EFFECT OF THE POLARITY OF SURROUNDING ON THE MICROSTRUCTURE OF POLY(METHYL METHACRYLATE) IN THE ANIONIC POLYMERIZATION

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Values corroborating views about the "protective" effect of tert-alkoxides on the growth centre in the anionic polymerization of methyl methacrylate were obtained by measuring the degree of influence on the stereoregularity of poly(methyl methacrylate) prepared by the anionic polymerization with n-butyllithium and tert-alkoxides as initiators in media having different solvation power. The "protective" effect on the growth centre prevents side reactions of the growth centre and makes possible polymerization at $+20°C$ up to 100% conversion, and also provides the constant character of stereoregularity during changes in the solvation power of the medium.

Alkali metal tert-alkoxides are advantageously used as initiators of the anionic polymerization of methyl methacrylates[1-3]. Their most marked advantages compared with organometallic compounds are: the possibility of polymerization at room temperature up to a 100% conversion; relatively low polymerization rate; elimination of side reactions between tert-alkoxide and the carbonyl group in methacrylate. The fact that the polymerization of methyl methacrylate initiated with *e.g.* n-butyllithium occurs at $+20°C$ only to low conversions owing to termination reactions is explained by the existence of protection of the growing polymeric centre due to a tert-alkoxide present in excess[3]. The strength of such complex between the growing polymeric centre and tert-alkoxide should be illustrated by this paper, in which we examine the effect of the solvation medium on the structure of the forming polymer.

EXPERIMENTAL

Chemicals. Methyl methacrylate (commercial product of Synthesia, Kolín) was freed from the inhibitor by shaking with a 2·4% soda solution, washed with water, dried with $CaCl_2$ and distilled twice on a column with 20 TP under reduced pressure in argon[4]. The monomer used in the polymerization was dried 24 h over calcium hydride and distilled. Only middle fractions (30% at utmost) in the last distillation immediately before polymerization were taken for polymerization, free from impurities according to the gas chromatographic recording (PYE apparatus, squalane as packing, PEGA as stationary phase, room temperature). Methyl and butyl methacrylates
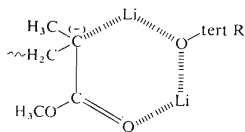
were prepared by the hydrogenation of the respective methacrylic acid esters[4]. Benzene and toluene(thiophene-free) were twice rectified with sodium under argon and stored over calcium hydride. Lithium tert-butoxide was prepared from tert-butyl alcohol and lithium metal[3] and purified by sublimation *in vacuo*[4]. Lithium tert-alkoxide was obtained from 2-methyl-2-pentanol by employing a similar procedure.

Polymerization and testing of polymers. Glass parts of the apparatus used both in the polymerization and in the preparation of the polymerization components were annealed evacuated, washed with argon free from moisture and oxygen, annealed and reevacuated before use. The flexible connections were doubled (inside polyethylene, outside softened poly(vinyl chloride) or rubber, argon flowing between the insulation tubing)[4]. All operations were performed in purified argon. The polymerization took place in glass lens-shaped dilatometers. The polymerization components were introduced into the dilatometers connected with a comb-like distribution frame in contact with vacuum and an argon inlet by using injection syringes in a countercurrent of argon at the same temperature in the following order: nonpolar solvent, initiator, saturated ester or tetrahydrofuran, and finally monomer. Packed dilatometers were closed or sealed. The polymerization was inhibited by methanol with acetic acid or by hydrochloric acid. Polymer solutions were precipitated or reprecipitated into methanol or hexane. The reprecipitated polymers were filtered off, washed and dried to constant weight at 40°C *in vacuo*. The conversion was calculated from volume contractions[5,6] or determined gravimetrically. Molecular weights were determined viscometrically in a diluting viscometer in benzene or chloroform at 25°C. Equations from ref.[7-9] were used in the molecular weight calculations. The structure of the polymers was characterized by determining iso-, syndio- and heterotriads in the polymer chain by NMR using a method described in ref.[10] and a JNM-3-60 apparatus. Precipitation of an acetone solution of the polymer into methanol was used for fractionation.
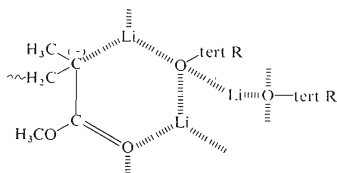
RESULTS AND DISCUSSION

The growth centre of the polymer chain in the initiation with lithium organometallic compounds and lithium alkoxides should be identical after several growth steps, independent of the way of initiation. However, this holds only on condition that the initiation reaction is much faster than the growth reaction and that all initiator is consumed in the initiation stage by the active growth centres, so that the growth reaction cannot be influenced by the initiator any more. This happens *e.g.* in the initiation with n-butyllithium, where all initiator is consumed in a fraction of second. The growth polymeric anion forms with the lithium counterion either a contact ion pair, an ion pair separated by the solvent, or freely solvated ions.

