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## ANIONIC POLYMERIZATION OF 2-METHOXYETHYL METHACRYLATE AND 2-(DIMETHYLAMINO)ETHYL METHACRYLATE

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It follows from a series of papers dealing with the polymerization of methyl methacrylate initiated with the alkali metals compounds, that the stereospecificity of polymers prepared in the same solvents depends on the alkali metal used<sup>1,2</sup>. Identical results were found during polymerization with alkoxides of the alkali metals<sup>3,4</sup>. It can be said, that by initiation with the lithium compounds in a non-polar medium an isotactic polymer is formed, whereas the use of sodium and potassium compounds leads to an atactic product or a polymer enriched by a syndiotactic component<sup>3</sup>. The stereospecificity of poly(methyl methacrylates) (*I*) prepared with organometallic compounds of lithium, sodium and potassium in both non-polar and polar media is in principle temperature-independent<sup>1</sup>. The effect of the medium upon the stereospecificity of a polymer is characterized by the fact that the non-polar solvent favours the formation of an isotactic structure, whereas the polymer formed in a polar medium is prevalingly syndiotactic. In solutions of medium polarity the equilibrium existing between a complex which favours the formation of an isotactic structure and a complex which controls the propagation to higher contents of syndio-structures leads to the formation of an atactic or a stereoblock polymer<sup>1,2,5</sup>.

As a rule, linear or cyclic ethers, pyridine *etc.* are used as the polar medium, that is, compounds which contain in their molecule electron donor elements (O, N), capable of participation in the formation of a transient complex which controls the stereospecific introduction of a monomeric unit into a growing polymer chain.

Similarly to the polarity of the medium, the direct presence of electron donor elements in the monomer<sup>6</sup> molecule also influences the microstructure of polymethacrylates obtained in the presence of butyllithium. During polymerization of methacrylates which contain in their ester group one of the above electron donor elements, the content of the individual stereoisomers in the

stereospecific composition of the polymer varies, similarly to the polymerization of methyl methacrylate in polar solvents, even if the polymerization is carried out in a non-polar medium under otherwise identical conditions.

The present paper refers to the polymerization of 2-methoxyethyl methacrylate and 2-(dimethylamino)ethyl methacrylate in the presence of lithium tert-butoxide, that is, esters containing nucleophilic elements (O, N) directly in the alkoxide residue at position 6 toward the growing anion. To prevent tert-alkoxide from affecting the stereospecificity of the polymers, comparative polymerizations of the above monomers were performed, using tert-butyllithium as the initiator. For this compound it can be assumed that no side reactions leading to the formation of a tert-alkoxide will occur, as it happens if butyllithium is used<sup>7</sup>.

## EXPERIMENTAL

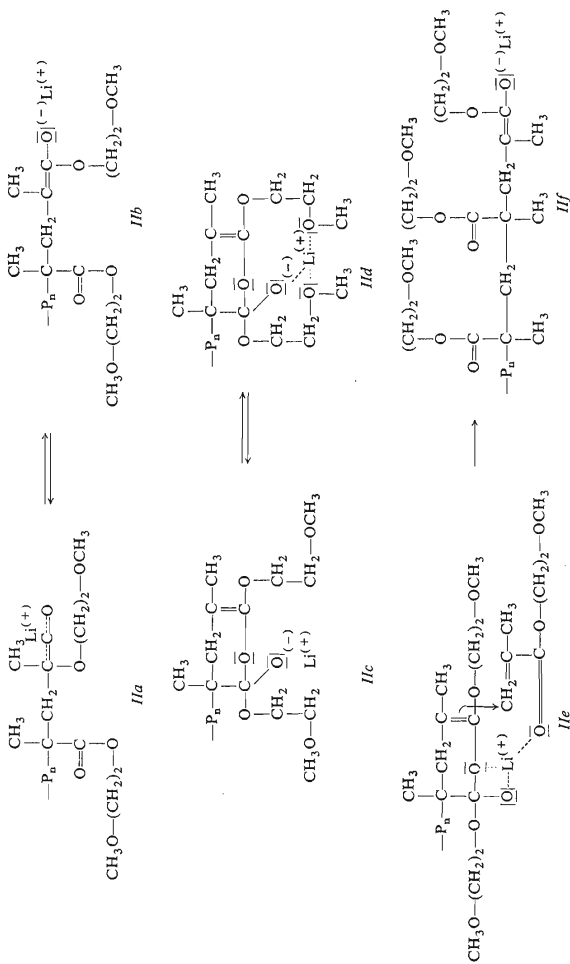
### Materials Used

2-Methoxyethyl methacrylate and 2-(dimethylamino)ethyl methacrylate were prepared by reesterification of methyl methacrylate with 2-methoxyethanol<sup>8</sup> or N,N-dimethylaminoethanol<sup>9</sup>. The esters thus obtained were purified by distilling twice *in vacuo* on a Vigreux column (15 theoretical plates). They were dried 24 h with calcium hydride prior to use, then distilled, and the middle fraction (approx. 40%, methoxy derivative b.p. 57°C/8 Torr, amino derivative b.p. 50°C/4 Torr) was again dried 24 h with calcium hydride. The purity of the monomers was checked by gas chromatography using a Pye apparatus on a column 1 m long, filled with Chromosorb coated GEXE (10%), with argon as carrier gas (37 ml/min) and a flame ionization detector. The temperature of the column was 98°C for the methoxy derivative and 108°C for the amino derivative.

