

THE COPOLYMERIZATION OF 2-METHOXYETHYL METHACRYLATE
WITH METHYL METHACRYLATE INITIATED
BY LITHIUM TERT-BUTOXIDE*

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The copolymerization of methyl methacrylate with 2-methoxyethyl methacrylate initiated by lithium tert-butoxide in benzene proceeds in two stages of growth which are, like the homopolymerization of 2-methoxyethyl methacrylate under the same conditions, separated by a plateau on the conversion curve. The rate of growth in the first stage as well as the length of the plateau are functions of the initial monomer mixture composition. The growth rate of the second stage is practically constant. The isotacticity of the copolymer resulting in the first stage decreases with increasing concentration of 2-methoxyethyl methacrylate in the monomer mixture and at equimolar composition of both monomers is approximately the same as that of poly(2-methoxyethyl methacrylate). In the second stage, a chiefly syndiotactic copolymer is formed even at a low concentration of 2-methoxyethyl methacrylate in the mixture. It is assumed that 2-methoxyethyl methacrylate participates in the formation of the active centres in the first growth stage and lowers their stereospecific efficiency for isotactic growth as well as their life time; it is also assumed that it forms a transition product with unreacted alkoxide, which is then rearranged into the active centres of the second stage differing in life time as well as in stereospecific efficiency from the first ones.

In our previous paper¹ dealing with the anionic copolymerization of methacrylate monomers we observed an unusual form of the conversion curve of the copolymerization of methyl methacrylate with 2-methoxyethyl methacrylate initiated by lithium tert-butoxide in benzene medium. It was found that the anomalous course of the copolymerization is caused by the peculiarity of the 2-methoxyethyl methacrylate-lithium tert-butoxide system, which then became subject of a more detailed study². The found facts led us to the opinion that this polymerization is controlled by two types of active growth centres which are formed consecutively in the polymerization mixture and differ in life-time as well as in stereospecific efficiency. This idea is supported by the anomalous dependence of molecular weight on the conversion as well as by the changes of the polydispersities of polymers which had been observed in the study of 2-methoxyethyl methacrylate polymerization initiated by lithium tert-butoxide.

This paper deals with the study of the copolymerization of 2-methoxyethyl methacrylate with methyl methacrylate, initiated by lithium tert-butoxide in benzene medium, and with the stereoregularity of the resulting copolymers.

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EXPERIMENTAL

The preparation and the purification of monomers, initiators and their solutions as well as the technique of polymerization in dilatometers under argon atmosphere were described earlier³⁻⁵. The chemical composition of copolymers as well as their stereoregularity were determined by NMR spectroscopy in the same manner as in the previous case. The stereoregularity is characterized by the percentual content of *I*, *H* and *S* triads determined from the heights or from the integrals of the respective signals of alphas-methyl protons, without discrimination between the two kinds of monomer units. The precision of this determination is substantially better for copolymers with one prevailing comonomer than for the intermediate ones, for which even the assignment of signals is less certain. The basic correctness of the analysis even in these cases is, however, documented by the continuity of the established dependencies in the whole series under study.

The molecular weights, the intrinsic viscosity and the distributions of the copolymers were determined by GPC in THF solution. Six separation columns filled by the porous silicagel "Sphérosil" (Produits Chimiques, France) of the types B, D, and E had the overall length of 720 cm. For the calibration of the system, polystyrene standards (Waters Ass., USA) and samples of poly(methyl methacrylate) of known molecular weight were used⁶. The resulting molecular weights were calculated using the same constants of the Mark-Houwink equation for the given polymer-solvent system⁶ as were used for the interpretation of the universal calibration curve⁷.

RESULTS

Copolymerization Kinetics

The conversion curve of the copolymerization of an equimolar mixture of the monomers under study, initiated by lithium tert-butoxide in benzene medium at 20°C

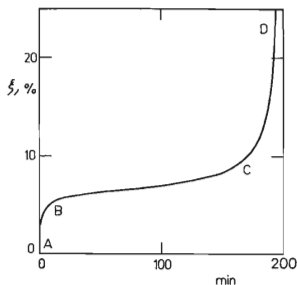


FIG. 1

The Conversion Curve of the Copolymerization of Methyl Methacrylate with 2-Methoxyethyl Methacrylate

The concentration of the monomers 1.585 mol/l, the initiator concentration 0.017 mol/l.

