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The Synthesis and Polymerisation of Macromonomers

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Problems concerning the synthesis and reactions of macromolecular monomers (macromonomers)-polymeric molecules containing at least one polymerisable, usually unsaturated, end group or a fragment capable of polycondensation reactions—are considered. They are usually obtained by a radical or ionic polymerisation method in which the use of special chain initiating or terminating agents as well as intense chain transfer ensures the introduction of the reactive group. Studies on the polymerisation and copolymerisation of macromonomers are surveyed and the characteristic features of these processes, determined by the low concentration of the reacting group and the presence of a polymeric substituent, are analysed. The applications of macromonomers in polymer engineering, mainly in the synthesis of cone, star, graft, and other hybrid polymers, are examined.
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I. INTRODUCTION

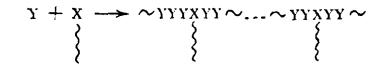
Reactive oligomers constitute a large family of polymers having at least one functional end group capable of further reactions. Macromolecular monomers or macromonomers (MM) are reactive monofunctional oligomers capable of participating in chain propagation reactions via these groups. The term macromonomer (or even more briefly "macromer") was introduced by Milkovich[1] as the trade name for a group of polystyrene oligomers with a wide variety of polymerisable end groups. According to a later definition,[2] macromers are short-chain polymers coupled quantitatively at one of the ends of the chain to polymerisable unsaturated groups. The unsaturation is naturally not the only possible source of the polymerisability of MM, since the end group can be cyclic or of another type, although the number of examples of such groups is small. These groups can be introduced into the MM molecule in the stage involving the initiation or limitation of the growth of the chain (chain transfer and termination) and also as a result of the conversion of one set of end groups into another.

In reality MM were known long before the time when this term appeared. Thus siloxane MM with styrene groups (polysiloxanestyrene MM) were synthesised as early as 1962 and were used to obtain polystyrene with grafted polysiloxane side chains.[3] All these features resemble the history of "living" polymers, which existed long before they came to be referred to by this term, but the introduction of the latter was extremely useful for the purposes of classification and the elucidation of preparative possibilities.

Thus a MM can be represented schematically as a polymer chain having one end group X capable of entering into chain propagation reactions:

although in a number of studies bifunctional and even polyfunctional oligomers of different type have also been classified as MM, which is incorrect.

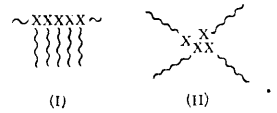
When preparative aspects associated with MM are considered, then MM are usually regarded as intermediates in the synthesis of graft copolymers with a vigorously defined structure, in particular as regards the length of the grafted chains:



(1)

where Y is a low-molecule-weight comonomer.

The homopolymerisation of the MM itself affords a regular comb polymer (I), while in the case of very low degrees of polymerisation the same reaction leads actually to a star polymer (II):



(I) (II)

Together with other familiar methods of preparative polymer chemistry, the procedures based on MM give rise to the prospect of obtaining polymeric products of the types indicated, whose nature is extremely varied. The possibility of combining in a single macromolecule units of the kind that cannot be joined together by direct or successive copolymerisation and other similar methods is of special interest. Thus macromonomers give rise to the possibility of overcoming the inability of certain monomers to polymerise via a single mechanism.

MM are identified by the usual methods, characterising mainly the molecular weight ($\overline{M}_n$) and the average functionality ($\bar{f}_n$) with respect to the groups X:

$$\bar{f}_n = \frac{\overline{M}_n N_x}{g},$$

where g is the mass of the sample analysed and N_x the number of functional groups found in the specimen. It is noteworthy that, in contrast to the telechelic polymers used in the synthesis of polymer networks, in the case of MM there is no need to attain a high functionality, although naturally in most synthetic studies the authors endeavoured to obtain compounds with a functionality close to unity. The deficiency of polyfunctional reactive oligomers as regards functionality usually has serious consequences when they are employed in the synthesis of polymeric materials.[4]

II. METHODS OF SYNTHESIS OF MACROMONOMERS

Polymerisable groups can be introduced into the macromolecule in virtually any stage of its formation process. In polymerisation such groups can be a direct result of a specific mechanism of chain initiation, destruction, or transfer and also of the introduction into the reactive mixture of special substances (chain initiating, terminating, or transferring agents). Finally, groups capable of subsequent polymerisation can be formed during the reaction of some other end groups which were present in the initial oligomers and in this case polycondensation oligomers can also be employed for the synthesis of MM.

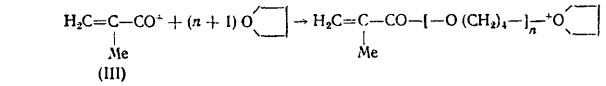
1. Polymerisation Methods

(a) Initiation

Initiation with subsequent "living" polymerisation is one of the most direct methods of synthesis of MM. It is necessary that the initiation under the influence of the initiator introduced should be the only reaction leading to the appearance of growing polymer chains and that side processes, including the polymerisation of the end group formed, should not occur. We shall consider certain examples of such syntheses.

Cationic polymerisation. Only a few monomers polymerise via the "living" mechanism under the conditions of cationic initiation. Some of them are used to synthesise MM.

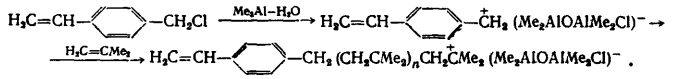
The polymerisation of tetrahydrofuran under the influence of the unsaturated acylium salt (III), i.e.



(III)

leads to a polymer the first of the end groups of which is the methacrylate group, while the second is available for the generation of any kind of functional group.[5] This method is suitable for the "living" cationic polymerisation of various monomers, because the oxocarbenium ions (III) can initiate the polymerisation of heterocycles such as acetals, sulphides, and amines.

A study,[6] whose authors were the first to synthesise polyisobutylene MM using as the initiator the *p*-vinylbenzyl chloride—Me_3Al—water system under conditions ruling out chain transfer, may serve as an example of the employment of the cationic polymerisation of vinyl monomers:



The number of styryl groups per chain in the MM synthesised was close to 1.0 according to UV spectrophotometric data (255 nm, $\varepsilon = 1.68 \times 10^4$ litre mol^{-1} cm^{-1}), but the authors[6] noted some decrease of functionality with respect to these groups when the synthesis was carried out at low monomer concentrations or with high degrees of conversion. In a modified method,[7] the initiator employed was therefore *p*-(β-bromoethyl)cumenyl chloride, which, after its incorporation in the chain, was converted into the styryl group by treatment with potassium t-butoxide.

Certain characteristics of the MM based on isobutylene obtained by these procedures are presented in Table 1, which also includes information about isobutylene MM synthesised by other methods.

The polymerisation of vinyl ethers on treatment with the $HI-I_2$ system takes place without chain termination and transfer and leads to monodisperse polymers. This fact was used to synthesise MM from ethyl vinyl ether:[11]

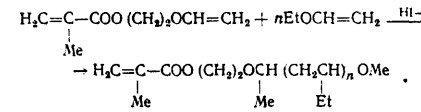
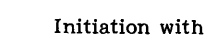
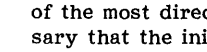
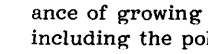
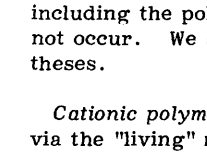
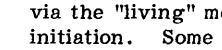


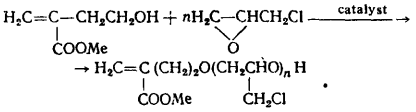
Table 1. Characteristics of MM based on polyisobutylene.

End group	Method*	$10^{-3}\bar{M}$	$\bar{f}_n$	Refs.
	A	10—30	—	[6]
	A	4.2—34.2	0.9—1.1	[7]
	B	1.6—3.2	0.95—1.04	[8]
	B	1.6—13.9	0.98—1.05	[8]
	C	27.0	1.0	[9]
	B	3.6	1.95**	[10]

*Methods for the introduction of end groups: A—initiation; B—reactions via end groups; C—method employing a combined agent—initiator and chain transfer agent ("inifer"[9]).
**A bifunctional derivative.

The polymerisation was carried out at −40 °C in toluene; chain termination was achieved by introducing methanol. The degree of polymerisation was varied by varying the ratio of the monomer and the initiator in the range 5—100. A study of the MM obtained by gel-permeation chromatographic (GPC) and NMR methods confirmed the proposed structure.

Recently, in the development of methods for the preparation of oligomers having a specified structure on cationic initiation, much hope was associated with the so called "activated monomer" mechanism, which makes it possible to avoid many typical complications, in particular macrocyclisation. This procedure, in which a proton-containing initiator "specifies" the polymer end group, has been used recently to obtain MM based on epichlorohydrin:[12]

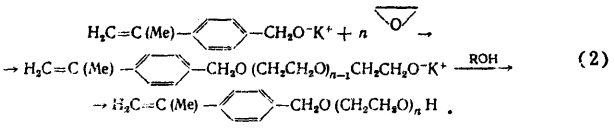


It is entirely possible that this approach is fairly universal.

