

**MICROSTRUCTURE OF POLY(METHYL METHACRYLATE)  
PREPARED BY ANIONIC POLYMERIZATION.  
EFFECTS OF ALKALI ALKOXIDES**

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Esters of isobutyric acid substituted by lithium, sodium or potassium in the  $\alpha$ -position, in some cases with the addition of tert-butoxides of alkali metals, were used to initiate polymerizations of methyl methacrylate. Analysis of the microstructure of the resulting polymers has confirmed that the tert-butoxides are coordinated by the growth centre and that the growth reaction is significantly affected by this interaction. It is assumed that at least part of the reacting monomer forms an adduct with the alkoxide primarily coordinated at the growth centre, thus affecting the stereoregularity of the growing polymer. In the system  $\alpha$ -lithio ester-sodium or potassium tert-butoxide, the effect of metal exchange upon the microstructure of the resulting polymer is described.

As a rough approximation, esters of isobutyric acid substituted by an alkali metal in the  $\alpha$ -position may be considered as models of the growth centre in anionic polymerization of methacrylate esters. Recently these compounds have been prepared in pure form and it has been found that they undergo more or less pronounced adduct formation with alkali alkoxides<sup>1,2</sup>. The  $\alpha$ -lithio esters were found to be added by a rapid reaction to the C=C double bond of methacrylate esters, without any appreciable amount of side products<sup>3</sup>. Therefore they may be used as suitable initiators of the polymerization of these esters, especially in studies of the mechanism of the mentioned reaction.

In polymerization of methyl methacrylate initiated by alkyllithium compounds the effect of lithium alkoxides has been proved<sup>4,5</sup>, but it could not be defined accurately because of overlapping effects of the products of initiator side reactions. Knowledge of similar effects of sodium or potassium alkoxides is scarce, in spite of the fact that these alkoxides are known to strongly affect polymerization<sup>6,7</sup>. Therefore in our studies of the mechanism of anionic polymerization of methacrylate esters, the role of alkali alkoxides seemed worth of attention. In this connection, the microstructure of poly(methyl methacrylates) prepared with initiators containing various  $\alpha$ -metallo esters and alkali alkoxides was compared.

In the following, the cyclic intermediate complex according to Cram<sup>8</sup> is considered as condition of isotactic growth of the polymer chain in anionic polymerizations of methacrylate esters. According to this mechanism, in the growth reaction the

counter-ion of the growth centre first coordinates the monomer molecule which is then added through the double bond in the next step. The coordination of the monomer has a definite steric arrangement, and therefore also the addition of monomer is sterically controlled. Therefore the microstructure of the formed polymer depends considerably on the type of the counter-ion and on its state. So *e.g.* in toluene solution, organolithium initiators lead to the formation of predominantly isotactic poly(methyl methacrylate), whereas with sodium or potassium organometallics, the content of the isotactic component is lower<sup>9,10</sup>. On the other hand, in solvating media like tetrahydrofuran, organolithium initiators yield predominantly syndiotactic polymers<sup>11</sup>. By analysis of microstructure it is therefore possible to obtain informations on the nature of the growth centre and on the growth reaction.

## EXPERIMENTAL

All operations with the organic compounds of alkali metals (including polymerization) were performed in an atmosphere of pure argon. Ethyl isobutyrate substituted by Li, Na or K were prepared and isolated according to<sup>1,2</sup>, the tert-butoxides according to<sup>12</sup>; the tert-butyl  $\alpha$ -sodio-propionate was used in the form of a reaction mixture of equivalent amounts of hexamethyldisilazylsodium and tert-butyl propionate. The rectified monomer was vacuum distilled with calcium hydride directly before use.

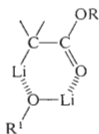
The polymerizations were carried out in ampoules at 20°C under stirring; after 1 hour the polymerization was interrupted by methanol and the polymer isolated by precipitation in heptane. This polymerization time was of sufficient length, because initiator systems with metallo esters lead to 95% conversion in less than 15 s (ref.<sup>13</sup>). The crude polymer was reprecipitated twice from heptane, dissolved in an equimolar mixture of *o*-dichlorobenzene and tetrachloroethylene and its NMR spectrum was then measured on the JEOL PS-100 spectrometer at 135°C. The stereoregularity of the polymer in terms of triads was calculated from the relative peak heights of the  $\alpha$ -CH<sub>3</sub> signals. The microstructure of methacrylate esters with higher alkyls was determined from the fine structure of the methylene band, with correspondingly lower accuracy. In butyl and octyl methacrylates, the tacticity value found in this way was near to the value determined for methyl methacrylate prepared with the same initiating system.

