SOME ORGANIC LITHIUM COMPOUNDS AS INITIATORS OF THE ANIONIC POLYMERIZATION OF METHYL METHACRYLATE

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The presence of α-lithio ketone in the initiation mixture formed by a reaction between butyllithium and methyl pivalate was demonstrated. In the initiation of the polymerization of methyl methacrylate α-lithio ketones exhibit high efficiency, which can be enhanced by the effect of lithium alkoxides, in particular of lithium tert-butoxide.

In the initiation of the polymerization of methacrylate esters, the reaction mixture of butyllithium and some carboxylic acids esters, *e.g.* methyl pivalate, exhibits a behaviour different from that of butyllithium alone[1]. For this reason, the initiating system was investigated in greater detail.

The reaction mixture of butyllithium (BuLi) and methyl pivalate (3 + 1 mol) was analyzed, and the content of organolithium compounds in the system was determined by titration with tert-butyl alcohol first[2]. It was found that the reaction of the initial components was completed already after five min, and that the titre of the mixture (corresponding to 34·5% mol.% of BuLi added, *i.e.* 1 mol) remained unchanged for at least 5 h. The IR spectrum of the mixture exhibited an absorption band of medium intensity at 1623 cm^{-1}, *i.e.* in a range in which lithio ketones exhibit a characteristic absorption[3]. The reaction mixture was then hydrolyzed, and the isolated main products, in addition to methanol, were 2,2-dimethyl-3-heptanone and 5-tert-butyl-5-nonanol, whose mutual ratio was 0·25 (*i.e.* 0·2 + 0·8 mol) (calculated from GLC data). A reaction scheme was suggested on the basis of these data:

$$(CH_3)_3CCOCH_3 + C_4H_9Li \rightarrow (CH_3)_3CCOC_4H_9 + CH_3OLi \qquad (A)$$

$$(CH_3)_3CCOC_4H_9 + C_4H_9Li \rightarrow (CH_3)_3COCHLiC_3H_7 + C_4H_{10} \qquad (B)$$

$$(CH_3)_3CCOC_4H_9 + C_4H_9Li \rightarrow (C_4H_9)_2C(OLi)C(CH_3)_3 \qquad (C)$$

The comparatively high content of ketone in the reaction mixture was assigned to steric factors of the reacting compounds, but predominantly to the fact that one part of ketone immediately after formation was obviously metalated with butyllithium in the position alpha (*B*). This reduced the reactivity of the carbonyl group of ketone, so that in the case of this lithio ketone no more butyllithium was added in the sense of reaction *C*.

When estimating the initiating activity of the individual components of the reaction mixture, great attention was concentrated on lithio-2,2-dimethyl-3-heptanone, because with compounds of this type one may expect a considerable initiating activity. Lithio-2,2-dimethyl-3-butanone[3] is readily available and adequately characterized in the isolated state, and it was therefore used in further experiments as the model compound.

Of the four lithium compounds which predominate in the reaction mixture of BuLi with methyl pivalate (*cf.* reactions *A*, *B*, *C*), two may be assumed to be weakly efficient initiators under the given conditions if used alone, viz., lithium methoxide and lithium 5-tert-butyl-5-nonoxide. It is known, however, that lithium alkoxides may interact with organolithium compounds, thus altering their properties[4–6]. Thus, *e.g.*, for butyllithium its interaction with lithium tert-butoxide was easy to demonstrate; on the contrary, lithium methoxide possessed only a low reactivity in this respect[4]. For these reasons, also lithium 5-tert butyl-5-nonoxide was prepared individually, and its interactions with BuLi or lithio-2,2-dimethyl-3-butanone were examined. In both cases, however, mutual interaction could not be demonstrated unambiguously using IR spectra or changes in solubility. On the contrary, the ability of lithio-2,2-dimethyl-3-butanone to interact with other lithium alkoxides was demonstrated using lithium tert-butoxide as an example, where it was reflected in a proncounced change in the IR spectrum[3]. The weak tendency towards interactions should thus be assigned at the expense of lithium 5-tert-butyl-5-nonoxide.