In the initiation of the polymerization of methyl methacrylate with lithium tert-alkoxides the rates of initiation and growth differ from each other by at least one order of magnitude. On the other hand, the duration of the initiation reaction can be counted in minutes. This makes possible addition of the initiator so far unreacted on the growing centre already formed, accompanied by the formation of a relatively stable complex having a probable structure

$$
\begin{array}{c}
H_3C \\
\sim\sim H_2C
\end{array}
\overset{(-)}{C}\cdots\text{Li}\cdots O\text{—tert R}
\quad
H_3CO\text{—}C\text{=}O\cdots\text{Li}
$$

Since tert-alkoxides are associated to various degrees according to the polarity of the medium, it is quite likely that the growing end is "wrapped" by several molecules of tert-alkoxide:

$$
\begin{array}{c}
H_3C \\
\sim\sim H_2C
\end{array}
\overset{(-)}{C}\cdots\text{Li}\cdots O\text{—tert R}
\quad
\text{Li}\cdots O\text{—tert R}
\quad
H_3CO\text{—}C\text{=}O\cdots\text{Li}
$$

Lithium tert-alkoxide is consumed in the initiation reaction to a very low degree, about 10%; the remaining alkoxide is probably bonded in the above complex. This complex, on the one hand, lowers the basicity of the growing anion; on the other, it considerably restricts its reaction with the ester group for sterical reasons. This reaction is a reaction terminating the growing chain, and in the case of a reaction with the ester group on the polymer gives rise to branched polymers. (In the initiation with *e.g.* n-butyllithium, where the growing centre is not protected, polymerization stops owing to the termination reaction already at low conversion, and the polymer is strongly branched[11]). Consequently, if the conditions of the polymerization of methyl methacrylate are chosen so that lithium alkoxide is virtually completely consumed in the initiation reaction, *e.g.* at extremely low concentrations of the initiator or with methyl or butyl isobutyrate, γ-butyrolactone or tetrahydrofuran used as the activator, the growing chain is terminated because of lack of free tert--alkoxide needed for the protection of the growing centre, the polymerization reaction stops before reaching a 100% conversion, and the polymer thus obtained is strongly branched[3,12].

The protection of the growing centre can also be reduced owing to the reesterification reaction between tert-alkoxide bonded on the growing centre and methyl methacrylate with formation of tert-butyl methacrylate and lithium methoxide, which because of its insolubility is separated from the polymeric system in the form of a fine precipitate. However, this reaction is very slow even at +20°C, and under the given conditions the protective tert-alkoxide is not exhausted even after several tens of hours.

The stabilizing character of the growing centre with lithium tert-alkoxides used as initiators is also reflected in the increased participation of iso-triads in the structure of poly(methyl methacrylate) compared with the initiation with n-butyllithium. In order to support the view about the degree of strength of adducts of lithium tert-alkoxides with the growing centre we investigated the effects of various conditions, and above all of the polymerization medium having different solvation power, on the tacticity of the forming polymer. It is generally known that in the anionic polymerization the stereoregularity very strongly depends on the metal in the initiator used, and predominantly on the solvation power of the polymerization medium, solvent in the first place.

Several papers[13-16] deal with the effect of the polarity of the medium on the tacticity of poly(methyl methacrylate) if usual organolithium compounds, butyllithium in the first place, are used in the reaction. Changes in tacticity have been observed if there was a change in the initial concentration of the monomer[13,15,16], at conversion and in the presence of solvating solvents. Although the stereoregularity values given in these papers differ under similar conditions, changes in stereoregularity are quite considerable. For instance, a change in the monomer concentration from 1·9 mol/l to 4·75 mol/l causes a decrease in the isotactic component from 87·5% to 70%, or in the presence of 3 mol/l of methyl isobutyrate the isotactic component is lowered from 76% to 34·5%.

In the polymerization of methyl methacrylate initiated with lithium tert-butoxide in toluene at 20°C (data *cf.* Table I) the tacticity of the forming polymer is independent of the monomer concentration within a range of 1·8 to 8·8 mol/l. Additions of the solvation solvent − isobutyrate − also do not affect the tacticity of the forming polymer within a range of 1·2 mol/l to 5·8 mol/l, while on the other hand in the initiation with butyllithium an addition of 2·7 mol/l of isobutyrate reduces the isotactic component from 71% to 29%.

The degree of strength of the protective complex of the growth centre is particularly pronounced if one considers the results of the polymerization of methyl methacrylate initiated with lithium tert-butoxide and with butyllithium in the presence of tetrahydrofuran (Table I). While the content of the isotactic component with butyllithium as initiator is low and decreases with increasing concentration of tetrahydrofuran, the content of the isotactic component of polymethacrylate prepared with lithium tert-butoxide as initiator is higher by almost 50% at a comparable concentration of tetrahydrofuran. This means that even such strong solvation agent as tetrahydrofuran is able to destruct only to a small extent the protective complex of tert--alkoxide with the growing centre, which controls the isotactic access of the entering monomeric unit.