Anionic polymerisation. The range of monomers polymerising via the "living" mechanism under the conditions of anionic initiation is much wider than in the cationic processes. Anionic polymerisation reactions of styrene and its derivatives, dienes (buta-1,3-diene, isoprene), 2- and 4-vinylpyridines, methacrylates (under conditions ruling out chain

transfer), certain cyclic ethers (usually epoxyethane), three- and four-membered cyclic sulphides, lactones, cyclosiloxanes,† and other less readily available groups of monomers can be used virtually without limitations for the synthesis of MM by the direct initiation procedure. The formation of living polymers is not the only precondition for the successful synthesis of MM: it is necessary that the initiation mechanism should ensure the incorporation of the future polymerisable group in the polymer chain.

For example, alkoxides derived from p-isopropenylbenzyl alcohol have been used to synthesise polyoxyethylene MM:[13]



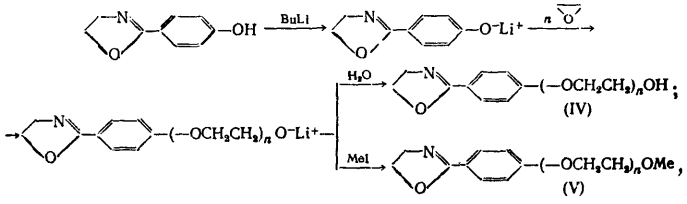
(2)

The MM, formed in 75–85% yield, had molecular weights in the range 2000–4500. They were characterised by different methods; it has been shown that the calculated and observed characteristics agree satisfactorily. The molecular weights of two specimens based on the data of Masson et al.[13] are presented below:

From the ratio of the monomer and initiator concentrations	2000	4500
From the titration of unsaturated groups	1850	5200
From ^{1}H NMR data—the ratio of the signals of the protons in the aromatic end groups and oxyethylene units	1700	4700
From the UV spectrum (250 nm, ϵ = 12700 litre mol^{-1} cm^{-1})	2000	4200
From light scattering data	2100	4500

The results of the study of Masson et al[13] show that the process does indeed proceed via mechanism (2), but a high functionality is hardly guaranteed in this instance, because any proton-containing admixture participates in this process as a coinitiator (see, for example, Sepulchre et al.[14]), generating chains without specified functional groups.

Polyoxyethylene MM with 2-oxazoline end groups, suitable for subsequent cationic polymerisation, were synthesised in an analogous way.[15] When the reactions are carried out in accordance with the scheme

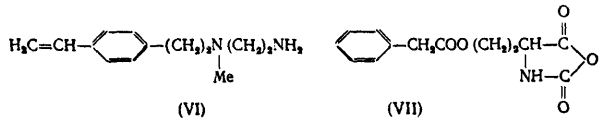


the MM (IV) and (V) are obtained, their degrees of polymerisation amounting to ~20 and 40 respectively according to gas-phase osometric data; a chain length of ~20 can also be obtained from the ratio of the peak areas of the methylene and aromatic protons in the NMR spectrum of compound (IV); compounds (IV) and (V) homopolymerise and copolymerise on treatment with BF_3 etherate.

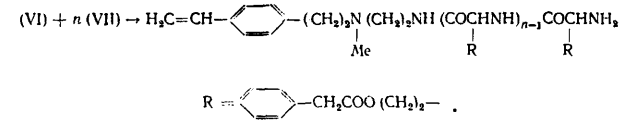
Here mention should also be made of the synthesis of reactive oligomers of epoxyethane and propene on treatment with alkoxides derived from allyl alcohol,[16] but in this case there is even less guarantee of the formation of MM homogeneous as regards functionality since intense chain transfer to the monomer is characteristic of the polymerisation of epoxypropane.

†Macrocyclisation at high degrees of conversion is characteristic of the last two groups of monomers.

It is known that the polymerisation of the *N*-carboxyanhydrides of α-aminoacids on treatment with primary amines proceeds in many instances with quantitative initiation via addition to the monomer. This has been used[17] for the synthesis of polyaminoacid MM, which are of great interest from the standpoint of their subsequent use for the preparation of biomedical materials. Amino-derivatives of styrene, for example compound (VI), were used as the initiators, while the monomer was the *N*-carboxyanhydride of γ-benzyl-L-glutamic acid (VII):

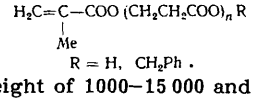


The polymerisation reaction via mechanism (3) leads to MM with a styrene end group:



(3)

Salts of various weak acids, which are effective only in the presence of activators such as crown ethers, are known to be suitable for the initiation of the polymerisation of β-propiolactone. The use for this purpose of the potassium methacrylate–dibenzo-18-crown-6 ether made it possible to obtain the corresponding MM:[18]

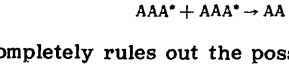


with a molecular weight of 1000–15 000 and with a quantitative functionality. An analogous approach is applicable also to epoxyethane.

b) Reactions Involving the Deactivation or Destruction of Active Centres

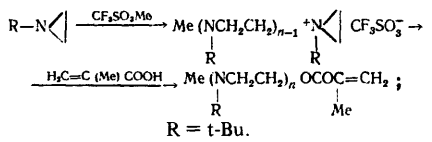
Cationic polymerisation. "Living" cationic polymerisation mechanisms, which constitute an essential condition for the quantitative introduction of the required end groups at the deactivation stage, has been established most reliably for heterocycles. It has been correctly stated recently,[19] in the analysis of the problem of the introduction of functional end groups under the conditions of cationic polymerisation with ring opening, that the main obstacle in this instance is chain transfer to the polymer, which should be eliminated or negligible. Macrocyclisation gives rise to analogous difficulties.

There are virtually no complications in the preparation of MM from tetrahydrofuran, cyclic sulphides, or aziridines if the process is carried out up to low degrees of conversion. At later stages of the process, chain transfer to the polymer complicates the synthesis of MM in these and similar systems and the problem is not limited to macrocyclisation, the broadening of the molecular weight distribution (MWD), and the impossibility of achieving total conversion. An even more serious obstacle is the disproportionation of living polymers, in which they are partly converted into a mixture of inactive and bifunctional growing macromolecules:



which completely rules out the possibility of obtaining MM homogeneous as regards functionality during their subsequent deactivation.

The use of sterically hindered monomers partly or fully suppresses the undesirable chain transfer to the polymer; one of the examples of this is provided by the successful synthesis of methacrylate MM from *N*-t-butylaziridine:[20]

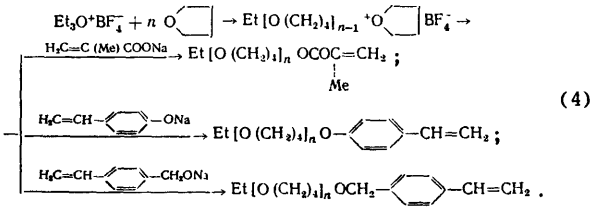


R = t-Bu.

Gas-phase osmometric and ^{1}H NMR data confirm the structure of the MM obtained, whose finite functionality was not determined in the above study.

Many different MM have been obtained from tetrahydrofuran, which is perhaps the most typical monomer polymerising via the cationic "living" mechanism.

MM have been synthesised[21–23] from tetrahydrofuran with methacrylate and styrene end groups via mechanism (4), the polymerisation being interrupted by introducing the appropriate reagents at a low degree of conversion:



(4)

Table 2. Characteristics of MM based on polytetrahydrofuran obtained by cationic polymerisation methods.

End group	Method*	$10^{-3}\bar{M}$	$\bar{f}_n$	Refs.
~OCH$_2$–C$_6$H$_4$–CH=CH$_2$	A	2.7–9.7	0.93–1.07	[21]
~OCH$_2$–C$_6$H$_4$–C(Me)=CH$_2$	A	2.3–8.0	—	[24]
~O–C$_6$H$_4$–CH=CH$_2$	A	4.5–9.9	0.90–1.12	[23]
~OCO–C(Me)=CH$_2$	A	8.0	0.98–1.00	[22]
~CO–C(Me)=CH$_2$	B	1.6–3.4	0.93–1.08	[5]
H$_2$C=C(R)–CO~OCO–C(R)=CH$_2$	C	17.0–55.4	1.71–1.96**	[25]

*Methods for the introduction of end groups: A–deactivation; B–initiation; C–the method of "inifers" (see the footnote to Table 1).
**Bifunctional derivative (R–H or Me).

Other functional groups have been introduced into polymers via procedures similar to scheme (4). Certain characteristics of MM based on tetrahydrofuran, obtained by the deactivation of living polymers and also by other ionic polymerisation methods, are listed in Table 2. Evidently in most cases, where the reaction is continued only up to a low degree of conversion, the target functionality is nearly obtained. There is no doubt that a wider assortment of polymerisable end groups is also possible.

Anionic polymerisation. The synthesis of MM by the method involving the directed deactivation of living anionic polymers was achieved for the first time in relation to polystyrene.[1,26,27] A multiplicity of different functional groups, capable of polymerisation via a multiple bond or with ring opening and also of polycondensation or polyaddition, were introduced.

The deactivation of macroanions leads to much more extensive possibilities than in the case of the analogous cations, because, as already mentioned, a much greater number of monomers polymerise in this instance with formation of living polymers. The realisation of these possibilities is illustrated in Table 3, where the majority of the MM obtained by this procedure at the present time are listed. The method for the introduction of functional groups in the synthesis of all the MM investigated is in principle the same and consists in the reaction of the nucleophilic living macroanion (usually in the state of an ion pair) with an electrophilic deactivator.#

Table 3. Characteristics of MM obtained by the deactivation of "living" anionic polymers.