Lithium tert-butoxide was prepared by a method described earlier and purified by sublimation<sup>7</sup>; tert-butyllithium was prepared and purified using usual procedures<sup>10</sup>. The purity of both compounds was determined after hydrolysis by acidimetric titration (99.9%). Toluene solutions of catalysts were used for polymerization, and their concentration was determined by acidimetric titration using phenolphthalein as indicator.

### Polymerization

The polymerization was carried out in toluene solutions of various concentrations, either in dilatometers (2-methoxyethyl methacrylate at 20°C and 0°C), or in special ampoules with two tubes. Both the ampoules and the dilatometers were dried at 130–140°C prior to use and then again dried by heating in a flame at  $10^{-2}$  Torr. The components of the polymerization mixture were added with syringes, to which pipettes provided with long needles had been connected. The individual components were added into the ampoules separately, that is, initiator and solvent into one tube, and monomer into the other. Both components were mixed only after they had been cooled to the polymerization temperature. All operations concerning purification of the chemicals and apparatus, preparation of solutions, filling of ampoules and dilatometers were performed in dry oxygen-free argon. The polymerization was stopped by adding a methanol solution of hydrogen chloride. Poly(2-methoxyethyl methacrylate) (II) was purified by precipitating twice into a tenfold volume of hexane and dried to constant weight at 40°C/0.01 Torr. Poly(2-(dimethylamino)ethyl methacrylate) (III) becomes insoluble in the presence of oxygen. This is why the following procedure was applied for the isolation and preparation of samples for the NMR analysis (using argon only): After the polymerization had stopped, the polymerization mixture was diluted directly in the ampoules with distilled chloroform, a small part of the solution was taken and precipitated into a tenfold excess of distilled and degassed hexane. After sedimentation



SCHEME I

of the polymer the hexane was removed by pipetting, and the polymers were dried at room temperature under a given pressure. From polymers thus isolated, solutions for spectral analysis were prepared directly by distilling the amount of deuteriochloroform per polymer calculated in advance.

### Spectroscopy

Tacticity of the polymers was determined using the nuclear magnetic resonance method applied by Bovey to poly(methyl methacrylate)<sup>1</sup> with a JNM-3-60 apparatus at a frequency 60 Mc. Measurements were performed with solutions having a concentration of about 10%; *II* was dissolved in the mixture tetrachloroethylene-*o*-dichlorobenzene (1 : 1) (and the NMR spectrum was recorded at 120°C), *III* was dissolved in deuteriochloroform (70°C). The contents of the individual stereoisomers were calculated from relative intensities of the  $\alpha$ -methyl bands using a procedure analogous to *I* (ref.<sup>1</sup>). Characteristic parts of both spectra are given in Fig. 1.

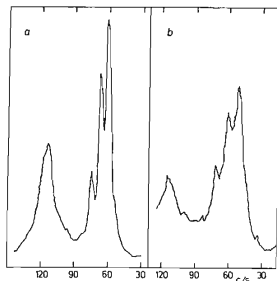


FIG. 1

The NMR Spectrum of Poly(2-methoxyethyl methacrylate) (*a*) and Poly(2-dimethylamino)ethyl methacrylate) (*b*)

### RESULTS AND DISCUSSION

Results of anionic polymerizations of methacrylates containing various alcoholic residues are summarized in Table I. In comparison with poly(methyl methacrylate) (*I*), the tacticity of poly(2-methoxyethyl methacrylate) (*II*) prepared with lithium tert-butoxide exhibits a considerable decrease in the content of the isotactic component, accompanied by an increase in both the syndiotactic and heterotactic fractions (Experiments No 1 and 2). In contrast with *I*, whose tacticity little depends on the polymerization temperature<sup>7</sup>, the microstructure of *II* is considerably temperature dependent (Experiments No 3, 4, 6, 8). A decrease in temperature suppresses the effect of the electron-donor atom in the alcoholic residue of the monomeric ester; at the same time the content of the isotactic component of the polymer increases up to a value which can be attained with *I*, prepared with lithium tert-butoxide or butyllithium at room temperature<sup>11</sup> (Experiment No 1). It has also been established that the tacticity of *II* is not affected by the degree of conversion (Experiment No 2—5, 7, 8). This finding, along with the results obtained by Iwakura and coworkers<sup>6</sup>, justifies the hypothesis of an intramolecular effect of the heteroatom in the alcoholic residue of the ester.