No essential change in the tacticity of poly(methyl methacrylate) prepared with lithium tert-butoxide as initiator could be detected even as a function of temperature

from $-60°C + 20°C$, of conversion, or of molecular weight for molecular weights ranging from 46000 to 448000 (Table II).

It can be stated, therefore, that of all the factors examined here, the stereoregularity of poly(methyl methacrylate) in the initiation with lithium tert-alkoxide varies only in the presence of a solvent possessing a strong solvation power (tetrahydrofuran), and moreover to a considerably smaller degree compared with the usual

TABLE I

Effect of Medium on the Stereoregularity of the Polymer in the Polymerization of Methyl Methacrylate in Toluene (20°C)

M monomer, I initiator, A activator: MIB methyl isobutyrate, BIB butyl isobutyrate, THF tetrahydrofuran.

[M]	[I]	Acti-	A	Conver-	Tacticity, %		
mol/l		vation	mol/l	sion %	I	H	S
		Initiator: lithium tert-hexoxide					
8·87	0·086	—	—	28	81	13	6
5·61	0·083	—	—	15	84	12	4
3·76	0·085	—	—	21	82	13	5
1·81	0·097	—	—	23	83	12	5
		Initiator: lithium tert-butoxide					
2·80	0·025	—	—	19	82	13	5
4·74	0·024	MIB	3·08	29	80	14	6
1·88	0·011	MIB	1·76	58	82	13	5
3·77	0·016	MIB	4·00	29	82	13	5
1·88	0·017	MIB	5·74	62	80	15	5
1·85	0·011	BIB	1·20	99	82	13	5
1·86	0·011	BIB	1·21	49	84	12	4
1·09	0·011	BIB	1·86	100	85	12	3
0·64	0·011	BIB	2·15	100	86	11	3
4·68	0·050	THF	4·40	11	58	21	21
		Initiator: butyl lithium					
8·45	0·045	—	—	30	52	25	23
0·10	0·012	—	—	22	71	17	12
0·74	0·022	MIB	2·77	100	29	30	41
0·93	0·005	THF	0·862	40	17	36	47
0·93	0·005	THF	3·695	65	10	34	56

organometallic lithium compounds. Constant values of the stereoregularity of poly-(methyl methacrylate) prepared with lithium tert-alkoxides as initiators under various conditions of the anionic polymerization in solution — at various monomer concentrations, temperatures, conversions, molecular weights — as well as polymerization in the presence of methyl and butyl isobutyrate corroborate the assumption that the growth centre of poly(methyl methacrylate) in the initiation with lithium tert-alkoxides is coordinated with the lithium tert-alkoxide present in excess. This adduct of the growing centre with lithium tert-alkoxide is so strong that it withstands the competitive solvation power of the increasing monomer and isobutyrate concentration and to a great extent also prevents the influence of such strong solvation agent as tetrahydrofuran. In addition to providing constant stereoregularity, such

TABLE II

Stereoregularity of the Polymer under Various Polymerization Conditions of Methyl Methacrylate (M) Initiated with Lithium Tert-butoxide(I)

T °C	[M]	[I]	Conversion %	$M_\eta \cdot 10^{-3}$	Tacticity, %		
	mol/l				I	H	S
			Solvent: benzene				
20	2·80	0·025	3·6	—	81	13	6
20	2·80	0·025	5·0	—	78	15	7
20	2·80	0·025	12·0	—	80	14	6
20	2·80	0·025	19·0	—	81	13	6
20	4·74	0·024	29·0	—	80	14	6
20	1·86	0·011	49·0	—	84	12	4
20	1·09	0·011	100	—	85	12	3
20	3·74	0·024	—	448	80	15	5
20	3·74	0·024	—	325	80	15	5
20	3·74	0·024	—	229	83	14	3
20	3·74	0·024	—	160	84	13	3
20	3·74	0·024	—	100	81	15	4
20	3·74	0·024	—	46	81	14	5
			Solvent: toluene				
20	4·68	0·025	—	—	81	14	5
0	4·68	0·025	—	—	82	13	5
−20	4·68	0·025	—	—	86	9	5
−40	4·68	0·025	—	—	87	9	4
−60	4·68	0·025	—	—	87	9	4

stabilized (protected) growing end of the polymer chain considerably reduces the possibility of side reactions of the polymeric centre with the ester group of the monomer or of the polymer, allowing to polymerize at $+20°C$ up to a 100% conversion, which cannot be achieved with usual organometallic compounds.

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