Polymer chain	Polymerisable group	$10^{-3}\bar{M}$	$\bar{f}_n$	Refs.
Polystyrene	~CH$_2$–C$_6$H$_4$–CH=CH$_2$*	3.8–6.0	0.95–1.10	[28]
Polyoxyethylene	~OCO–C(Me)=CH$_2$	2.0–4.5	0.87–1.10	[13]
Poly(methyl methacrylate)	~CH$_2$–C$_6$H$_4$–C(Me)=CH$_2$	1.9–7.0	0.87–1.06	[29,30]
,,	~CH$_2$CH=CH$_2$	1.3–1.4	—	[29,30]
Polyamide**	~CH$_2$–C$_6$H$_4$–CH=CH$_2$	3.7–3.8	0.93–1.07	[31]
Polyvinylpyridine	~(CH$_2$)$_2$OCO–C(Me)=CH$_2$	3.5–6.2	0.70–0.94	[32]
,,	~CH$_2$–C$_6$H$_4$–C(Me)=CH$_2$	1.1–4.3	0.70–0.93	[32]
Polydimethylsiloxane	~C$_6$H$_4$–CH=CH$_2$	3.1–7.4	0.90–1.02	[33]
,,	~(CH$_2$)$_3$OCOC(Me)=CH$_2$	3.2–7.7	0.92–1.05	[33]

*MM based on polystyrene with the groups ~CH=CH$_2$, ~C(Me)=CH$_2$, ~OCH=CH$_2$, ~C$_6$H$_4$–CH=CH$_2$, ~CH(O)CH$_2$, ~OCOC(Me)=CH$_2$, ~OCOCH=CH–COOH, ~CH$_2$COOCH=CH$_2$, and ~CH(OH)=CH$_2$OH have been obtained,[1,26,27] but have not been characterised quantitatively.
**Polymer of 8-oxa-6-azabicyclo[3.2.1]octan-7-one.

The probability of side reactions, i.e. the non-selectivity of the reaction involving the introduction of the functional group, increases with increasing reactivity of the anion. Its conversion into a less active form yields in many instances positive results, of the kind achieved, for example, by the preliminary conversion of the polyvinylpyridine carbanion into an oxa-anion by reaction with epoxyethane.[32]

#The polymerisation of a bicyclic oxalactam, which proceeds via the activated monomer mechanism, is an exception;[31] in this instance the anion of the deactivator attacks the growing end of the chain.

Radical polymerisation. One of the possible mechanisms of chain termination in radical polymerisation is disproportionation of the macroradicals in accordance with the scheme

$$2\sim CH_2\dot{C}HX \rightarrow \sim CH{=}CHX + \sim CH_2CH_2X\ .$$

This reaction leads to a polymeric product, half of the macromolecules of which contain an unsaturated end group. This termination mechanism predominates in the polymerisation of methyl acrylate, methyl methacrylate, and other monomers.[34] We may note that, owing to the higher activation energy than in the recombination reaction, the contribution of the disproportionation to the destruction of macroradicals increases with increasing temperature. However, the tendency towards the formation of symmetrically substituted double bonds does not give rise to prospects for the use of such MM owing to their low reactivity.

(c) Chain Transfer

The synthetic applications of the chain transfer reaction as a method for the introduction of functional groups require that it should proceed effectively, predominating among other reactions limiting the length of the polymer chain. It is desirable that the chain transfer agent should not influence the polymerisation kinetics, i.e. that the new species arising in the chain transfer step should initiate the next chain. In essence, this is merely the definition of true chain transfer. Chain transfer systems and agents acting according to this principle have long been known, especially in radical polymerisation.

There are several radical and ionic polymerisation processes in which MM are formed via a mechanism natural for these processes, i.e. without the introduction of any special chain transfer agents. The most obvious variant of this method of synthesis of MM is polymerisation with intense chain transfer to the monomer. Generally speaking, two cases are possible, for example, for vinyl monomers:

$$\sim CH_2\dot{C}HX + H_2C{=}CHX \begin{cases} \xrightarrow{a} \sim CH_2CH_2X + H_2C{=}\dot{C}X\ ; \\ \xrightarrow{b} \sim CH{=}CHX + Me\dot{C}HX\ . \end{cases} \quad (5)$$

If there are no other initiation and termination processes in the given system, the double bond is fixed in the initial (pathway *a*) or terminal (pathway *b*) fragment of the chain. Chain transfer of type (5) in processes of different chemical nature proceeds with transfer of a hydrogen atom, proton, hydride ion or, more rarely, a larger species.

Cationic polymerisation. Two types of chain transfer reactions lead to MM in cationic polymerisation—chain transfer to the monomer and elimination of a proton from the active fragment of the growing macromolecule.

Chain transfer to the monomer is characteristic of the cationic polymerisation of certain unsaturated compounds. It has long been known, for example, that the cationic polymerisation of isobutene results in the formation of a macromolecule containing unsaturated groups at the end of the chain.[35,36] A more detailed analysis demonstrated that the number of such groups in the polymer is equal to the total number of macromolecules to within 5% (in the range of molecular weights 700–2000),[37] i.e. intense chain transfer takes place via the mechanism:

$$H_2C{=}CMe_2 \xrightarrow{\text{initiator}} X\,(CH_2CMe_2)_{n-1}CH_2\overset{\displaystyle Me}{\underset{\displaystyle Me}{C^+}} \xrightarrow{H_2C=CMe_2} \begin{cases} \rightarrow Me\,(CH_2CMe_2)_{n-1}CH_2C(Me){=}CH_2\ ; \quad \text{(VIII)} \\ \rightarrow Me\,(CH_2CMe_2)_{n-1}CH{=}CMe_2\ . \quad \text{(IX)} \end{cases} \quad (6)$$

NMR data have shown[37] that, together with groups (VIII) and (IX), other isomeric structures are formed in the MM via a reaction involving mechanism (6) but the entire wide variety of the different kinds of terminal unsaturation reduces exclusively to groups of type (VIII) when di-t-butylpyridine is used in the reaction as a cationic trapping agent.[38]

The cationic polymerisation of styrene[39] and α-methylstyrene[40] also leads to polymers with unsaturated end groups. They are formed in high yields in the polymerisation of styrene by CF_3SO_3H in non-polar media.[41] It has been established[42] that the yield of double bonds in acenaphthylene polymers formed via the cationic mechanism is quantitative.[42]

Reactions involving chain transfer to the monomer with formation of polymers having unsaturated end groups proceeds also in the polymerisation of certain heterocycles—ε-caprolactone,[43] oxepan,[44] and 2,2-dimethyloxetan.[45]

Transfer to the chain transfer agent, specially introduced into the system, has been used to obtain bifunctional MM. It has long been established[46] that acid anhydrides, for example, acetic anhydride, act as effective chain transfer agents in the polymerisation of tetrahydrofuran, which makes it possible to regulate the chain length and the composition of the end groups. This same procedure has been used recently to obtain bifunctional acrylate and methacrylate MM:[25,47]

$$[H_2C{=}C(R)CO]_2O + \sim CH_2\overset{+}{O}\langle\square\rangle \rightarrow \sim CH_2O(CH_2)_4COC(R){=}CH_2 + H_2C{=}C(R)CO^+ +$$
$$+ H_2C{=}C(R)CO^+ + nO\langle\square\rangle \rightarrow H_2C{=}C(R)CO[(CH_2)_4O]_{n-1}(CH_2)_4\overset{+}{O}\langle\square\rangle\ ; \quad (7)$$
$$R = H, Me\ .$$

There is a purely formal analogy between reaction (7) and polymerisation under the influence of "inifers"—substances which act simultaneously as initiators and chain transfer agents and introduced into polymer practice by Kennedy.[48] In the studies already quoted[8–10] this method has been used to synthesise various polyisobutylene MM (see Table 1).

The use of effective proton trapping agents—the so called "proton sponges", especially di-t-butylpyridine which gives rise to effective proton transport—is also promising in this instance.

Anionic polymerisation. The best known instance of the direct formation of MM in ionic polymerisation is provided by processes involving substituted oxirans.[49] The increased acidity of the hydrogen atoms in the molecules of these monomers, on the one hand, and the presence of the highly nucleophilic alkoxide anions, on the other, increase sharply the rate of the processes involving chain transfer to the monomer:

$$\sim CH_2CH(R)O^- + H_2C\underset{O}{-}CHR \rightarrow \sim CH_2CH(R)OH + H_2C{=}C(R)O^-$$
$$H_2C{=}C(R)O^- \xrightarrow{\text{monomer}} H_2C{=}CH(R)O\sim \ldots \sim CH_2CH(R)O^-\ , \quad (8)$$

whose contribution is extremely significant for the anionic polymerisation of the majority of substituted epoxides. We may recall that their oligomerisation processes are usually employed to generate hydroxylated telechelate polymers for the synthesis of polyurethanes and in this sense reaction (8) prevents the attainment of the required functionality.