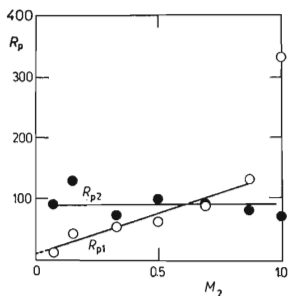


FIG. 2

The Copolymerization Rate in the First (R_{p1}) and in the Second (R_{p2}) Growth Stage, respectively, as a Function of the Initial Monomer Mixture Composition

M_2 the mole fraction of 2-methoxyethyl methacrylate in the initial monomer mixture.

(Fig. 1), is very similar to that of the homopolymerization of 2-methoxyethyl methacrylate under the same conditions². It consists of two growth stages (the first one A to B, the second one C to D) which are separated by a plateau (B to C). Table I shows the results of copolymerizations of monomer mixtures of different composition. It is clear that in the first stage, the growth rate is a function of the initial monomer mixture composition while in the second stage, it is practically composition – independent (Fig. 2). Change of the initial monomer mixture composition alters the form of the conversion curve as well as the length of the plateau (Fig. 3). Maximum

TABLE I

The Copolymerization of the Mixtures of Methyl Methacrylate (M_1) with 2-Methoxyethyl Methacrylate (M_2)

M_1 and M_2 the mole fractions of the monomers in their initial mixture, c concentration of initiator, ξ conversion, R_{p1} and R_{p2} polymerization rates of the first and the second stage, in $\text{mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$, m_2 the content of 2-methoxyethyl methacrylate in the copolymer, p the length of the conversion curve plateau.

Run No	M_1 mol/l	M_2 mol/l	M_2 mol. %	c mol/l	ξ %	R_{p1} $10^{-5} \text{ mol} \cdot \text{l}^{-1} \text{ s}^{-1}$	R_{p2} $10^{-5} \text{ mol} \cdot \text{l}^{-1} \text{ s}^{-1}$	m_2 mol. %	p min
1	3.369	0.269	7.4	0.018	16.1	12	91	9	60
2	2.994	0.549	15.5	0.018	21.9	42	131	16	70
3	2.243	1.096	33.0	0.018	19.7	56	74	35	140
4	1.585	1.585	50.0	0.017	23.0	62	100	43	150
5	0.935	2.066	69.0	0.030	33.8	89	90	72	200
6	0.369	2.482	87.0	0.020	34.2	133	84	90	130

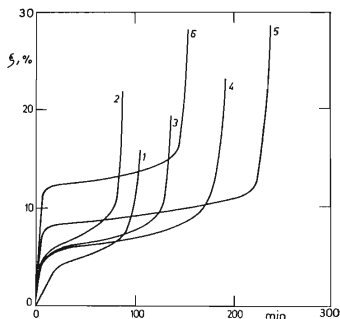


FIG. 3

The Copolymerization Conversion Curves of the Various Mixtures of Methyl Methacrylate with 2-Methoxyethyl Methacrylate

The numbers of the curves correspond to those of the runs in Table I.

length of this plateau is observed for approximately equimolar composition of the initial monomer mixture.

The Stereoregularity of Copolymers

As in the case of the homopolymers of 2-methoxyethyl methacrylate², changes of the stereoregularity of its copolymers with methyl methacrylate appear in connection with the marked changes of reaction rate as seen on the conversion curves. In Table II, a set of samples of copolymers with variable composition, corresponding to different parts of the conversion curve, is characterized. It can be seen that the stereoregularity is changed markedly at the end of the plateau of the conversion curve and at the beginning of the second growth stage, in the whole range of the monomer mixture composition. The dependence of the content of the isotactic triads on the initial monomer mixture composition for the first as well as for the second growth stage is shown in Fig. 4. A marked decrease of the isotacticity of the copolymer with increasing content of 2-methoxyethyl methacrylate in the extent of 0 to 30 molar per cent can be seen here for the first growth stage. Further in-

