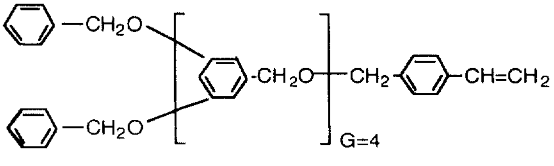


(114)[290]

Macromonomers containing oligosaccharides with styryl or methacrylate end groups, **115** for example, were prepared for specific recognition toward cells.[291–293] A dendrimer with a polymerizable group, **116**,[294] or a hyperbranched macromonomer, was also synthesized, where G = 4 means a fourth generation, carrying 2^4 or 16 arms on the outermost surface.



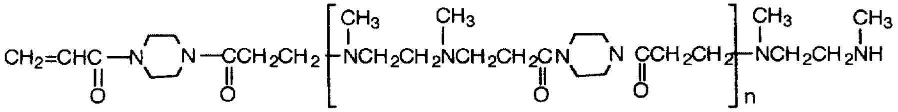
(115)[292]



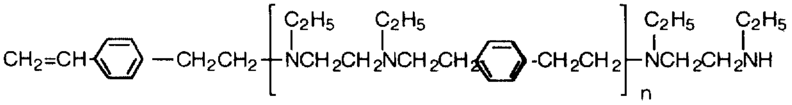
(116)[294]

5.16. *Macromonomers prepared by polyaddition*

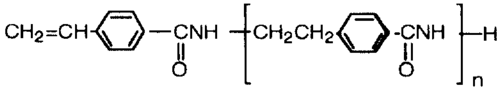
Polyaddition involving vinyl groups provides a direct route to macromonomers as already decribed for **15**. Other examples include nitrogen-containing macromonomers such as polyamideamines (**117**), polyamines (**118**), polyamides (**119**), polyguanamines (**120**) and silicon-containing macromonomers (**121–123**), which can be useful as functional intermediates for biocompatible and intelligent materials.



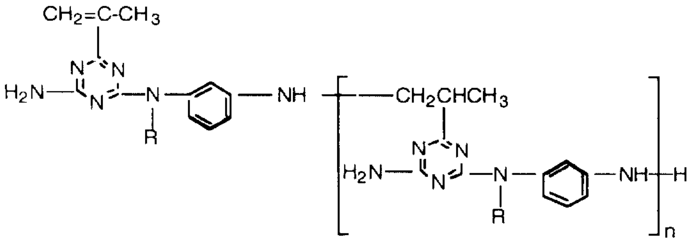
(117)[295,296]



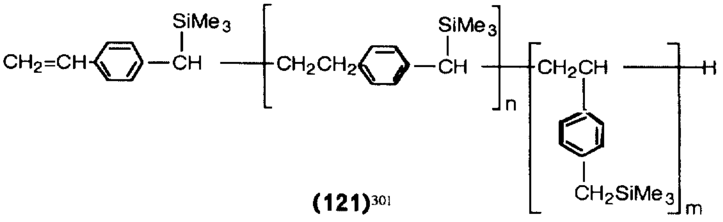
(118)[297,298]



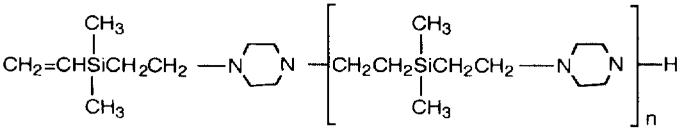
(119)[299]



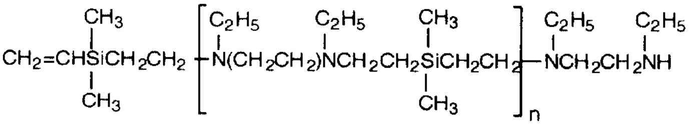
(120)[300] (R = C_2H_5, $C_{18}H_{37}$)



(121)[301]

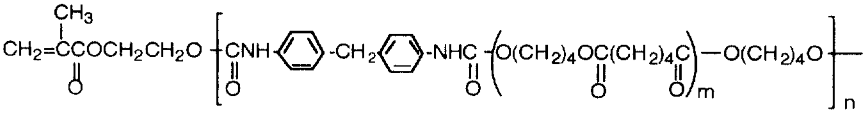


(122)[302]

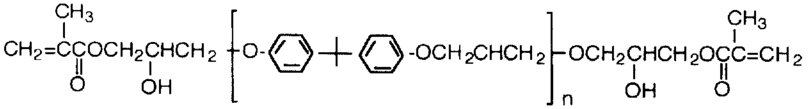


(123)[304]

Some other macromonomers via the polyaddition route have also been prepared by end-group transformations from a polyurethane to **124**, or from a epoxy-bisphenol adduct to **125**, for example:



(124)[305]



(125)[306-308]

6. CONCLUSIONS

For two decades, a large number of macromonomers have been prepared and used for the syntheses of various types of branched polymers and copolymers. In this article, the author intended to review fundamental aspects related to polymeric design, including syntheses (Section 2), characteristic behaviors in polymerization and copolymerization of typical macromonomers (Section 3), and the construction of comb or star and graft polymers (Section 4). Finally, many examples of macromonomers as classified by type of constituting monomers are listed (Section 5). An understanding of macromonomer reactivity and of the characterization and properties of the branched polymers derived still remain to be studied further. Macromonomers will hopefully continue to serve as good probes to understand polymer–polymer reactions and branched polymers, in general. The architectures of novel branched polymer systems by the use of macromonomers are also of growing interest. We have many kinds of building blocks available as the trunk and branch components, with a wide range of properties ranging from hard to soft, hydrophobic to hydrophilic, speciality to commodity, and so on.

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