These reactions have been studied in greatest detail in relation to epoxypropane, where two variants of terminal double bonds are possible:

$$\underset{(X)}{H_2C{=}CH{-}CH_2O{\sim}} \qquad \underset{(XI)}{Me{-}CH{=}CH{-}O{\sim}} .$$

Under the polymerisation conditions, the allyl groups (X) isomerise to the *cis*-propenyl groups (XI).[50] The maximum number of unsaturated groups does not, however, exceed 50–55% and their content depends on the temperature of the synthesis, the radius of the alkali metal counter-ion, which has been omitted in scheme (8), and also on the concentration of alcohol in the polymerisation system.[51,52] Reactions (8) have been observed also in the polymerisation of substituted glycidyl ethers: up to 87% of unsaturated macromolecules are formed in the polymerisation of, for example, *o*-chlorophenyl glycidyl ether and up to 79% in copolymerisation with epoxypropane.[52]

Since the introduction of polyether fragments into the macromolecules is of practical interest, the set of problems associated with chain transfer as a method of synthesis of MM requires a more serious analysis.

Chain transfer to the monomer is characteristic under certain conditions of the polymerisation of ethylene under the influence of Ziegler type catalysts,[53,54] which creates the possibility of the controlled conversion of ethylene into C_6–C_{20} α-olefins, which can then be used as MM. Mainly vinyl end groups are then formed and these then partially isomerise to internal double bonds. The fractions of vinyl groups β in ethylene oligomers are listed below:[54]

n	6	8	10	12	14	16	18
β, mole %	90.4	88.4	86.4	85.5	84.8	84.1	82.5

Variation of the monomer pressure, of the nature of the solvent, and other conditions makes it possible to increase the functionality with respect to these groups almost to 100%. The possibility of the quantitative epoxidation of α-olefins obtained by this method is of great interest,[55] because the subsequent copolymerisation of such MM opens a way to polyethers with hydrocarbon side chains.

Radical polymerisation. The formation of reactive oligomers (introduction of functional groups) with the aid of the chain transfer reaction has been the object of many investigations. The successful insertion of reactive groups into macromolecules via a chain transfer agent specially introduced into the system depends on the reactivity of the monomer (M) and the corresponding macroradical and also on the reactivity of the chain transfer agent (SH) in chain transfer and reinitiation processes:

$$\begin{array}{l} SM_nM^{\cdot} + SH \rightarrow SM_{n+1}H + S^{\cdot} \\ \uparrow{\scriptstyle nM} \qquad\qquad\qquad \uparrow{\scriptstyle M} \\ SM^{\cdot} \leftarrow \end{array} . \qquad (9)$$

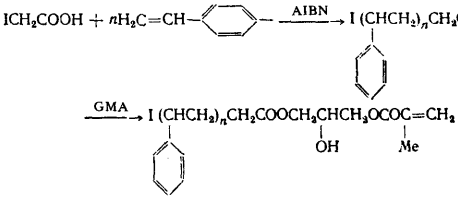
Thus the effectiveness of the reinitiation is low for inactive monomers, which give rise instead to reactive macroradicals, which are more reactive than the radical S in Scheme (9).

One of the most thoroughly investigated transfer processes having a practical application is the telomerisation of ethylene by CCl_4:[56]

$$CCl_4 + nH_2C{=}CH_2 \xrightarrow{R} \underset{(XII)}{CCl_3(C_2H_4)_nCl} .$$

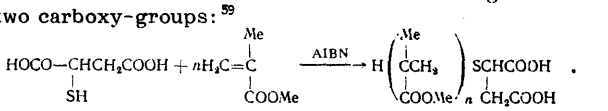
A wide variety of reactions of the telomer (XII) are possible and it can be regarded as the intermediate in the synthesis of MM. There are examples of the use of the telomerisation of various monomers for the direct synthesis of MM.[57–62]

The radical polymerisation of styrene and methyl methacrylate in the presence of iodoacetic or thioglycolic acids leads to a monocarboxylate polymer, into which functional groups have been introduced.[57,58] For example, styrene has been telomerised by treatment with azobisisobutyronitrile (AIBN) with subsequent introduction of functional groups by means of glycidyl methacrylate (GMA) in accordance with the scheme:



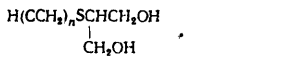
The reaction leads to the corresponding MM (with molecular weights of 4300–7700) in yields up to 90%.[58]

The use of thiomalic acid as the telogen makes it possible to introduce into the macromolecule a telechelic fragment with two carboxy-groups:[59]



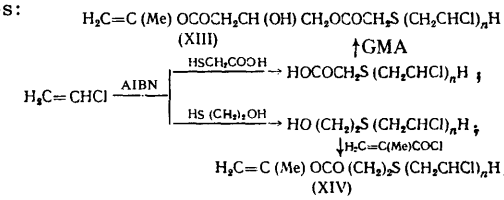
The authors[59] emphasise that this is the first synthesis of MM for subsequent polycondensation with diols, diamines, etc.

MM containing the diol group at one end of the poly(methyl methacrylate) chain have been obtained analogously using thioglycerol:[60]



These MM can also be used in polycondensation or polyaddition reactions, for example, for the synthesis of modified polyurethanes.[60]

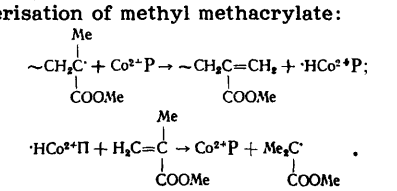
Radical telomerisation with subsequent introduction of unsaturated groups has been used recently to synthesise vinyl chloride and vinylidene chloride MM.[61,62] In the case of vinyl chloride, two different telogens were used and correspondingly two agents for the introduction of functional groups:



The products (XIII) and (XIV) have been comprehensively characterised—they have molecular weights in the range 1000–2400 and copolymerise with standard monomers.

We shall now return to chain transfer to the monomer. By itself, this reaction is unable to ensure the required functionality under the usual conditions. In fact, for example, in the usual polymerisation of methyl methacrylate (in bulk at initial concentration 1 M, 50 °C, and rates of initiation in the range 10^{-8}–10^{-6} mol litre^{-1} s^{-1}), f_n with respect to unsaturated end groups does not exceed 0.3–0.4, which can be shown by estimates based on kinetic parameters.[34]

A sharp acceleration of chain transfer by catalysts has been observed and studied in detail recently.[63] It has been shown, for example, that in the presence of cobalt complexes of porphyrin $Co^{2+}P$, a hydrogen atom is transferred with a high efficiency from the radical to the monomer in the polymerisation of methyl methacrylate:



There are a number of pieces of evidence (obtained by NMR, electrochemical, etc. methods) for this mechanism, which results in the formation of a substituted methyl methacrylate group in each macromolecule.

(d) Other Polymerisation Methods

The polymerisation of acrylamide is initiated by lithium alkyls via a mechanism involving the abstraction of a proton with retention of the vinyl group:[64]

$$H_2C{=}CHCONH_2 + RLi \rightarrow RH + \underset{(XV)}{H_2C{=}CHCONH^-Li^+}\,.$$

The latter is then introduced into the chain of the poly-β-alanine (nylon-3) formed:

$$(XV) + nH_2C{=}CHCONH_2 \rightarrow H_2C{=}CHCONH\,(CH_2CH_2CONH)_n^-Li^+\,.$$

The highest functionality ($\bar{f}_n = 0.95-1.10$) with respect to these groups has been shown to be attained[64] on initiation with t-butyl-lithium. The MM formed polymerises under the influence of radical and ionic initiators.[65]

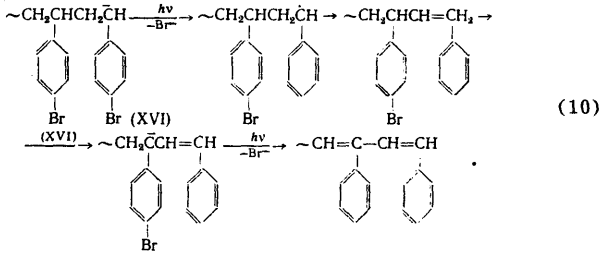
The polymerisation of *N*-carboxyanhydrides on treatment with amines, which proceeds with retention of the initial group of the initiator at the end of the macromolecule, was examined previously. In the case of a number of monomers (for example, β-propiolactone, epoxyethane, etc.) and tertiary amines, the polymerisation is complicated by the instability of the primary zwitter-ionic active centres:

$$R_3N + \underset{\quad=O}{\overset{\quad O}{\square}} \rightarrow R_3\overset{+}{N}CH_2CH_2COO^- \xrightarrow{n\ \square=O} R_3\overset{+}{N}CH_2CH_2\,(OCOCH_2CH_2)_nCOO^- \rightarrow$$

$$\rightarrow H_2C{=}CH\,(OCOCH_2CH_2)_nCOO^-H\overset{+}{N}R_3\,.$$

This instability leads to the appearance of unsaturated end groups in the macromolecules, which is analogous to the method of synthesis of olefins via the Hofmann rearrangement. In the polymers of β-propiolactone,[66] epoxethane,[67] and glycidyl phenyl ether,[68] there is a double bond in each macromolecule. It is essential to note that only the acrylate end groups of poly-β-propiolactone formed via this mechanism are of real interest from the standpoint of the possibility of the subsequent employment of MM.