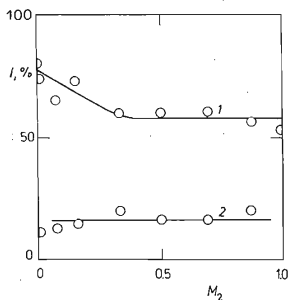


FIG. 4

The Dependence of the Content of Isotactic Triads (I) in the Copolymers of Methyl Methacrylate with 2-Methoxyethyl Methacrylate, on the Monomer Mixture Composition (the concentration of the monomers 2.8–3.7 mol/l)

1 in the first growth stage; 2 in the second growth stage; M_2 the mole fraction of 2-methoxyethyl methacrylate in the initial mixture.

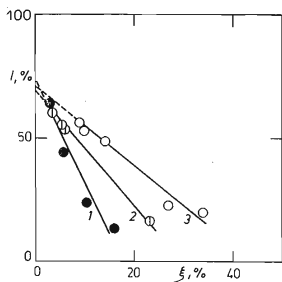


FIG. 5

The Dependence of the Content of Isotactic Triads (I) in the Copolymers of Methyl Methacrylate with 2-Methoxyethyl Methacrylate (M_2) on the Conversion (ξ)

The concentration M_2 in the initial monomer mixture (mol per cent): 1 7.5, 2 50, 3 87.

crease of the concentration of this monomer causes only a slight change of the stereoregularity of the polymer product. The stereoregularity of the copolymers depends, however, very markedly on conversion in the whole range of their chemical composition. This dependence is especially marked in products with prevailing

TABLE II

The Microstructure of the Copolymers of Methyl Methacrylate (M_1) with 2-Methoxyethyl Methacrylate (M_2) (concentration of initiator 0.015–0.030 mol/l)

M_1 , M_2 mole fractions of the monomers in their initial mixture, ξ conversion, m_2 the content of M_2 in the copolymer, stop — the region of termination (Fig. 1).

M_1 mol/l	M_2 mol/l	M_2 mol. %	ξ %	Tacticity of triads %			m_2 mol. %	Stop
				I	H	S		
3.707	0.027	0.7	2.9	74	14	11	— ^a	A—B
3.707	0.027	0.7	5.2	52	22	26	— ^a	B—C
3.707	0.027	0.7	22.0	14	29	57	— ^a	C—D
3.369	0.275	7.5	2.6	65	19	41	10	A—B
3.369	0.275	7.5	3.1	58	21	21	10	B
3.369	0.275	7.5	5.8	44	23	33	9	B—C
3.369	0.275	7.5	10.6	23	26	51	9	C—D
3.369	0.275	7.5	16.1	13	26	61	9	C—D
2.995	0.552	15.5	3.0	73	17	10	17	A—B
2.995	0.552	15.5	4.3	68	19	13	17	B
2.995	0.552	15.5	7.0	59	21	20	19	B—C
2.995	0.552	15.5	12.1	31	25	44	18	C
2.995	0.552	15.5	21.9	15	28	57	16	C—D
2.245	1.100	32.8	3.2	60	24	16	35	A—B
2.245	1.100	32.8	4.5	57	27	16	36	B
2.245	1.100	32.8	5.2	46	24	30	35	B—C
2.245	1.100	32.8	7.7	38	25	37	35	B—C
2.245	1.100	32.8	19.7	20	28	52	37	C—D
1.585	1.585	50.0	3.6	60	20	20	58	A—B
1.585	1.585	50.0	5.4	55	25	20	57	B
1.585	1.585	50.0	6.4	53	25	22	57	B—C
1.585	1.585	50.0	7.6	50	25	25	58	B—C
1.585	1.585	50.0	23.3	16	28	56	57	C—D
0.370	2.480	87.0	8.7	56	26	18	91	A—B
0.370	2.480	87.0	9.7	53	26	21	89	B—C
0.370	2.480	87.0	13.8	49	26	25	91	B—C
0.370	2.480	87.0	26.7	23	28	49	88	C—D
0.370	2.480	87.0	34.2	20	28	52	89	C—D