## RESULTS AND DISCUSSION

In Table I the results of the polymerization of methyl methacrylate initiated by various types of alkali metal compounds are summarized. As expected, the microstructure of the obtained polymer depended on the type of counter-ion and on the structure of the initiator, the latter effect being the least pronounced in potassium compounds. So the microstructures of the poly(methyl methacrylates) formed by the action of lithium, sodium and potassium isobutyrate differed considerably from each other, as well as from the polymers obtained with the aid of tert-butoxides of the respective alkali metals. An addition of alkali tert-butoxide to the  $\alpha$ -metallo ester of the same metal had a perceptible effect on the microstructure and yield of polymer, in spite of the fact that other properties of the initiator system were determined by the

metallo ester component of the initiator (*i.e.* mainly the rate of an attainment of limit conversion). The change of microstructure was always in the direction of the values obtained with *tert*-butoxide alone, and it increased with the increasing ratio (alkoxide/metallo ester). *E.g.* for the ratio  $[(\text{CH}_3)_3\text{CONa}]/[\textit{tert}\text{-butyl sodiopropionate}] \sim 4$ , the microstructure was equal to that obtained with sodium *tert*-butoxide alone. These results indicate interaction of alkali *tert*-butoxides with the growth centre and the important role of the coordinated alkoxides in the growth reaction. The described dependence of the microstructure change on the ratio alkoxide/metallo ester indicates that the growth centre is either able to coordinate several molecules of the alkoxide simultaneously or that the coordination of the alkoxide is an equilibrium reaction.

Polymerization of methacrylate esters initiated by alkali *tert*-butoxides alone proceeds under the conditions given for the metallo esters only to a small extent and at a considerably slower rate (Table I). However, conditions are known under which alkali *tert*-alkoxides are effective initiators of methacrylate ester polymerization<sup>14,15</sup>. In the case of methyl methacrylate polymerization initiated by lithium *tert*-butoxide, mechanistic considerations have led to the assumption that part of the alkoxide unused for initiation is bound by the growth centre<sup>16</sup>. Similar conclusions were suggested also by the behaviour of models of the growth centre, *i.e.* of alkyl  $\alpha$ -metalloisobutyrate interacting with alkali alkoxides<sup>1,3</sup>. In infrared spectra of lithium compounds these interactions were manifested by changes of skeletal vibrations involving the C—O—Li bond in lithium *tert*-butoxide at  $974\text{ cm}^{-1}$  and of the  $\alpha$ -lithiocarboxyl group in the metallo ester. It is therefore possible to assume participation of these groups in the formation of the adduct, and its structure then may be schematically depicted as



The real structure of the complex growth centre will naturally be more complicated; besides other effects, like *e.g.* coordination with penultimate carboxyl group of the polymer chain, or various “intraaggregate” electron transfers, also the tendency of alkali alkoxides and of metallo esters to the formation of higher aggregates<sup>17,18</sup> may be of importance.

According to these ideas, the growth centre in this type of polymerization is “enveloped” by alkoxide molecules. In the propagating reaction according to the Cram mechanism the entering monomer molecule could also be coordinated to the

“enveloping” alkoxide and only in the subsequent reaction step, after the reorganization of the adduct, it would be added to the growing polymer chain. Such a mechanism is in good agreement with the experimental results, because the growth centre with the coordinated alkoxide molecules does yield polymers with a microstructure near to the microstructure found for alkoxide alone (Table I).

The interaction of carboxylic acid esters with sodium and potassium alkoxides has been described and some of the adducts have been isolated<sup>19</sup>. This interaction was also manifested in the infrared spectrum of these systems<sup>20</sup> mainly by the lowering of the frequency of the carbalkoxyl band by 10–20 cm<sup>-1</sup>. Therefore coordina-

TABLE I

Microstructure and Yield of Polymer in Polymerization of Methyl Methacrylate Initiated by  $\alpha$ -Metallo Esters (toluene, 20°C, 1 h) and Their Mixtures with Alkali Alkoxides

[Monomer] = 0.627 mol/l, [monomer]/[metallo ester] = 120. Unusual symbols: iB isobutyrate, P propionate. Symbols:  $\bar{i}$ ,  $\bar{s}$  mean length of isotactic and syndiotactic sequence, respectively,  $\rho$  persistence ratio.