A novel method for the generation of double bonds has been devised in a study of the photochemical decomposition of living poly-*p*-bromostyrene:[69]



(10)

Under certain conditions, the reaction leads to the formation of polymers with 1,3-diphenylbuta-1,3-diene end groups in quantitative yield and it has been shown that the MM formed (molecular weight 50 000) are readily converted into high-molecular-weight comb polymers with anionic initiators. The photochemical reaction (10) can also proceed further, leading ultimately to polyphenylacetylene.

The relatively easy rupture of the poly(methyl methacrylate) chain on mechanical treatment has also been used to synthesise products resembling MM.[70] Ultrasonic treatment in benzene in the presence of *p*-divinylbenzene and subsequent deactivation of the system with methanol result in the formation of MM with molecular weights in the range 130 000–230 000 and functionalities of 2.2–12.0. They possess a broad molecular weight distribution and are highly inhomogeneous as regards functionality. Copolymers with styrene and methyl methacrylate have been obtained from them.[70]

2. Polyaddition and Polycondensation

There is a very limited number of examples of the application of the polyaddition and polycondensation reactions for the synthesis of MM. The point is that in the majority of processes of this type, the lengthening of the polymer chain is achieved by employing bifunctional monomers and the nature of the end groups is determined by statistical factors and the reactant ratio. The excess of one of the reactants or the use of a monofunctional terminating agent makes it possible to guarantee with a high degree of accuracy the nature of only the two end groups. These methods are hardly used in the synthesis of monofunctional MM.

An apt example, which indicates the new possibilities which have appeared in this field, is provided by the catalytic polyaddition with participation of secondary diamines and divinylbenzene:[71,72]

$$\underset{(XVII)}{C{=}CH{-}\langle\rangle{-}CH{=}CH_2} + n\underset{(XVIII)}{NH\,(R){-}X{-}N\,(R)\,H} \rightarrow H_2C{=}CH{-}\langle\rangle{-}(CH_2)_2 - \underset{(XIX)}{\left[N\,(R){-}X{-}N\,(R)\,(CH_2)_2{-}\langle\rangle{-}(CH_2)_2\right]_{n-1}N\,(R){-}X{-}N\,(R)\,H}\,. \quad (11)$$

The first stage in scheme (11) is rapid and quantitative. The residual vinyl group is then highly passivated, as a result of which it is possible to achieve the preliminary synthesis of the stoichiometric adduct (XX) and its subsequent poly-addition:

$$(XVII) + (XVIII) \rightarrow \underset{(XX)}{H_2C{=}CH{-}\langle\rangle{-}(CH_2)_2N\,(R){-}X{-}N\,(R)\,H} \rightarrow (XIX)\,. \quad (12)$$

Analysis of the resulting polyamine MM by gas–liquid chromatography and ^{13}C NMR[71] indicates molecular weights in the range 1800–6600, which corresponds to degrees of conversion of 0.84–0.93 in reaction (11).

Reactions of types (11) and (12) can be used also for the introduction of various groups, for example, crown ethers, into the macromolecule, which has been used successfully in one investigation.[73]

Polycondensation has not so far provided examples of the synthesis of MM.

3. The Reactions of the Functional Groups of Macromolecules

It is possible to obtain MM by the quantitative replacement of any end group by one capable of polymerisation. Such a reaction requires the activation of the group to be substituted by the use of a reactive agent for the introduction of functional groups, so that the method involving the deactivation of living polymers is in this sense more natural. On the other hand, in the methods based on the modification of the end groups, it is possible to use a much greater range of reactions. The main requirement which they must meet is complete conversion.

Historically, the first example of the synthesis of MM refers to precisely this field. In 1962 Greber and Reese[3] achieved the reaction

$$Me_3Si\,(OSiMe_2)_4Cl + ClMg{-}\langle\rangle{-}CH{=}CH_2 \rightarrow$$

$$\rightarrow Me_3Si\,(OSiMe_2)_4{-}\langle\rangle{-}CH{=}CH_2 + MgCl_2\,.$$

and obtained polydimethylsiloxane MM in ~50% yield, which were then copolymerised with styrene.

Subsequently a number of communications concerning the introduction of a wide variety of polymerised fragments by the reaction of end groups with the corresponding agents for the introduction of functional groups were published. One of the convenient methods for the introduction of such functional groups is the use of poly(ethylene glycols) (PEG) and its monofunctional analogues, whose hydroxy-groups are readily activated. In particular, the synthesis of oligoacrylate esters, widely used for the synthesis of three-dimensional polymers, is based on these reactions.[74]

There is no doubt that the attempt to obtain monofunctional MM by the same methods as a result of the selection of the corresponding stoichiometry should lead to a mixture of products. This remark applies fully, for example, to a study[75] where a number of glycols were esterified via the scheme

$$H(OC_2H_4)_nOH + HOCOCH{=}CH_2 \xrightarrow{H^+} H(OC_2H_4)_nOCOCH{=}CH_2 ,$$

but the monofunctionality of the final product was not reliably established.

The only real possibility of the synthesis of MM involves therefore the use of the initial monofunctional polymers and the factors which determine the choice of method for the direct introduction of functional groups in the polymerisation stage of the replacement of groups in the finished polymer is the stability of the polymer chain as regards the action of the corresponding reagents and the attainment of the required functionality.

We shall consider several of the latest examples of the synthesis of MM using these reactions. Mono- and divinyl-ethers of PEG have been synthesised with high degrees of conversion:[76,77]

$$H(OC_2H_4)_nOH + HC{\equiv}CH \xrightarrow[180^\circ]{Na} \begin{cases} \rightarrow H(OC_2H_4)_nOCH{=}CH_2 , \\ \rightarrow H_2C{=}CH(OC_2H_4)_nOCH{=}CH_2 . \end{cases} \quad (13)$$

These are of interest from the standpoint of the subsequent synthesis of macromolecules with crown ether rings in the chain. Reaction (13) is accompanied by the degradation of the main chain, as shown by the results of the chromatographic analysis, presented below, of a mixture of bifunctional oligomers with different chain lengths n according to the data of Mathias et al.:[77]

Initial PEG	Products			
	$n=2$	$n=3$	$n=4$	$n=5$
$n=3$	43%	57%	—	—
$n=4$	23%	33%	44%	—
$n=5$	—	27%	64%	8%

In this connection an assortment of milder conditions is necessary, in particular, the use of phase transfer catalysts.[76] The same approach can be applied to monofunctional polymers.

Monofunctional allyl[78] and acrylate[79] derivatives of oligoethers, i.e.

$$Ar(OCH_2CH_2)_nONa + HOCOCH{=}CH_2 \rightarrow Ar(OCH_2CH_2)_nOCOCH{=}CH_2 , \quad (14)$$
$$Ar = C_9H_{19}C_6H_4, Ph$$

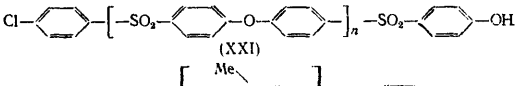
as well as their styrene derivatives,[79] i.e.

$$Me(OCH_2CH_2)_nONa + ClCH_2{-}C_6H_4{-}CH{=}CH_2 \rightarrow$$
$$\rightarrow Me(OCH_2CH_2)_nOCH_2{-}C_6H_4{-}CH{=}CH_2 .$$

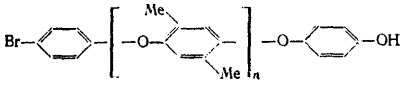
have been obtained by analogous methods, i.e. by the activation of hydroxy-groups with alkali metals.

Detailed analysis of the acrylate MM formed by capillary gas chromatographic and high performance liquid chromatography yields the distribution of the MM with respect to chain lengths but at the same time an appreciable amount of the initial school is detected, which shows that reaction (14) does not go to completion.

Fundamentally new types of MM have been obtained recently by the introduction of functional groups into polyethersulphone (XXI) and poly(2,6-dimethyl-1,4-phenylene oxide) (XXII):[80]

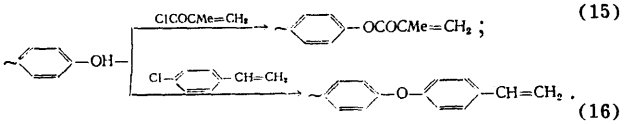


(XXI)



(XXII)

The method of synthesis of the polymers ensured in both cases the presence of one phenolic end group, which was then converted into methacrylate or styrene groups in accordance with the schemes:



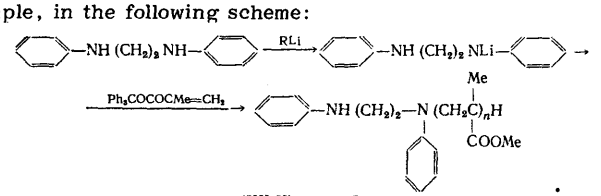
(15)

(16)

Reaction (15) was carried out in the presence of 4-*NN'*-dimethylaminopyridine and triethylamine and reaction (16) was carried out under phase transfer conditions.