^a Lower than the sensitivity threshold of the measurement.

methyl methacrylate, as can be observed in Fig. 5. At very low conversions (2–3 per cent.), the isotacticity of all copolymers is practically the same, irrespective of the relative amounts of both monomers. By extrapolation of these lines to zero conversion, approximately 80 per cent of isotactic triads are found, which corresponds to the isotacticity of poly (methyl methacrylate) prepared under the same conditions. The gradient of the decrease of isotacticity with conversion is thus the highest if the content of 2-methoxyethyl methacrylate in the initial monomer mixture is low.

Molecular Weights, Their Distribution and Polydispersity of the Copolymers

Anomalous dependencies of the molecular weights, of their distributions as well as of the polydispersities of the copolymers on conversion were observed, in connection with kinetic and structural changes. As can be seen in Table III and Fig. 6, the average molecular weights decrease at the beginning of the plateau on the conversion curve. A new increase of \bar{M}_w and \bar{M}_n values with increasing conversion does not begin till the second growth stage. Table III also shows the polydispersity index values, which increase at the beginning of the plateau. In the second growth stage, this increase is pronounced and it tends, in some cases, to enormous values; these could, however, be caused by the branching of the resulting polymer. The differential distribution curves of copolymers with variable composition (Fig. 7) exhibit a broadening in the range of the conversion curve plateau, and in some samples with conversion in the second growth stage a clearly bimodal distribution of molecular weights.

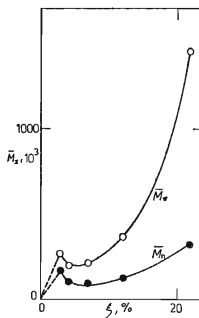


FIG. 6
The Dependence of \bar{M}_w and \bar{M}_n of the Copolymer on the Conversion (ξ)

Initial monomer mixture: 15.5 mol per cent of 2-methoxyethyl methacrylate.

DISCUSSION

Our results clearly show that the copolymerization of methyl methacrylate with 2-methoxyethyl methacrylate proceeds in a similar manner as the homopolymerization of 2-methoxyethyl methacrylate under the same conditions. (The copolymerization parameters $r_1 = 1.51$ and $r_2 = 2.10$ for mole fractions M_1 and M_2 of methyl methacrylate and 2-methoxyethyl methacrylate, respectively, in the dependence of R_{p1} on M_2 clearly show the steepest decrease of R_{p1} for M_1/M_2 between 0 and 1. This means that the change of reaction rate due to the variation of the monomer mixture composition in the first growth phase is not caused by differences in the individual propagation rates⁵ only, but must be caused by a change in the nature of the active centres.

In the polymerization of methyl methacrylate initiated by lithium tert-butoxide in nonpolar hydrocarbon medium, the efficiency of the initiator is relatively low. The unreacted alkoxide, however, participates in the chain propagation by forming a protective complex with the growth centres⁸. This protective cover prevents chain termination by reaction with the ester groups of the monomer or the polymer and makes possible polymerization with these initiators up to high conversions at room temperature; it is also cause of the slower rate of polymerization as compared to systems initiated by organolithium compounds of the type R—Li.

In polymerizations initiated by lithium tert-butoxide, increase of the solvation ability of the reaction medium, as compared to nonpolar hydrocarbons, brings about a higher reaction rate, but also a slowing down or even stopping of chain growth after a definite time. The cause of this phenomenon may be found in the stripping of the growth centre by the polar solvent interacting with the excessive alkoxide⁹.

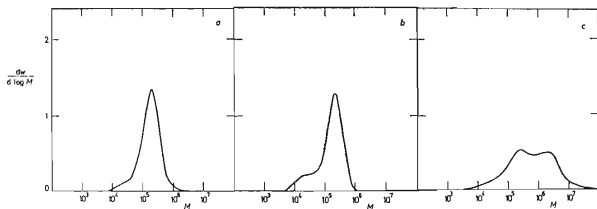


FIG. 7

The Differential Distribution Curves of the Copolymers with 50 mol per cent. of 2-Methoxyethyl Methacrylate in the Initial Monomer Mixture

Conversion, per cent (terminated in the area — see Fig. 1: a 3.6 (A—B), b 7.6 (B—C), c 23.3 (C—D).