Polymers *I* and *II*, which were prepared with tert-butyllithium at 20°C, exhibit different structural compositions; polymers *II* have a decreased content of the isotactic component by approximately the same values as in the case of initiation with lithium tert-butoxide (Experiment No 13, 14). No effect of the concentration of the organometallic initiator upon the microstructure of the polymers could be observed (Experiment No 14, 15). In contrast with the polymers prepared with an alkoxide, these polymers do not exhibit any dependence of the microstructure upon the polymerization temperature within the range under investigation (Experiment No 15, 16).

Similar results were obtained for the polymerization of 2(dimethylamino)ethyl methacrylate in the presence of the same initiators (Experiment No 12, 17). However, the decrease in the content of the isotactic fraction of the polymers prepared with lithium tert-butoxide is smaller by about 30% (with respect to *I*), and the increase in the syndiotactic component is lower by 25% than in *II*, which can be due to the influence of comparatively bulky methyl groups at the nitrogen atom and a smaller electron-donor effect of the nitrogen atom in comparison with the oxygen atom. The dependence of microstructure on the polymerization temperature is roughly the same as

TABLE I

Effect of the Polymerization Conditions on the Structure of Polymethacrylates

[C] Concentration of the initiator, [M] concentration of the monomer,  $\xi$  degree of conversion.  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOR}$ :  $R_I$  = methyl,  $R_{II}$  = 2-methoxyethyl,  $R_{III}$  = 2-(dimethylamino)ethyl.

Exp. No	R	[M]	[C]	T °C	$\xi$ %	Tacticity of the polymer		
						% of triads		
Initiation with lithium tert-butoxide								
1	$R_I$	3.74	0.023	20	41	77	7	16
2	$R_{II}$	3.05	0.0304	20	44	21	48	31
3		3.05	0.0304	20	30	24	45	31
4		3.05	0.0304	0	90	12	58	30
5		3.05	0.0304	0	13	14	57	29
6		3.05	0.0304	-20	56	58	21	21
7		3.05	0.0304	-40	36	73	12	15
8		3.05	0.0304	-40	16	76	10	14
9	$R_{III}$	5.20	0.0515	20	—	55	20	25
10		5.20	0.0515	0	—	64	15	21
11		5.20	0.0515	-20	—	51	22	27
12		5.20	0.0515	-40	—	80	10	10
Initiation with tert-butyllithium								
13	$R_I$	3.75	0.176	20	13	56	16	28
14	$R_{II}$	3.05	0.0305	20	61	6	60	34
15		3.05	0.003	20	10	4	65	31
16		3.05	0.003	-20	37	7	59	34
17	$R_{III}$	5.20	0.0051	20	—	22	43	35

for *II* prepared under identical conditions. At low temperatures ( $-40^{\circ}\text{C}$ ), an almost pure isotactic polymer is formed during polymerization with an alkoxide. The dependence of the tacticity upon the degree of conversion was not measured owing to the difficult treatment of the polymers; however, it can be expected in analogy with *II* that conversion will have no influence upon the tacticity of the polymers. If we assume the existence of the cyclic complexes according to Cram<sup>12,13,14</sup> (cf. Scheme 1), as a condition for the formation of an isotactic chain, it can be supposed that during polymerization of 2-methoxyethyl and 2-(dimethylamino)ethyl methacrylates the probability of the formation of Cram's cycles will be reduced because of the effect of the electron donor atoms in the alcoholic residue of both monomeric esters, which will lead in its turn to a decrease in the probability of an isotactic growth (structure *IIId*). As is shown by the experimental results the growth of the isotactic chain is not quite precluded. It can be assumed that structure *IIc* is in equilibrium with structure *IIId*, capable of forming Cram's cycles. The participation of the electron donor atom from the alcoholic residue of the ester in the formation of a cyclic complex is apparently conditioned by its approaching to the lithium cation.

The pronounced temperature dependence of the microstructure of poly(2-methoxyethyl methacrylate) and poly(2-(dimethylamino)ethyl methacrylate), prepared with lithium tert-butoxide as initiator (in contrast with tert-butyl-lithium as initiator) can be explained in terms of the existence of an equilibrium between a complex of the growing centre with alkoxide, on the one hand, and a complex of the growing centre with the electron donor atom in the alcoholic residue of the monomeric ester, on the other. This equilibrium can be strongly temperature dependent; the equilibrium is shifted to the side of the alkoxide complex with decreasing temperature and therefore the influence of the heteroatom from the alcoholic residue of the monomeric ester on stereoregularity is suppressed.

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