The initial polymers (XXI) and (XXII) as well as the MM based on them have been investigated in detail by IR spectroscopy and ^1H and ^{13}C NMR. The equality of the signal intensities of the halogenophenyl and phenolic groups or the unsaturated groups demonstrates the presence of the planned MM structure. The complete absence of absorption due to the OH groups in the terminal phenolic fragments in the IR spectra demonstrates additionally that the introduction of functional groups is complete.[80]

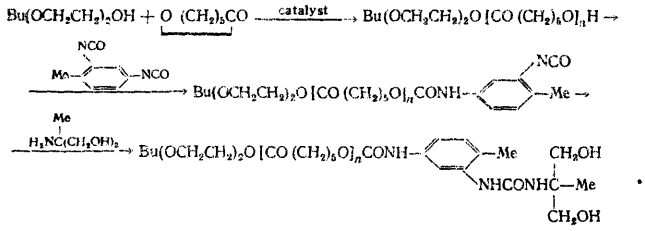
One may quote the example of the synthesis of poly(methyl methacrylate) optically active MM[81] as an example of the wide variety of the possibilities and prospects for the synthesis of MM. Such MM are of undoubted interest as the starting materials for the creation of chiral sorbents and chromatographic phases. The polymerisation of racemic triphenylmethyl methacrylate on treatment with lithium initiators in the presence of chiral diamines leads to polymers having high optical activities with different signs—$[\alpha]_D$ ranges from −354° to +194°. The end groups of the polymers are determined by the initial lithium amide initiator, for example, in the following scheme:



(XXIII), $n = 45$

The subsequent reaction of compound (XXIII) via the N—H bond with methacryloyl chloride leads to a MM whose acrylamide end groups have been clearly identified by IR spectroscopy. These MM copolymerise with methyl methacrylate via a radical mechanism.

In a number of instances the specific synthesis of MM presupposes special regulation of the nature of the end group already in the stage involving the formation of the polymer in order to be able to replace it subsequently. One of the illustrations of this approach may be provided by the synthesis of the MM from ε-caprolactone:[82]



The MM obtained can enter into polyaddition reactions via the two hydroxy-groups in the terminal fragment. They are used to synthesise modified polyurethanes.

Having completed the consideration of the problems of the synthesis of MM, we may note that in recent years a set of methods have been devised for the introduction of polymerisable groups (mainly styrene and acrylate groups) into macromolecules of different types both directly in the stage of their synthesis and via secondary reactions. The methods involving the deactivation of living polymers lead to MM with the highest functionalities. In those cases where this procedure is impossible, good results can be achieved with the aid of reactions via the end groups but here too the feasibility of the quantitative introduction of the corresponding group (or groups) must be inherent in the precursor polymer.

III. POLYMERISATION OF MACROMONOMERS

It has been assumed *a priori* that the capacity of MM for polymerisation and copolymerisation with other monomers must be complicated by a number of factors. The impossibility of achieving high MM concentrations in the reaction medium as a result of their high molecular weight should be regarded as the first although the most trivial of these. The low MM concentrations can in the first place give rise to thermodynamic prohibitions of polymerisation, particularly in those cases where the polymeric substituent is attached directly to the double bond, which as a rule decreases sharply the heat of polymerisation. Under homopolymerisation conditions, this factor should reduce the rates and average degrees of polymerisation of MM and the MM copolymerisation processes always proceed for this reason under conditions where there is an excess of the "small" comonomer. The second factor is diffusion-dependent limitations, which in the given instance extend also to chain propagation via the reaction between the macromolecules.

The polymeric substituent can naturally exert a strong steric and polar influence on the reactivity of the double bond. In this sense the MM with styrene and acrylate groups are most preferred especially if the polymer chain is on the periphery, i.e. in the benzene ring or in the ester fragment respectively.

Finally, one must reckon with the possible instability of the polymer chains of the MM in relation to the active centres propagating the polymerisation. For example, polyoxyethylene is known to exhibit a tendency to be cleaved by radical, cationic, and even anionic agents. The polymer chains of MM based on lactones and siloxanes, in which chain dissociation and macrocyclisation reactions take place readily, cannot be regarded as fully stable in relation to ionic initiators. Because of these causes, the tendency to introduce into the MM groups capable of polymerisation via a radical mechanism predominates.

Purely polymeric effects, such as, for example, the matrix influence of the MM chain on the growth of new macromolecules (the orientation of the monomers and their polymerisation in the bound state, the formation of stereocomplexes, and other matrix growth mechanisms) as well as the thermodynamic incompatibility of the initial and final chains, which may be manifested both by the segregation into separate phases and by purely kinetic effects, are also possible.

All these complications occur to some extent in processes involving MM. For example, the MM formed via the chain transfer mechanism in the radical polymerisation of methyl methacrylate[63] does not copolymerise directly with the initial monomer apparently owing to steric hindrance and thermodynamic prohibition. The characteristic features of the kinetics of the polymerisation of poly(tetrahydrofuran-styrene) MM and the low chain lengths of the polymers obtained can be accounted for by the low concentration of the MM.[83] The copolymerisation of acrylic acid with polyoxyethylene-methacrylate proceeds in a significantly different manner in the pH ranges corresponding to the comonomers bound in a complex or in a free state.[84]

The kinetics and thermodynamics of the homopolymerisation of MM have, however, been so far investigated to an extremely insignificant extent, which precludes a more detailed analysis of the above features of these processes. Much more attention has been devoted to the copolymerisation of MM, because it is the main pathway to polymers of practical interest.

1. Copolymerisation With Participation of Macromonomers

Copolymerisation is the main procedure in the synthesis of polymers based on MM. Radical initiation is regarded as the most preferred in view of its universality. The usual equation for the composition of the copolymer of a "small" monomer (M_1) with a macromonomer (M_2) has to be modified because of the low concentration of the MM:[85]

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]} \simeq r_1\frac{[M_1]}{[M_2]} ,$$

which corresponds to the case of the so called "ideal" copolymerisation ($r_1r_2 = 1$) and leads to a simple kinetic equation:

$$r_1 = \ln(1-\alpha_1)/\ln(1-\alpha_2), \qquad (17)$$

where α_1 and α_2 are the degrees of conversion of the monomers M_1 and M_2 respectively. This evidently simplifies the determination of the reactivity of the monomer M_1, but hinders and frequently altogether precludes the determination of the reactivity of the MM. The copolymerisation of MM has beeen analysed by gas–liquid chromatography.[86]

It is also easy to show that only single MM units should be incorporated in the chain during copolymerisation. Indeed, the probability of the formation of the diad M_2M_2 and hence its fraction in the comonomer

$$f_{M_2M_2} = r_2\frac{[M_2]}{[M_1]}\left(1+r_2\frac{[M_2]}{[M_1]}\right)^{-2} \simeq r_2\frac{[M_2]}{[M_1]}$$

are very small and the following probabilities can be obtained for the average block lengths:

$$\bar{p}_1 = 1 + r_1\frac{[M_1]}{[M_2]} \gg 1 ;$$

$$\bar{p}_2 = 1 + r_2\frac{[M_2]}{[M_1]} \simeq 1 .$$

In other words, the copolymerisation considered is as a rule close to statistical copolymerisation and the variation of the constants r_1 and r_2 rarely alters this situation, because the aim of the tactics employed is usually to make sure that the polymerisable groups of the MM have structures identical to that of the "small" comonomer.

Table 4 presents the copolymerisation constants for systems with participation of MM. In the main, they refer to the "small" comonomer and in this case we obtain information about the reactivity of the MM, because

$$1/r_1 = k_{12}/k_{11} \quad (18)$$

is the ratio of the rate constants for the addition of the MM and the "small" comonomer to the radical of the latter. The quantities r_2 are of great interest from the standpoint of the analysis of the complications caused by the macromolecular nature of the MM, but they are known only in rare cases.

Table 4. The reactivities of monomers in radical copolymerisation processes with participation of MM.

MM (M_2) *	Comonomer (M_1)	r_2**	r_1**	Refs.
Poly(ethylene oxide)-styrene	Styrene	1.04 (1.00)	1.18 (1.00)	[87]
"	Butyl acrylate	0.60 (0.48)	0.11 (0.15)	[87]
Poly(ethylene oxide)-methacrylate	Styrene	0.46 (0.46)	0.41 (0.52)	[88]
Polystyrene-methacrylate	Styrene	—	0.61 (0.66)	[89]
"	Butyl acrylate	—	0.82 (0.35)	[89]
Polyisobutylene-styrene	Styrene	—	1.2—6.6***	[90]
"	Methyl methacrylate	—	0.48—0.58****	[90]
Polyvinylpyridinemethacrylate	Butyl acrylate	—	8.3	[91]
Polydimethylsiloxane-styrene	Styrene	—	1.1 (1.0)	[92]
"	Methyl methacrylate	—	0.60 (0.52)	[92]

*The first part of the name of the MM refers to the chain structure and the second to that of the end group.

**The values for low-molecular-weight models are given in brackets.

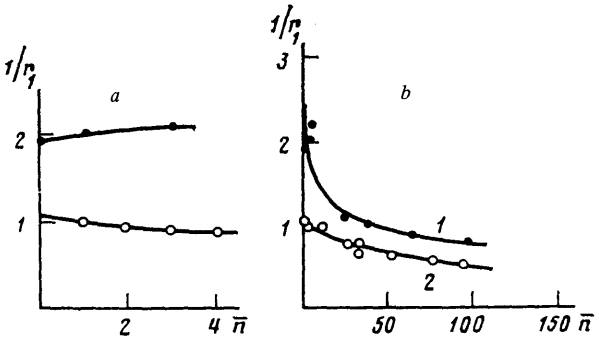
***When the MM chain length is varied.

