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Abstract

Full Text

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Study of the Electrical Conductivity of Solutions of Lithium Alkyls in Connection with the Polymerization Process

It is known that, in the polymerization of isoprene in nonpolar solvents under the action of metallic lithium or organolithium compounds, a polymer is formed containing about 95% 1,4-cis units and about 5% 3,4-units ([1–3]). The corresponding compounds of other alkali metals do not give stereoregular polymers. The formation of stereoregular polyisoprene under the action of LiR is associated with the formation of a six-membered cyclic complex of the initiator molecule with the monomer

$$\begin{array}{c} CH_3 \\ CH - C \\ CH_2 \quad CH_2 \\ \cdots \quad \cdots \\ R - Li \end{array}$$

in which the monomer is forcibly oriented in the cis form ([3]). Here the specific features of the structure of the electronic shell of lithium are manifested; in contrast to sodium and potassium, lithium is inclined toward s,p-hybridization.

The introduction into the system of various substances of electron-donor character—for example, simple ethers, dialkyl sulfides, or tertiary amines—has a substantial influence on the microstructure of the polymer formed: with increasing concentration of electron donors the content of 1,4-cis units decreases, and the content of 3,4- and 1,4-trans units (1,2-units for butadiene) increases ([1–5]). The formation of significant amounts of 1,4-trans and 3,4-units is always observed in those cases where an increase in the polarity of the metal–carbon bond may be expected; for example, not only in the case of electron-donor additives, but also when LiR is replaced by NaR or KR. An increase in the polarity of the C—Li bond should lead to an increase in the electrical conductivity of the solutions.

The purpose of our work was to measure the electrical conductivity of solvent—initiator (LiR) and solvent—initiator—electron donor systems.

Purified benzene and hexane were used as solvents. The initiators LiC_2H_5 and

Fig. 1. Apparatus for measuring the electrical conductivity of lithium alkyl solutions. 1 –vessel for mixing, 2 –electrodes, 3 –measuring tube for dosing solvent, 4 –vessel with THF, 5 –measuring tube for dosing THF

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Li-n-C_4H_9 were prepared by the method described in ([6]). Tetrahydrofuran was used as the electron donor. Before use, THF was treated with alkali, distilled, dried, and kept over sodium.

Initially the electrical-conductivity measurements were carried out with direct current. Various measuring cells with platinum cylindrical electrodes were used, with a cell constant from 0.025 to 0.06 cm^{-1}. The resistance was measured with an E-6 teraohmmeter, which made it possible to measure resistances up to 10^{11} ohm with an accuracy of several percent. Subsequently we abandoned this method and used an AC bridge circuit, which excluded the possibility of electrode processes occurring in the conductometric cell. The elements of the bridge

the circuit, in addition to the cell, were: a GZ-33 audio generator, an R315-P resistance box, an R513 capacitance box of the MERP type, and an S1-1 oscilloscope (null instrument). The capacitance box, connected in parallel with the resistance box, served to compensate the capacitance of the measuring cell. Measurements were carried out at a frequency of 100 Hz. The relative accuracy of the measurements at resistances on the order of 10^7 ohms was 0.2%.

Calibration of conductometric cells with small values of the cell constant cannot be carried out by the usual method–by determining the resistance of a cell filled with a KCl solution of known concentration–because of the considerable capacitance of the double layer. To determine the constant, we measured the resistance of the working and auxiliary cells filled with absolute ethyl alcohol; after this the auxiliary cell was calibrated by the usual method (using a KCl solution), its constant being two orders of magnitude greater than the constant of the working cell (k). Thus, k was found from the formula: $k = k'R/R'$, where k' is the constant of the auxiliary cell; R and R' are, respectively, the resistances of the working and auxiliary cells filled with ethyl alcohol.

Fig. 1. Apparatus for measuring the electrical conductivity of lithium alkyl solutions.
1 –vessel for mixing, 2 –electrodes, 3 –measuring tube for dosing solvent, 4 –vessel with THF, 5 –measuring tube for dosing THF

For thorough drying and degassing of the glass apparatus, a TsVL-100 diffusion pump was used, providing a vacuum on the order of 10^{-6} mm Hg. The construction of the cell made it possible to carry out all operations with the initiator solutions–dosing, dilution, concentration–without access of air. These

Figure 2

Figure 2: Figure 2

operations were carried out either in vacuum or in an atmosphere of pure argon dried over triisobutylaluminum.

The ampoule with lithium alkyl and the break-seal were placed in vessel 1 (Fig. 1), previously etched and filled with dry argon. Diluted lithium alkyl solution in benzene or hexane was poured into measuring tube 3. Then vessel 1 was evacuated for a long time with the aid of the diffusion pump. After this, the required amount of solvent was recondensed from measuring tube 3, and the ampoule with lithium alkyl was broken. The resulting solution was concentrated or diluted likewise by recondensation. Dosing of THF from vessel 4 was carried out analogously with the aid of measuring tube 5.

