

ACTIVE CENTRES IN THE ANIONIC POLYMERIZATION OF METHOXYPOLYETHYLENEGLYCOL METHACRYLATES

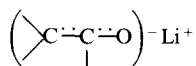
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Abstract—The nature of the propagation sites in the anionic polymerization of methoxypolyethyleneglycol methacrylates in the presence of Li counterion has been studied through i.r. spectra of the model compounds, Li derivatives of isobutyric acid esters, $(\text{CH}_3)_2\text{CLiCOO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ with n from 1 to 4, and of 2,2,4-trimethylglutaric acid esters. The wavelength of the absorption band of lithioisobutyrate, due to the vibration of the



grouping, is independent of the nature of the solvent. This fact has been explained by intramolecular solvation of Li^+ by the polyetheral alcoholic residue. The spectra of the metalated trimethylglutarates give evidence of concurrent solvation of Li^+ by the alkoxy carbonyl group in the γ -position and the alcoholic residue of the ester group bound to the metalated carbon atom. When the number of ethyleneoxide units in the polyetheral chain is increased, the coordination of Li^+ to it prevails over the interaction with the γ -alkoxycarbonyl group.

INTRODUCTION

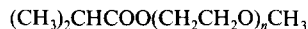
The reactivity of active centres in the anionic polymerization of both polar and non-polar monomers is strongly influenced by the solvent since its properties govern the equilibria between the ionic species. Thus, metal cations are coordinated by polar solvents with electron donor heteroatoms in the molecule resulting in increased reactivity of the respective ion pairs. The same effect can be achieved with additives capable of forming stable complexes with positive ions. The acyclic cation-binding agents widely used in recent years (the podands), although not possessing the selectivity of coronands and cryptands, interact no less effectively with metal ions owing to the cooperative action of the oxygen atoms in the polymer chain. Further, the pseudocycles formed around the cations are conformationally more flexible than the respective macrocycles.

It is of interest to study the reactivity of active centres in the anionic polymerization of polar monomers endowed with acyclic moieties capable of binding metal cations. As is known, the active centres in the anionic polymerization of ethylene oxide are solvated by the generated polyetheral chain [1] so that the propagation rate is not solvent dependent [2]. Intramolecular solvation was also found in the anionic polymerization of 2-vinylpyridine, the cation being coordinated to the nitrogen atom in the pyridine ring [3, 4]. The high isotacticity of poly(methyl methacrylate) obtained in non-polar solvents with Li counterion is explained by the chelation of Li^+ with the terminal and penultimate carbonyl functions [5, 6]. In THF, conclusive evidence for the formation of such a chelated structure is still absent [7].

The purpose of the present study was to examine the influence of the length of polyetheral chains attached to methacrylic acid on the structure of the active centres in the polymerization with lithium counterion of the respective methacrylates. This can be conveniently studied by i.r. spectroscopy since the spectral changes in the region of the carbonyl group vibrations provide evidence of carbonyl oxygen coordination to the metal cation. Lithium derivatives of appropriate esters of 2,2,4-trimethylglutaric acid were used as model compounds for the active centres in the polymerization of methoxypolyethyleneglycol methacrylates. The influence of the polyetheral chain length was previously studied with the aid of lithium $(\text{CH}_3)_2\text{CHCOO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ where $n = 0-4$.

EXPERIMENTAL

Isobutyrate of general formula



with $n = 1-4$ were synthesized from isobutyryl chloride and the monomethyl ethers of the glycols. Similarly, methacrylic esters were prepared from methacryloyl chloride and the monomethyl ethers of ethyleneglycol and diethyleneglycol. All esters were purified by vacuum distillation and dried over CaH_2 .

All operations for the metalation of the esters of isobutyric acid, the preparation of 2,2,4-trimethylglutaric acid esters and their metalation were carried out in vacuum. Hexane and THF were also dried in vacuum. Hexane was dried over Na-K alloy and subsequently by a solution of butyllithium; THF was distilled from "blue" potassium solution.

The metalated esters were prepared following the procedure of Lochmann *et al.* [8] with lithium diisopropyl

amide. The metalation was performed for 2 hr at -40° in hexane and for 30 min at -80° in THF. Since the diisopropyl amine obtained in the process did not affect the absorption bands in the i.r. spectra of the metalated esters, it was not extracted from the reaction mixture.