****When the solvent is varied.

The data in Table 4 demonstrate in the first place the absence of any appreciable polymeric effects in copolymerisation, because in most cases the constants r_1 are close to those characteristic of the same pairs of low-molecular-weight monomers (indicated in brackets in Table 4) and the same applies to the few values of r_2 in Table 4. Systems where microphase separation occurs in consequence of the incompatability of the MM macromolecules and the polymer obtained are an exception. This applies to a considerable extent to, for example, copolymerisation of the polyisobutylene-styrene MM with styrene and methyl methacrylate.[90] A particularly marked effect is exerted by the increase of the molecular weight of the MM (from 4200 to 48 000), which leads to an increase of r_1 from 1.2 to 6.6 in the copolymerisation with styrene; in the latter case the reaction mixture is appreciably opalescent. Similar phenomena have been observed also in other systems.[27,88]

The incompatibility of the polymers may play an even greater role in emulsion copolymerisation, because in this case there is a possibility of the formation of several phases and the rate of diffusion of the MM may prove to be the decisive factor. In particular, it has been shown that the emulsion copolymerisation of styrene with the polyisobutylene-styrene MM takes place with formation of the graft copolymer only in monomer drops, while the usual variant leads to polystyrene and the MM which failed to react.[93]

In the absence of explicit phase separation, the antagonism between the macromolecules of the growing polymer (consisting mainly of M_1) and the MM may be manifested by certain kinetic effects. Ito et al.,[88] who investigated in detail the dependence of the reactivity of poly(ethylene oxide) MM on the chain length (see Figure) tend towards this view. It can be seen from Fig.*a* that, in the region of short chains, there is virtually no dependence of n_1 on chain length, which indicates an insignificant inductive and steric influence of the substituent on the reactivity of the polymerisable group in the MM. In the region of great chain lengths (up to 10^2) (Fig.*b*), a monotonic decrease of $1/r_1$ is observed, which most probably indicates the corresponding decrease of the reactivity of the MM in relation to the growing macromolecule, i.e. a decrease of k_{12} in Eqn.(18). These changes are attributed to the kinetic effect of the excluded volume in intermacromolecular reactions. However, quantitative agreement with the theory of this effect has not been obtained and the idea of macromolecular antagonism has been formulated.[88]



The reactivities of poly(ethylene oxide) MM of different lengths ($\bar{n}$) in the radical copolymerisation with styrene (M_1);[88] MM with methacrylate (curves *1*) and *p*-vinylbenzyl (curves *2*) end groups.

It is essential to note that, overall, the approach to the study of the problem of the reactivity of the end groups in polymers via the investigation of the copolymerisation of MM is perhaps more correct than analysis of the processes involving the conversion of telechelate polymers into network polymers.[4] The theory of copolymerisation has been developed in detail, which makes the first approach even more justified.

On passing to the ionic copolymerisation of MM, which has not so far been touched upon, solvation interactions, matrix effects, etc. should be manifested to a considerable extent.

IV. APPLICATIONS OF MACROMONOMERS IN POLYMER ENGINEERING

The synthesis of graft copolymers clearly predominates in the preparative applications of MM. Strictly speaking, this field as a whole arose owing to the need to combine in a single macromolecular system at least two different frequently opposite properties, which cannot always be achieved by methods involving the successive copolymerisation of different monomers and block or graft copolymerisation. In graft polymers, there is a possibility of significantly different ratios of the main and grafted chains. The relatively greater freedom of the latter compared with the corresponding fragments in block copolymers leads in many instances to more favourable conditions for microphase separation, which results in qualitatively new mechanical properties of the material.

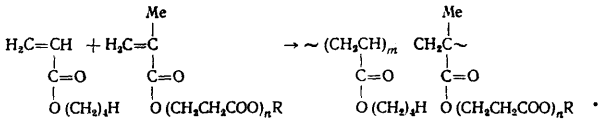
Virtually all the MM whose synthesis and polymerisation were examined in previous sections have been used to obtain graft copolymers with different "small" comonomers. The homopolymerisation of MM, leading to strictly regular comb polymers, has attracted significantly smaller and purely theoretical interest, although it is evident that in this sense the MM method is promising for the formation of liquid crystal materials.

We shall now consider the principal trends in the synthesis of graft copolymers based on MM.

It is known that the introduction of a rubber-like phase into plastics (polystyrene, materials based on epoxy-resins) increase their impact strength. A fundamentally new procedure has been proposed by Kennedy and Lo,[93] who achieved an increase by a factor of 2.5 of the impact strength of polystyrene by introducing into the latter, in the formation stage, approximately 10% of grafted polyisobutylene fragments, using the appropriate MM. The microphase separation and the enhancement effect were observed only for MM with relatively high molecular weights ($\bar{M}_n = 5 \times 10^4$). According to the authors,[93] an advantage of this method over the traditional introduction of rubbers (usually polybutadiene) is the high stability of the properties of the material as a function of time, including its stability in relation to the action of natural factors, for example, UV irradiation. The results of this study can hardly be regarded as final and it leads to new prospects for the solution of problems of this kind.

Another physicomechanical modification procedure, which is the direct opposite as regards the results achieved, involves the introduction of crystallisable fragments into elastomers. Microphase separation leads in this case to the formation of thermally reversible cross-links and to materials of the type of thermoelastoplastics. Polymeric fragments based on lactones, which are highly crystalline and give rise to a high rate of formation of the given phase, are of great interest in this connection. Their use in block copolymers is known.[94,95]

The graft copolymers of poly-β-propiolactone with butyl acrylate were first synthesised recently[18] via MM using the scheme



They do indeed have the properties of unfilled acrylate rubbers. The copolymers obtained by treatment with AIBN have molecular weights in the range 30 000–60 000 and contain 46–80 wt.% of the ester fragments of poly-β-propiolactone, which corresponds on average to 1.7–3.5 grafted chains per macromolecule. In terms of their mechanical properties—strength and elongation on rupture (12 MPa and 380% respectively)—these materials approach filled rubbers based on butyl acrylate (12 MPa and 250% respectively). The properties of thermoelastoplastics based on the above MM are fully restored after the "fusion–crystallisation" cycle and have attracted evident interest.

A number of examples of the directed modification of traditional polymeric materials by means of the macromonomer techniques have been described in a recent communication by Milkovich,[1,27] who is undoubtedly a pioneer in this field. He employed polystyrene MM with methacrylate groups having molecular weights ranging from 11 000 to 16 000. The copolymers of such MM with ethyl and butyl acrylates, obtained in solution or in suspension, exhibit markedly the properties of reinforced rubbers with microphase separation, in which the rigid polystyrene domains simulate a solid filler. The majority of the copolymers are thermoplastic and their mechanical properties improve significantly when subjected to shearing influences, for example, extrusion, apparently as a result of the creation of a more homogeneous physical network. The principal mechanical characteristics of a series of ternary MM copolymers (molecular weight 16×10^3) with a 1 : 1 mixture of ethyl and butyl acrylates according to Milkovich's data[1] are given below:

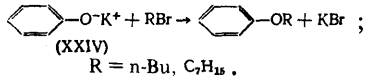
MM content, wt.%	25	30	40	45	50
Yield point, MPa	—	1.9	8.3	12.4	18.0
Tensile strength, MPa	9.0	11.7	15.2	17.2	20.7
Limiting elongation, %	730	550	400	350	240

With increase of the content of MM, the copolymers undergo a change in a set of properties, being converted from thermoplastic elastomers capable of effective recovery of properties (20–30% MM) to flexible thermoplastic materials with high yield points and tensile strengths (35–45%) and finally to thermoplastic materials capable of being moulded and having a high tensile strength (45–55%).

The introduction of polystyrene MM into polyacrylonitrile (10 and 50 wt.% of the MM) makes it possible to improve significantly the conditions for the formation of films by casting methods at 150 °C. Positive effects following the introduction of MM have been observed also in the properties of poly(vinyl chloride).[27]

Other types of studies involving graft copolymers are associated with imparting various specific properties to materials. Many heterochain polymers are known to exhibit a high solvating power in relation to cations[96,97] and they are therefore used widely, together with crown ethers, as sorbents, solubilising additives, phase transfer catalysts, etc. Polyoxyethylene is perhaps of greatest interest and there have been a number of studies designed to produce the appropriate materials on the basis of its MM.[98,99]

Cross-linked polymeric sorbents based on network styrene–divinylbenzene copolymers, containing free suspended polyoxyethylene chains, have been obtained using MM.[98] It is possible to overcome in this way the low mechanical stability of the cross-linked polyoxyethylene, which precludes its direct employment as a chromatographic sorbent. The solvating power of network graft copolymers, containing different amounts of MM, have been studied in relation to the Williamson reaction



(19)

R = n-Bu, C_7H_{15}.

This reaction is extremely sensitive to the solvation of the cation and the ion pair (XXIV) and this is why it has become the traditional kinetic test for the solvating power of the medium.[96,100,101]

The pattern in the activation of reaction (19) by a cross-linked polymeric catalyst and also by analogous graft copolymers proved to be extremely complex. In the case of networks, the activation effect depends on the content of the MM, the degree of cross-linking, the porosity, and also the degree of swelling of the polymer and its thermodynamic compatibility with the medium and the alkyl bromide. In particular, the maximum in the dependence of the rate of reaction on the content of the MM in the network, which occurs at 5 mole %, has been attributed[98] to the character of the distribution of the reactants in the network polymer–liquid phase system. Overall, this interesting study[98] merely leads to a new approach to the synthesis of phase transfer catalysts based on polyoxyethylene, without solving the many other problems in this field.