TABLE III

The Molecular Weight, the Intrinsic Viscosity and the Polydispersity Index of the Copolymers of Methyl Methacrylate (M_1) with 2-Methoxyethyl Methacrylate (M_2)

M_2 the content in the initial monomer mixture, ξ conversion, stop — the region of termination (Fig. 1).

M_2 mol. %	ξ %	Stop	$\bar{M}_w \cdot 10^{-3}$	$\bar{M}_n \cdot 10^{-3}$	$[\eta]$ dl/g	\bar{M}_w/\bar{M}_n
7.5	2.6	A-B	97	48	—	2.01
7.5	3.1	B	103	47	—	2.18
7.5	5.8	B-C	102	43	—	2.35
7.5	10.6	C-D	244	59	—	4.14
7.5	16.1	C-D	694	98	—	7.03
15.5	2.9	A-B	266	166	0.544	1.60
15.5	4.3	B-C	196	101	0.415	1.95
15.5	7.0	B-C	208	90	0.432	2.30
15.5	12.1	C-D	346	118	0.693	3.09
15.5	21.9	C-D	1 457	320	2.405	4.55
32.8	3.2	A-B	156	90	0.340	1.72
32.8	4.5	B	177	93	0.379	1.91
32.8	5.2	B-C	188	84	0.399	2.24
32.8	7.7	B-C	144	56	0.313	2.57
32.8	19.7	C-D	812	116	1.405	7.03
50.0	3.6	A-B	202	101	0.425	2.00
50.0	5.4	B-C	181	97	0.385	1.86
50.0	6.4	B-C	184	93	0.392	1.97
50.0	7.6	B-C	178	65	0.380	2.74
50.0	23.3	C-D	1 672	131	2.554	12.80
68.8	7.7	A-B	249	174	0.517	1.43
68.8	8.9	B-C	201	119	0.425	1.70
68.8	20.7	C-D	893	289	1.547	3.08
68.8	33.8	C-D	1 174	469	2.554	2.50
87.0	8.9	A-B	326	166	0.650	1.96
87.0	9.7	B	330	202	0.660	1.63
87.0	13.8	B-C	429	289	0.832	1.50
87.0	26.7	C-D	1 371	445	2.243	3.08
87.0	34.2	C-D	1 379	547	2.333	2.55

We propose a similar process for the system of 2-methoxyethyl methacrylate with lithium tert-butoxide, where the polymerization starts immediately after the mixing of the reaction components, proceeds with a high velocity but terminates after a relatively short time. As in the case of a solvating medium, the protective cover of the active centres is probably destroyed here by the coordination of the excessive alkoxide with the polar monomer. The effect is the same, *i.e.* the first stage of the polymeriza-

tion of 2-methoxyethyl methacrylate by lithium tert-butoxide is terminated after approximately 10 minutes at normal temperature, prior to reaching full conversion^{2,5}.

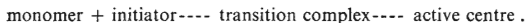
In the case of the copolymerization of 2-methoxyethyl methacrylate with methyl methacrylate, unprotected reaction centres are probably formed even at a very low content of 2-methoxyethyl methacrylate in the initial monomer mixture; this follows from the fact that the existence of two more or less separated growth stages can be observed even with less than 10 mol per cent. of 2-methoxyethyl methacrylate in the monomer mixture.

The stereoregularity of the copolymers of methyl methacrylate with 2-methoxyethyl methacrylate is characterized in comparison with poly(methyl methacrylate), by a lower content of isotactic triads and a higher content of syndiotactic triads, both being up to a point dependent on the initial mixture composition. As can be seen from Fig. 4, in the first growth stage the decrease of the isotacticity of the copolymer in dependence on the monomer mixture composition is pronounced in the interval from 0 to 30 mol per cent. of 2-methoxyethyl methacrylate but remains practically unchanged beyond it. An explanation of this fact may be sought partly on the basis of our earlier conclusions, combined with the idea of the cyclic growth centre of isotactic poly(methyl methacrylate), published by Cram and Kopecky some years ago^{10,11}.