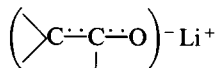
Bis[methoxyethyl] and bis[methoxyethoxyethyl]2,2,4-trimethylglutarate were prepared as follows. Lithium diisopropyl amide (0.1 mol) was prepared under vacuum in 100 ml of hexane. Isobutyrate (0.1 mol) were slowly added to it at -40° and with constant stirring. Within 2 hr the ester was quantitatively metalated and only the band of the Li derivative appeared in the i.r. spectrum. The reaction mixture was cooled to -80° and diluted with an equal volume of THF. 0.09 mol of methoxyethyl- or methoxyethoxyethyl methacrylate in 80 ml of THF were added dropwise to the solution. In 30 min the reaction mixture was inactivated by methanol. Solvents were distilled off and the product was purified by subsequent vacuum distillation on a column.

I.R. spectra of the metalated esters were recorded at various temperatures on the apparatus Specord UR-20.

RESULTS AND DISCUSSION

1. Metalated isobutyric acid esters of general formula $(\text{CH}_3)_2\text{CLiCOO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ with $n = 0-4$

On metalation of the isobutyric acid esters with lithium diisopropyl amide, the initial absorption of the ester group in the i.r. spectrum decreases or eventually disappears while a new band of the same intensity appears at lower frequency (Fig. 1). This new band results from vibrations of the



grouping, its wavelength depending on the length of the polyetheral chain (Table 1).

It is noteworthy that the solvating capacity of the medium influences the frequency of the i.r. absorption band only in the case of methylisobutyrate ($n = 0$). The same effect has been observed by Lochmann *et al.* [9] who reported even larger shifts of the absorption band of lithiomethylisobutyrate induced by changing the solvent (from 1692 cm^{-1} in nujol to 1676 cm^{-1} in THF).

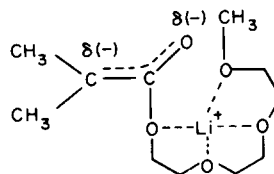
In contrast, however, the wavelength of the absorption bands of lithioisobutyrate with $n > 0$ prove to be independent of the solvent. This can be explained by intramolecular solvation of Li^+ by the polyetheral alcoholic residue. On the basis of quan-

Table 1. I.R. absorption bands of lithioisobutyrate of general formula $(\text{CH}_3)_2\text{CLiCOO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$. The initial esters with $n > 0$ absorb at 1736 cm^{-1}

<i>n</i>	Solvent*	
	Hexane	Hexane:THF = 5:1
0	1680 cm^{-1}	1675 cm^{-1}
1	1674 cm^{-1}	1674 cm^{-1}
2	1673 cm^{-1}	1673 cm^{-1}
3	slightly soluble	1672 cm^{-1}
4	slightly soluble	1672 cm^{-1}

*At 20° in hexane, at -25° in hexane:THF.

tum chemical calculations [10], ^{13}C -NMR measurements [11] and evaluation of the interionic distance in the ion pairs of poly(methyl methacrylate) [12], it is generally agreed that the counterion is located nearer to the oxygen than to the α -carbon atom. This allows the polyetheral chain in the isobutyrate with $n > 0$ to wrap around the cation and to form a "pseudo" cycle resembling the macrocycles of the coronands. The oxygens in the "pseudo" cycle are coordinated to Li^+ thus reducing its interaction with the anion. As a result, the absorption band of the ion pair shifts to lower frequencies in the i.r. Coordination of the alcoholic residue to the counterion is further confirmed by the bathochromic shift of the absorption bands of its etheral groups in the region $1000-1200 \text{ cm}^{-1}$ (Fig. 1).



The complexation constant in the fluorenyllithium coordination with glymes was shown to increase with the number of oxygens up to glyme-4 [13, 14]. Similarly, the absorption band of lithioisobutyrate shifts to lower frequencies in the i.r. spectrum up to the ester with $n = 3$ but remains unchanged when the polyetheral chain is further lengthened. This is indicative of the optimum size of the "pseudo" cycle formed on coordination of the oxygen atoms with the lithium counterion as being characteristic of the ester with four oxygens in the alcoholic residue.