The ability of systems of this kind to immobilise the corresponding reagents has been demonstrated in relation to gels obtained from MM of type (XXV) and methyl methacrylate with addition of 3–5% of cross-linking agents:[99]

$$MeO(CH_2CH_2O)_nCOC(Me)=CH_2,$$

(XXV)

$n = 4-7$.

In the swollen state, such gels are optically transparent, which permits a spectrophotometric study of the degree of binding by the latter of alkali metal picrates as a convenient model (see, for example, Arkhipovich et al.[102]), and also of the state of the latter in a polymeric solvating medium. Experiments have shown that the equilibria

$$\text{gel} + \text{PiNa} \overset{K_1}{\rightleftarrows} \text{Gel.PiNa},$$

$$\text{gel.PiNa} + \text{glyme} \overset{K_2}{\rightleftarrows} \text{gel} + \text{glyme.PiNa}$$

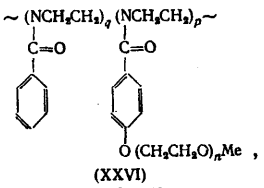
in dioxan and chloroform are strongly displaced towards sodium picrate (PiNa) immobilised in the network. The constants K_1 and K_2 proved to be ~300 litre mol^{-1} and 0.1–0.4 for networks based on MM of type (XXV) and glymes of similar length; the constants change somewhat as the chain length is altered.

These data indicate the higher solvating power of glymes in the polymer than in solution, although this is hardly likely to be achieved owing to cooperative effects, because glymes with this chain length are themselves fairly effective solvating agents.[103,104]

Spectroscopic studies[99] of the state of picrates in gel films have also confirmed the high level of solvation, because the spectra obtained correspond to solvate-separated ion pairs; the wavelengths of the absorption maxima are 368, 374, 377, and 378 nm for Li^+, Na^+, K^+ and Cl^+ respectively after the removal of the solvent. It has been suggested that the gels obtained and other analogous gels are promising for the study of the reactions of the reagents with the state solvated by macromolecules.

One of the important applications involves the creation of effective surfactants using MM. Comb polymers with a hydrophilic base and hydrophobic grafted chains (and conversely) have been used fruitfully for a long time for the steric (antropic) stabilisation of various dispersions, emulsifications, etc. (see, for example, Barrett[105]), but the approach using MM greatly simplifies the formation of such substances and extends the range of the possible structural variants. Polymers of this type are also of interest for the modification of the surfaces of polymeric materials and the solution of the problem of their compatibility. There have been several studies illustrating these possibilities.[92,106-109]

Using polyoxyethylene MM of types (IV) and (V), Kobayashi et al.[106] synthesised graft copolymers with the structure (XXVI):



(XXVI)

$n = 19-43$.

Owing to the presence of hydrophilic (polyoxyethylene) and hydrophobic (polyphenyloxazoline) fragments, these copolymers exhibit a high surface activity at the air–water interface. The surface tensions (γ, dn cm^{-1}) of water and 1% solutions at 28.5 °C are given below:

Water	71.4
MM	56.9
MM homopolymer ($p = 3$)	54.8
The copolymer (XXVI) ($p/q = 1:8.5$)	28.8

It has been suggested that these non-ionogenic surface-active graft copolymers would prove to be effective stabilisers of dispersions and also antistatic agents when they are introduced into plastics, like the analogous block copolymers.[107]

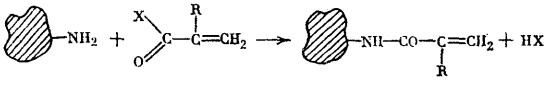
Extremely interesting and very promising surface effects have been observed after the introduction into polystyrene or poly(methyl methacrylate) films of small amounts of the corresponding graft copolymers containing hydrophilic polyamide[108] or, conversely, hydrophobic polydimethylsiloxane fragments.[92,109] Measurement of the wetting angles in water for polystyrene films obtained by casting onto glass plates has shown, for example, that the polyamide (see the footnote to Table 3) blocks are concentrated on the surface adjoining glass even when their content in the film is ~0.2%. This has been confirmed also by IR total internal reflection Fourier spectroscopic data. The surface of the film turned towards air does not differ in any way from that of the usual polystyrene.

The opposite picture has been observed for the system comprising poly(methyl methacrylate) and the graft copolymer of methyl methacrylate with polydimethylsiloxane-methacrylate.[110] In this case the siloxane blocks are concentrated on the "air" surface of the film, rendering it markedly hydrophobic; cos θ, where θ is the wetting angle, changes from 0.5 to −0.2 when not more than 0.5 wt.% of the siloxane component is introduced. The other surface of the film is also somewhat enriched in the graft copolymer and its distribution with respect to the thickness of the film follows clearly from IR reflectance spectroscopy. This effect, caused by the macroscopic separation of the copolymer in the bulk phase, is extremely stable and is almost fully retained after prolonged washing of the surface with n-hexane—an effective solvent for polydimethylsiloxane. In the case of similar modification of surfaces by static or block siloxane copolymers and also siloxane homopolymers, such washing eliminates the hydrophobic effect almost completely.

Presumably the application of biphilic graft copolymers constitutes a promising means of influencing the compatibility of polymers in composites, the character and stability of the microphase separation, and the modification of polymer films and fibres.

The biphilic property is one of the main qualities of graft copolymers widely used in the synthesis of biomedical materials. By virtue of MM, a series of new approaches have been discovered in this field also.

Plate and co-workers[111-113] have been consistently developing the immobilisation of biologically active compounds (BAC)—proteins, enzymes, etc.—on macromolecules or in cross-linked hydrophilic gels via intermediate "macromonomers". The principle of the method consists in the synthesis of MM by the acylation of BAC, i.e.



(BAC) (XXVII)

and the subsequent copolymerisation of the resulting acrylamide MM with an appropriate comonomer in the absence or presence of a cross-linking agent. It is possible to graft compound (XXVII) to various materials, for example, under the influence of γ-radiation. The functionality of the MM (XXVII) naturally depends on the number of the initial amino-groups in the BAC and on the degree of their substitution, which has been considered in detail in novel studies by this group of workers (see the review of Plate et al.[112]).

An important condition for the attainment of the final aim is the retention by the BAC of its activity at all the stages of the immobilisation process. It has been shown in relation to human serum albumin[113] and a number of other proteins that the BAC retain their secondary structure and that their binding centres are unaffected on modification.

The approach considered made it possible to create new effective sorbents for biospecific chromatography and materials with improved haemocompatibility, which is adequate even for making artificial veins. An important consequence of these studies is also clear-cut correlations between the haemocompatibility of the polymer and the effectiveness of its action on the clotting system of blood.

Another application concerned with the creation of biomedical materials, employing purely synthetic MM, has also been developing effectively.[17,73,114–116] The introduction of polyaminoacid, polyamine, polyamide, and also polysaccharide fragments, exhibiting "biological" affinity, into the usual polymers, most often polystyrene, which plays the role of an inert hydrophobic carrier, makes it possible to obtain two-phase materials which constitute the base for the creation of biosorbents, specific membranes, and anticlotting coatings.

The problem of the separation of *B*- and *T*-lymphocites, which is one of the key problems in modern chemical immunology, has attracted much interest recently.[117] The materials created on the basis of MM exhibit a high selectivity in such separation and are being studied vigorously. The selectivity coefficients A_B/A_T of the adsorption of the corresponding cells on polystyrene and graft copolymers with polyaminoacids [see Scheme (3)] and polyamine fragments (XIX), based on the results of several studies,[114–116] are presented below:

Polystyrene (PS)	—	1.18
PS with grafted polyaminoacid	(26%)	1.54
Ditto	(50%)	2.15
PS with grafted polyamine	(9%)	4.47
Ditto	(15%)	2.89
"	(25%)	2.45
"	(50%)	3.16

The mass content of the graft copolymers is indicated in brackets. Their selectivity is frequently antagonistic to the overall absorption of lymphocites on columns of this type.[115] However, the latest estimates have shown that the population of *T*-lymphocites can be obtained in yields up to 50% and with a purity of approximately 95% (for example, by employing the copolymer of polystyrene with a 9% content of polyamine). For this purpose, the columns are additionally modified by proteins, for example, albumin[115] or additives regulating the hydrophilic properties of the material.

Overall, the biomedical applications of MM have been developing most vigorously in recent times.

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Thus a new field, which has significantly enriched synthetic polymer chemistry, has arisen among reactive oligomers and has been developing vigorously. The use of MM containing one polymerisable end group, frequently an unsaturated group, made it possible to obtain a number of fundamentally new comb and graft polymers. Methods for the introduction of functional groups—initiation and deactivation in ionic polymerisation and radical telomerisation—have been developed in detail. The first reviews of studies in this new field have already appeared.[118,119] Presumably this field and also the synthesis of block copolymers, developing in parallel, will serve as sources of new polymeric materials for various purposes.

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