After these introductory and model experiments, the individual compounds were tested as initiators of the polymerization of methyl methacrylate. Up to now, only limiting conversions of the monomer reached after a given time have been evaluated, together with some properties of the polymers obtained, such as molecular mass and microstructure. The results are summarized in Table I; in the first place, they confirm our assumption regarding the high initiation efficiency of lithio ketones. Judging by the polymer yield, at 20° lithio ketones considerably exceed the efficiency of butylithium. This is obviously due to the fact that compared with BuLi, lithio ketones are less basic owing to the possibility of a mesomeric stabilization of the negative charge, which has as consequence a smaller extent of side reactions with MMA at this temperature. At a reduced temperature (−40°) this difference disappears, because the extent of side reactions of BuLi is decreased here. The lower basicity of lithio ketone is reflected in a lower overall rate of polymerization (approximately one half) at this temperature.

Pronounced changes in the polymerization process can be seen with the initiating system containing, in addition to lithio-2,2-dimethyl-3-butanone, also lithium tert-butoxide. Thus, at −40°C the overall rate of polymerization increases considerably (about four times), the molecular mass of the polymer becomes lower, and the distribution width of molecular masses also changes to a considerable extent. Also, at 20°C the limiting conversion of the monomer in the presence of lithium alkoxides increased pronouncedly. These effects are obviously caused by the presence of lithium

TABLE I

Polymerization of Methyl Methacrylate in Toluene

[MMA] 0·63 mol/l; [MMA]/[Initiator][a] 120, Symbol ξ-yield of crude polymer.

Initiating system (molar ratio)	T °C	t h	ξ %	$\overline{M}_w$. 10^{-3}	$\overline{M}_n$. 10^{-3}	$\overline{M}_w/\overline{M}_n$	Microstructure, %		
							I	H	S
C_4H_9Li	—40	1	92·4	323	73·9	4·4	65·2	20·5	14·3
$(CH_3)_3CCOCH_2Li$	—40	1	29·5	380	21·0	18·1	81·8	14·9	3·3
$(CH_3)_3CCOCH_2Li$	—40	2	90·1	521	43·0	12·1	—	—	—
$(CH_3)_3CCOCH_2Li$	—40	4	99·4	445	60·0	7·4	—	—	—
$(CH_3)_3CCOCH_2Li$	—40	8	100	556	46·0	12·1	86·0	10·1	3·9
$(CH_3)_3CCOCH_2Li + (CH_3)_3COLi$ (1 : 1)	—40	1	100	141	38·0	3·7	86·2	9·4	4·4
C_4H_9Li	20	1	12·2	—	—	—	—	—	—
$C_4H_9Li + (CH_3)_3COLi$ (1 : 1·5)	20	1	8·3	—	—	—	—	—	—
$C_4H_9Li + (CH_3)_3CC(OLi)(C_4H_9)_2$ (1 : 1·5)	20	1	15·2	—	—	—	—	—	—
$(CH_3)_3CCOCH_2Li$	20	1	53·5	26·6	10·5	2·5	65·0	26·2	8·8
$(CH_3)_3CCOCH_2Li + (CH_3)_3COLi$ (1 : 1)	20	1	87·9	53·2	20·1	2·6	67·5	21·7	10·8
$(CH_3)_3CCOCH_2Li + (CH_3)_3CC(OLi)(C_4H_9)_2$ (1 : 3)	20	1	69·0	59·6	25·9	2·3	80·2	15·2	4·6

[a] BuLi or lithio ketone.

tert-butoxide which interacts both with the initiator[3] and with the propagation centre[7]. This gives rise to propagation centres possessing different properties, and may also affect the rate constants of initiation and propagation, which results in the formation of polymers with the given parameters. A similar effect on the polymerization of MMA with lithium tert-butoxide has been observed for the polymerization of MMA initiated with lithio esters[8]. Lithium tert-butoxide alone does not initiate the polymerization of MMA under the given conditions. In all these polymerizations the effect of lithium tert-butoxide was more pronounced than that of lithium 5-tert-butyl-5-nonoxide, in agreement with the weak tendency of the other alkoxide towards interactions as observed using the IR spectra.

The content of isotactic triads in all polymers prepared in this study was very high (Table I), which is quite usual for the polymerizations of MMA initiated with organolithium compounds in hydrocarbon solutions.