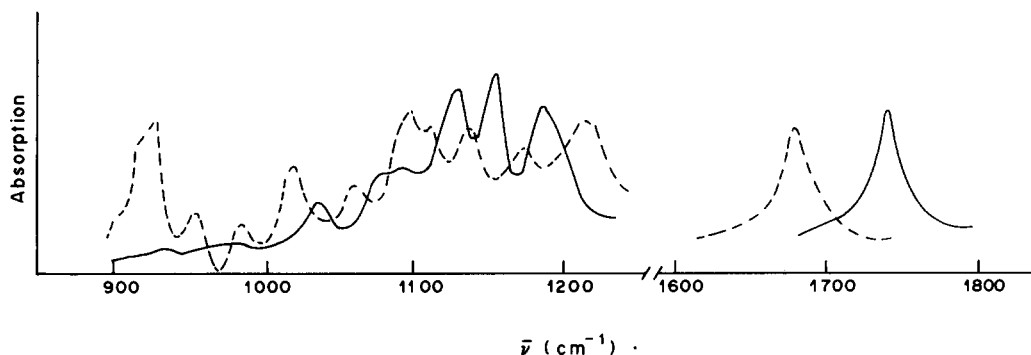


Fig. 1. I.R. spectra of methoxyethyl isobutyrate in hexane at 20° . (—) Methoxyethyl isobutyrate; (---) Li derivative.

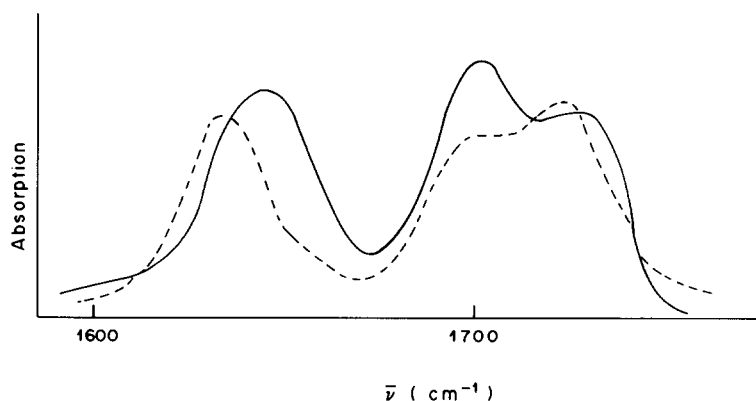
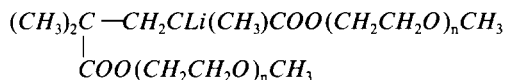


Fig. 2. I.R. spectra of lithio-bis[methoxyethyl]2,2,4-trimethylglutarate. (—) At 20° in hexane; (----) at -30° in THF.

II. Metalated esters of 2,2,4-trimethylglutaric acid of general formula



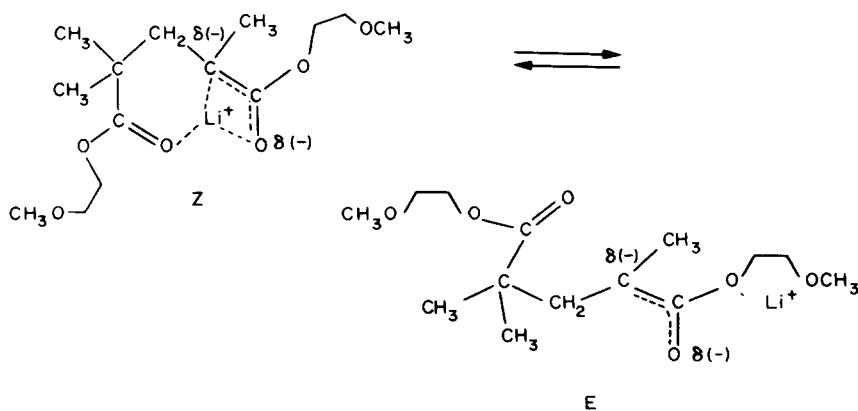
with $n = 1$ or 2

These are model compounds for methoxyethyl and methoxyethoxyethyl methacrylate polymers. The studies of their Li derivatives would contribute to an understanding of the mode of coordination of Li^+ in the polymerizations of the corresponding methacrylates. It has been shown that coordination of Li^+ to the carbonyl groups of the last and the penultimate unit is of substantial importance for isotactic polymethacrylate chain propagation [5, 6, 15] and that the presence of substituents reducing this interaction essentially decreases the polymer stereoregularity [16, 17].

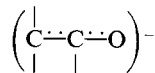
I.R. spectrum of the reaction mixture recorded after the interaction of bis[methoxyethyl]2,2,4-trimethylglutarate with lithium diisopropyl amide is presented in Fig. 2.

As seen from the spectra of lithiotrimethylglutarate with $n = 1$ (Fig. 2), three absorption bands appear in the region of carbonyl group vibrations, their frequencies and relative intensities being solvent dependent (Table 2).