According to Cram, isotactic addition of a monomer unit to the chain is controlled by the six-membered cyclic formation composed of the ultimate and penultimate monomer units, coordinating with the lithium counter-ion. The stereospecific effect of this Cram's cycle can be perturbed by an electron donating oxygen atom of the ester group of 2-methoxyethyl methacrylate which participates in its formation, as was found earlier by us⁴. The stereospecific controlling function of the complex is thus perturbed, the lithium atom is blocked by the polar 2-methoxyethyl groups and is thus unable to coordinate with the approaching monomer unit, leading to a marked decrease of the content of isotactic triads in comparison with poly(methyl methacrylate). In the formation of the cyclic growth centre of the 2-methoxyethyl methacrylate-methyl methacrylate copolymer, both monomers participate. As can be seen from the dependence of the microstructure on the composition of the copolymer (Fig. 4), one molecule of 2-methoxyethyl methacrylate as its structural unit is enough to disturb the stereospecific control of the Cram's complex, since the content of the isotactic triads in the copolymer with 30–50 mol per cent of 2-methoxyethyl methacrylate is the same as in the 2-methoxyethyl methacrylate homopolymer. This means that each 2-methoxyethyl methacrylate unit acts twice in the disturbing manner: once as a penultimate unit and once as an ultimate one, each time participating in the formation of Cram's cycle.

All these considerations relate to the first stage of polymerization, *i.e.* to the area A–B on the conversion curve (Fig. 1). The generation of the active growth centre

of the second growth stage, *i.e.* of the area C–D, shows some similarities to the methyl methacrylate–sodium *t*-butoxide system in a nonpolar medium¹². The growth of the polymer takes place after an induction period, the length of which is a function of the initial concentrations. The resulting polymer is syndiotactic or atactic. We established that in the polymerization of 2-methoxyethyl methacrylate, initiated by lithium *tert*-butoxide, the dependence of the length of the conversion curve plateau on the initial monomer concentration – similarly as the induction period in the polymerization of methyl methacrylate by sodium *tert*-butoxide – can be described by the relation $P_{\text{ind}} = K[M_0]^{-1/2}$. The formation of the active growth centre in the methyl methacrylate–sodium *tert*-butoxide system is supposed to be a two-stage reaction of the monomer with the alkoxide initiator proceeding through a metastable transition complex according to the following scheme:



It is possible that the active centres of the second growth stage of the polymerization of 2-methoxyethyl methacrylate with lithium *tert*-butoxide follow similar rules; the length of the plateau on the conversion curve can be then considered the measure of the stability of the transition complex. This idea is based on the mentioned similarities of both polymerization systems but there is no conclusive evidence of it as yet.

The curves of the differential molecular weight distribution of the copolymers (Fig. 7) show, like those of the 2-methoxyethyl methacrylate homopolymers, a marked change of the distribution in the second growth stage. The bimodality of the distribution curves is much more pronounced than in the case of the 2-methoxyethyl methacrylate homopolymers; this may, however, be caused by the fact that the copolymers were analyzed with a new, more efficient six-column GPC system instead of the four-column system used in the former case. The broadening of the distribution curves of the copolymers on the side of low-molecular weights, which takes place in the region of the conversion curve plateau, and the bimodality in the second stage of the polymerization may be considered a further support of our idea of the two-fold mechanism of the polymer growth. The existence of the two growth stages in the polymerization of 2-methoxyethyl methacrylate was proved in our preceding paper; the above described very similar course of the copolymerization of this monomer with methyl methacrylate under similar conditions indicates that the growth of the 2-methoxyethyl methacrylate–methyl methacrylate copolymer will follow similar rules as the homopolymerization of 2-methoxyethyl methacrylate. Even though the conditions of the copolymerization system are somewhat more complicated, the successive formation and function of the two types of active centres may be considered very probable.

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