A more detailed elucidation of the initiating system BuLi + carboxylic acids esters requires more experiments. Even now, however, it may be said that lithio ketones are one of the efficient components of the given system: their efficiency is quite considerable, especially near 20°C. Polymerizations initiated with lithio-2,2-dimethyl-3-butanone in the presence of lithiumt tert-butoxide offered another example of the influence of lithium alkoxides on the initiation and propagation reactions.

EXPERIMENTAL

All operations involving organic lithium compounds were carried out in purified argon. GLC analyses were performed with a Perkin–Elmer 30 apparatus, IR spectra were recorded with a Perkin–Elmer 457 spectrometer. The molecular mass distributions of polymers were determined by GPC in a THF solution, using an apparatus built at the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, and provided with columns packed with Styragel.

Methyl pivalate and methyl methacrylate (MMA) were dried with calcium hydride and rectified. A benzene solution of butyllithium (BuLi) was prepared from butyl chloride and lithium powder. Its standardization was carried out acidimetrically and by titration with a toluene solution of tert-butyl alcohol, using *o*-phenanthroline as indicator, which allows the actual concentration of organometallic compound to be determined[2]. The same procedure was employed in the titration of the mixture after the reaction of BuLi with methyl pivalate. The preparation of lithio-2,2-dimethyl-3-butanone has been described in an earlier paper[3]; the preparation of lithium tert-butoxide has been reported in ref.[4]. The solvents (benzene, toluene) were rectified and distilled in the presence of sodium benzophenoneketyl immediately before use.

Reaction between Butyllithium and Methyl Pivalate

To a solution of BuLi (0·443 mol) in benzene (1·01 mol/l), methyl pivalate (0·148 mol) was added with stirring at 20°C. The mixture was acidified with acetic acid after 1 h, the filtrate was extracted with water, dried and concentrated *in vacuo*. Distillation of the evaporation residue yielded: 1·62 g of 2,2-dimethyl-3-heptanone, b.p. 51·0—55·5°/0·00193 MPa, GLC purity 95·1%, IR spectrum 1710 cm^{-1} (C═O), n_V^{20} 1·4162 (ref.[9] n_D^{20} 1·4163); 20·75 g of 5-tert-butyl-5-nonanol, b.p. 108·5—109·5°C/0·00193 MPa, b.p. ref.[10] 105·5—7°/0·00147 MPa, GLC purity 99·8%, IR spectrum 3630 and 3505 cm^{-1} (O—H), n_D^{20} 1·4484 (ref.[10] n_D^{20} 1·4488). The overall yield of both products was 77·3% (with respect to methyl pivalate).

Preparation of Lithium 5-Tert-butyl-non-5-oxide

a) To 5-tert-butyl-5-nonanol (0·00916 mol) in benzene (9 ml), a solution of butyllithium (0·00942 ml) in benzene (1·03 mol/l) was added dropwise with stirring at 20°C. The microcrystalline precipitate was isolated after one hour, Yield 94% of lithium-5-tert-butyl-5-nonoxide; Li content (acidimetrically): found 3·31%, calculated 3·36%.

b) A mixture of lithium powder (0·00504 mol), 5-tert-butyl-5-nonanol (0·004 mol) and benzene (12 ml) was boiled under reflux with stirring until lithium was almost dissolved (some 15 h), the solution was filtered while hot, and the crystals precipitated on cooling were isolated in a yield of 81%. Li content: found 3·32%, calc. 3·36%. The IR spectra of both products were identical.

Polymerization of Methyl Methacrylate

The reaction mixture of butyllithium and methyl pivalate used in the initiation of polymerization was prepared by adding dropwise 0·0067 mol of ester to a 1·03M benzene solution of BuLi (0·020 mol of BuLi) at 20°C with stirring. After one hour the concentration of the initial BuLi was adjusted to 0·161 mol/l by the addition of toluene, and the solution was immediately used for initiation. The polymerizations were carried out in ampoules closed with a threeway cock under conditions given in Table I. After a chosen time, the polymerization was stopped with methanol, and the polymer was precipitated with light petroluem. For the molecular weight and microstructure determinations, the raw polymer was precipitated twice with petroleum ether from a solution in toluene.

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