In solutions of bis[methoxyethyl]2,2,4-trimethylglutarate, an equilibrium exist between two forms designated Z and E:

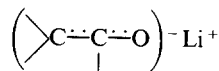


In the Z-form, Li^+ is coordinated to the γ -alkoxy carbonyl group the absorption of which is shifted to lower frequencies 1700–1704 cm^{-1} . Due to the formation of the six-membered coordination ring, the coulombic interaction between the cation and the



grouping strongly diminishes so that the absorption band of the ion pair in hexane undergoes a bathochromic shift of 26 cm^{-1} compared with its absorption in hexane solution of lithiomethoxyethyl isobutyrate. In THF, this band is shifted to still lower frequencies, while the band for the coordinated γ -alkoxy carbonyl group decreases by the increased intensity of the free carbonyl absorption. This indicates that THF molecules are capable of coordinating Li^+ and thus reducing considerably its interaction with the γ -alkoxy carbonyl group.

The i.r. spectrum of lithiotrimethyl glutarate with $n = 2$ (Fig. 3) is very different from the pattern described. Four absorption bands appear in it, assigned as follows. The band at 1640 cm^{-1} arises from the vibrations of the



grouping with Li^+ taking part in the six-membered coordination ring with the γ -alkoxy carbonyl group.

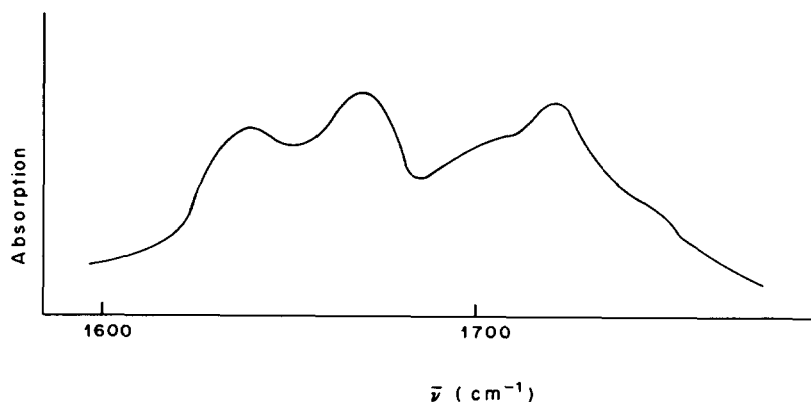


Fig. 3. I.R. spectrum of lithio-bis[methoxyethoxyethyl]2,2,4-trimethylglutarate in THF at -25° .

Table 2. Absorption bands in the i.r. spectra of lithio-bis[methoxyethyl]2,2,4-trimethylglutarate

Solvent	$\bar{\nu}$ (cm^{-1})		
Hexane, 20°	1648	1704	1723
Hexane:THF = 5:1, 25°	1638	1700	1724
THF, -25°	1633	1700	1724

The band at 1673 cm^{-1} is due to the same grouping when the cation is coordinated to the ethereal oxygens in the alcoholic residue of the monomer. It appears at the same wavelength as in the spectrum of the corresponding isobutyrate. The absorption at 1705 cm^{-1} results from the vibrations of the γ -alkoxy carbonyl group coordinated to the cation, while the vibrations of the free carbonyl group give rise to the band at 1724 cm^{-1} .

The differences between the i.r. spectra of metalated trimethylglutarates with $n = 1$ and 2 gives evidence of concurrent solvation of Li^{+} by the alkoxy carbonyl group in the γ -position and the alcoholic residue of the ester group bound to the metalated carbon atom. When the number of ethereal oxygens is insufficient (for $n = 1$), the coordination of the cation to the γ -alkoxy carbonyl group is stronger. When, however, the polyethereal chain contains an additional ethyleneoxide unit ($n = 2$), its coordination with Li^{+} becomes more effective and prevails over the interaction with the γ -alkoxy carbonyl group. As a result, for $n = 2$ an intensive absorption appears in the i.r. spectrum of the glutarate at 1673 cm^{-1} , i.e. at the same frequency as for the ion pair of the corresponding isobutyrate. The reduced interaction of the cation with the γ -carbonyl group is confirmed by the increased absorption frequency in THF of the ion pair in the six-membered ring (1633 cm^{-1} for $n = 1$ but 1640 cm^{-1} for $n = 2$).

The results of this study present further evidence for the idea of autosolvation of the active centres in

the anionic polymerization of polar monomers endowed with groups which are capable of coordinating to the metal counterion. Thus, without affecting the solvating capacity of the medium, by appropriate changes in the monomer substituents similar effects on the reactivity of the respective ion pairs can be achieved as are observed in the presence of cation binding compounds.

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