Initiating system <sup>a</sup>	Yield %	Microstructure, %			$\bar{i}$	$\bar{s}$	$\rho$
		I	H	S			
Li-EtiB	46	71	21	8	7.60	1.75	1.42
Li-EtiB + t-BuOLi	53	74	19	7	8.99	1.77	1.48
Li-EtiB + 3t-BuOLi	95	74	19	7	8.79	1.74	1.45
t-BuOLi <sup>b</sup>	100	81	13	6	13.5	1.92	1.68
Na-EtiB	65	54	36	10	4.00	1.56	1.12
Na-EtiB + t-BuONa	97	33	38	29	2.74	2.55	1.32
Na-t-BuP	54	50	40	10	3.52	1.54	1.07
Na-t-BuP + t-BuONa	97	28	39	33	2.43	2.65	1.27
Na-t-BuP + 2t-BuONa	99	22	38	40	2.13	3.10	1.26
Na-t-BuP + 3t-BuONa	100	19	37	44	2.05	3.34	1.27
Na-t-BuP + 6t-BuONa	100	18	36	46	1.97	3.50	1.26
t-BuONa <sup>c</sup>	13	19	36	45	2.06	3.50	1.26
K-EtiB	96	28	51	21	2.11	1.84	0.98
K-EtiB + t-BuOK <sup>d</sup>	90	30	49	21	2.21	1.86	1.01
t-BuOK <sup>e</sup>	89	32	41	27	2.56	2.32	1.22
Li-EtiB + t-BuONa	88	50	34	16	3.94	1.94	1.30
Na-EtiB + t-BuOLi	80	54	33	13	4.22	1.77	1.25
Li-EtiB + t-BuOK	92	28	51	21	2.07	1.84	0.97
K-EtiB + t-BuOLi	85	31	49	20	2.27	1.82	1.01

<sup>a</sup> Numbers at alkoxides indicate number of mol of alkoxide per mol of metallo ester; <sup>b</sup> [monomer] = 4.68 mol/l, [monomer]/[alkoxide] = 312, polymerization time 5 h; under conditions given in legend no polymer was formed; <sup>c</sup> [monomer]/[alkoxide] = 20. <sup>d</sup> [monomer]/[metallo ester] = 240. <sup>e</sup> [monomer]/[alkoxide] = 40.

tion of the monomer to the enveloping alkoxide may be assumed to be of importance in the propagation reaction.

The presence of tert-butoxides containing a different alkali metal than the metallo ester had a different effect upon the microstructure of the poly(methyl methacrylate). Lithium tert-butoxide practically did not affect the microstructure of the polymer prepared under the action of ethyl sodio- or potassioisobutyrate. On the other hand, the addition of sodium or potassium tert-butoxide in a polymerization initiated by ethyl lithioisobutyrate was manifested by a profound change of the microstructure of the polymer, which was near to the characteristic values found for polymers prepared with the corresponding sodio or potassio esters only. This result lead us to the hypothesis that in initiating systems composed of the lithio ester and the tert-butoxide of a heavier alkali metal, a metal-metal exchange reaction takes place; under preparative conditions such a reaction was described by the scheme<sup>2</sup> ( $M = \text{Na, K, Cs}$ ;  $R = \text{especially } \text{C}_2\text{H}_5$ ):



The products of this exchange reaction undergo only weak mutual interaction, without substantial effect on the microstructure of the polymer, as shown in Table I. In polymerization of methacrylate esters, initiated by the system  $\alpha$ -lithio ester-tert-butoxide of heavier alkali metal, the growth centre may therefore accept as counter ion in dynamic equilibrium even a heavier alkali metal.

A further characteristic parameter of stereopolymers is the distribution of stereo-sequences in the polymer chain (block character). It is sometimes described by the persistence ratio  $\rho$ , defined as  $\rho = 1/(u + w)$  where  $u$  and  $w$  are parameters of 1st order Markov statistics<sup>21</sup>. The persistence ratio may assume values from 0.5 (for alternating stereopolymer) over 1.0 (for statistical stereopolymer) to  $\infty$  (for maximum block character of stereopolymer).

From Table I it is further apparent that for poly(methyl methacrylates) prepared with the system metallo ester + tert-butoxide of the same alkali metal the persistence ratio was higher than for a polymer obtained with the metallo ester of the same metal only, and it was near to the value found in polymers prepared with the respective alkoxide only. Similarly initiating systems based on  $\alpha$ -lithio esters and tert-butoxides of heavier alkali metals yielded poly(methyl methacrylates) with a persistence ratio near to the values found for polymers prepared with  $\alpha$ -sodio or potassio esters only. The above described interactions in the system metallo ester-alkali metal tert-butoxide were thus similarly reflected also in the block character of the resulting polymers. The growth centre with a coordinated tert-butoxide of the same alkali metal yields a polymer with a higher block character; for such a centre the probability of maintenance of a certain type of steric addition of monomer is thus

higher. In initiator systems containing organic compounds of alkali metals the block character of poly(methyl methacrylate) decreased in the series  $\text{Li} > \text{Na} > \text{K}$ , the potassium-organic compounds yielding a completely atactic statistical stereopolymer.

The above results demonstrate the importance of alkali metal alkoxides in the growth reaction of anionic polymerization of methacrylate esters. Modifications of the initiating system by addition of alkoxide may be used to tailor the microstructure of the polymer in a broad range. Due to the relations between microstructure and physical and chemical properties of polymethacrylate esters, a possibility of modifications of polymer properties is clearly indicated.

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