Figure 2 presents the concentration dependence of the specific electrical conductivity ($\varkappa$) of solutions of LiC_2H_5 in benzene (curve 1) and Li-n-C_4H_9 in hexane (curve 2) at 20°. The saturation of the concentration curve for ethyllithium is caused, apparently, not only by a decrease in the degree of dissociation, but also by an increase in the degree of association. The literature contains numerous indications of the strong tendency of organolithium compounds toward association with the formation of associates of various degrees of complexity (7, 8). As follows from Fig. 2, in the case of lithium butyl an unusual concentration dependence is observed (there are inflection points on the curve), possibly connected with the formation of associates with different electrical conductivities.

Figure 3 presents the temperature dependence of the specific and molar electrical conductivity of lithium butyl solutions of different concentrations.

in hexane. With increasing concentration, the slope of the straight lines χ—t increases, whereas the slope of the straight-line temperature dependence of the molar conductivity λ ($\lambda = 1000\,\chi/C$, where C is the concentration in mol/l) can, to an accuracy of 10-15%, be regarded as independent of concentration for the indicated ranges of temperatures and concentrations. Under these conditions the mean temperature coefficient of the molar conductivity is equal to $(1.8 \pm 0.3) \cdot 10^{-8}\ \Omega^{-1} \cdot \mathrm{cm}^2 \cdot \mathrm{mol}^{-1} \cdot \mathrm{deg}^{-1}$. Because of complicating factors associated with association of lithium alkyl molecules, it is not possible, on the basis of the data obtained, to calculate the ionization constant of the monomeric form LiR.

Fig. 2. Concentration dependence of the specific electrical conductivity of lithium alkyl solutions.
1—LiC_2H_5 in benzene, 25°; 2—Li-n-C_4H_9 in hexane, 25° (a, b—points obtained respectively during concentration and dilution); 3—Li-n-C_4H_9 in hexane, 40°.

The greatest interest is presented by a study of the influence of electron-donor additives on the electrical conductivity. It was shown that the introduction

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

of tetrahydrofuran into a solution of lithium ethyl in hexane leads to a sharp increase in electrical conductivity (Fig. 4). At the molar ratio $THF/LiC_2H_5 = 5$, the electrical conductivity increased 20-fold in comparison with the electrical conductivity of solutions not containing tetrahydrofuran. At the ratio $THF/LiC_2H_5 = 55$, the electrical conductivity increased by approximately 1000 times.

Fig. 3. Temperature dependence of the specific (a) and molar (b) electrical conductivity of solutions of Li-n-C_4H_9 in hexane for various concentrations (mol/l): 1—0.076, 2—0.115, 3—0.151, 4—0.214, 5—0.278.

Fig. 4. Effect of an electron donor (THF) on the electrical conductivity of a LiC_2H_5 solution at 25°. [EtLi] = 0.15.

Thus, direct measurement of the electrical conductivity of alkyllithium solutions shows that the formation of a coordination bond between

with lithium and the electron-donor compound leads to an increase in the degree of dissociation of the ion pair:

$$R^- - \left[\mathrm{Li}\,(:\,\mathrm{O}\ \ )_n\right]^+$$

The results obtained on the influence of electron-donor additives on the electrical conductivity of the system clearly illustrate the transition from a coordination-anionic polymerization mechanism to a "free-ionic" mechanism, with the consequent change in the microstructure of the polymers—a transition from 1,4-cis to 3,4(1,2)- and 1,4-cis-trans units.

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CITED LITERATURE

1. A. V. Tobolsky, C. E. Rogers, *J. Polymer Sci.*, **40**, 73 (1959).

2. H. Hsieh, A. V. Tobolsky, *J. Polymer Sci.*, **25**, 245 (1957).

3. R. S. Stearns, L. E. Forman, *J. Polymer Sci.*, **41**, 381 (1959).

4. V. A. Kropachev, B. A. Dolgoplosk, N. I. Nikolaev, DAN, **115**, 516 (1957).

5. K. B. Piotrovskii, Abstracts of the IX Conference on General Problems of the Chemistry and Physics of High-Molecular Compounds, January, 1957.

6. T. V. Talalaeva, K. A. Kocheshkov, ZhOKh, **23**, 392 (1953).

7. K. B. Piotrovskii, M. P. Ronina, DAN, **115**, 737 (1957).

8. T. L. Brown, D. W. Dickerhoof, D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).

Note: Figure translations are in progress. See original paper for figures.