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POLYMERIZATION OF BUTADIENE BY POLYBUTADIENYLLITHIUM IN THE PRESENCE OF TETRAHYDROFURAN

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Abstract—Polymerization of butadiene by polybutadienyllithium (PBLi) has been studied in THF for concentrations of PBLi between 10^{-4} and 10^{-2} mol/l in the range 20– −70°, and also in a non-polar medium using THF as an added electron donor at various THF/PBLi ratios. The kinetic order with respect to PBLi in THF was 0.5 and the activation energies of the overall process and the propagation on free carbanions were 7.5 and 6.7 kcal/mol respectively. Rate constants for propagation on the free carbanions were calculated at three temperatures and rate constants for propagation on contact ion pairs were determined at two THF/PBLi ratios. Data on the kinetics of polymerization and the microstructure of the polymers suggest that contact ion pairs and free carbanions participate in propagation reactions.

INTRODUCTION

There are many publications on the polymerizations of dienes by organolithium compounds in THF-solution [1–8]. Nevertheless the nature of the active centres (AC), in the sense of the participation of ion pairs and free ions, remains controversial. Some authors [2, 3] suggest that ion pairs are the main type of AC in the polymerization of butadiene and isoprene in THF and disregard the participation of free carbanions in the propagation reaction. Bywater *et al.* [7, 8] investigated the polymerization of isoprene in THF by *n*-BuLi, established the participation of both ion pairs and carbanions in the propagation and estimated their contributions to the overall propagation constant. They applied the same concept to results for butadiene polymerization in THF-solution by living chains [5, 6]. It must be also noted that the available data concerning the polymerization of butadiene in THF are largely fragmentary and are not sufficient for a profound understanding of the process. It should be emphasized that so far no systematic investigation of the polymerization of butadiene in non-polar media containing small amounts of THF has been described although some data have been presented [9].

The present work deals with the polymerization of butadiene by polybutadienyllithium (PBLi) in THF and in non-polar medium with THF as added electron donor.

EXPERIMENTAL

THF was purified by successive boiling over KOH and metallic K followed by drying three times in all-sealed system with a liquid K-Na alloy up to the formation of "blue" solutions. After purification with H_2SO_4 and oleum and distillation, hexane and isooctane were dried twice in all-sealed system with concentrated *n*-BuLi. PBLi was obtained in isooctane from sec-BuLi and butadiene in a ratio of 1:8. The polymerization was studied dilatometrically in sealed systems under high vacuum (1.10^{-6} mm Hg) with vigorous stirring and thermostatting using a special cryogenic apparatus. The concentrations of monomer and PBLi were 1.3–1.5 and 10^{-2}–10^{-4} mol/l respectively. The polymerizations were carried out in dilatometric ampoules consisting of two chambers, one used for the preparation of the PBLi complex with THF and the other was used for collecting the monomer and the solvent. When initiator concentrations below 10^{-3} mol/l were used, its solution was prepared by introducing into the dilatometer an exact amount of previously prepared solution of high concentration (5.10^{-3} mol/l) followed by dilution by distilling in solvent. The component mixing was entirely carried out at −78° to avoid decomposition or isomerization of the initiator.

Very good agreement between experimental and theoretical values of molecular weight of the polymers suggests complete consumption of the initial PBLi in the propagation reaction.

RESULTS AND DISCUSSION

The use of PBLi excluded the initiation step and ensured the study of the propagation reaction only. The reaction orders in PBLi at 20, 0 and −30° were 0.42 ± 0.08, 0.39 ± 0.01 and 0.43 ± 0.08, respectively. These values are not in agreement with the data of Morton [2] who found first order with respect to both *n*-BuLi and monomer. The reaction orders in PBLi found by us under these conditions were close to 0.5 suggesting that the overall propagation constant ($k_p = v/m_0n_0$, were v is the propagation rate and m_0 and n_0 are the concentrations of the monomer and PBLi, respectively) can be described by Eqn (1) [10] provided the reaction order in monomer is 1:

$$k_p = k_{\pm} + k_{-} K_d^{0.5} n_0^{-0.5} \tag{1}$$

Here $k_{\pm}$ and k_{-} are the propagation constants corresponding to the ion pairs and carbanions respectively and K_d is the constant for the electrolytic dissociation of PBLi in THF.

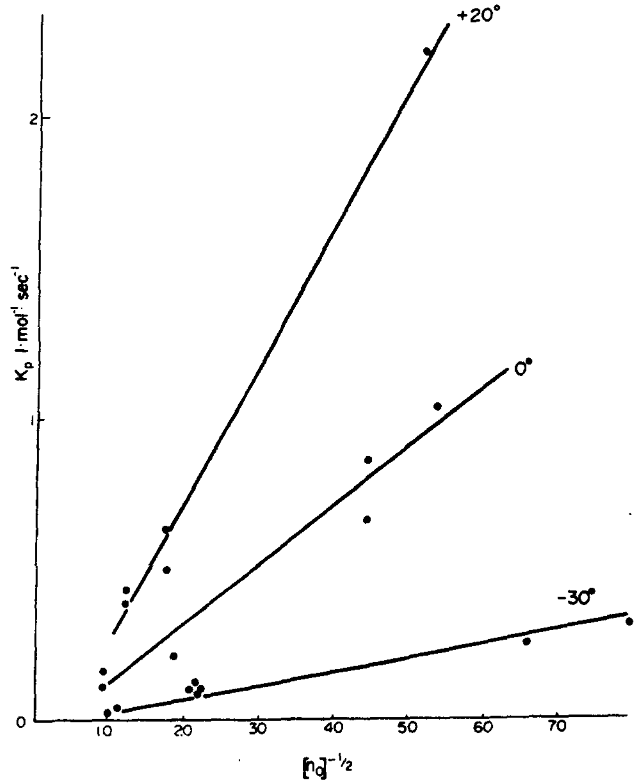

Fig. 1. Overall propagation rate constant k_p vs concentration of PBLi. $m_0 \simeq 1.5$ mol/l, THF used as solvent.

This conclusion is supported by the increase of k_p with decrease in [AC], this dependence being proportional to $n_0^{-0.5}$ (Fig. 1). The values of $k/K_d^{0.5}$ for 20, 0 and $-30°$ were calculated according to Fig. 1. Using the K_d values found before for PBLi in THF (l/mol.10^{-10}), viz. 5.13 (20°), 5.44 (0°) and 5.78 ($-30°$) [11], we estimated the k_- values as 2040 ± 100, 860 ± 100 and 210 ± 100 l/mol·sec, respectively. Extrapolation to 30°, by using the temperature dependence, leads to $2.7 \cdot 10^3$ l/mol·sec which is close to that established by Bywater $2.8 \cdot 10^3$ l/mol·sec [8] for polymerization of isoprene.

The energy of activation (E) of the overall propagation reaction could be estimated from the temperature dependence of k_p. For an experimental series with n_0 equal to 10^{-2} and to 10^{-4} mol/l, the E values were 7.0 ± 0.5 and 7.6 ± 0.3 kcal/mol respectively. The energy of activation (E') for carbanions was obtained similarly. This value (6.7 kcal/mol) virtually coincided with that estimated by Sigwalt [12] for the system butadiene-cumyl sodium-THF (6.5 kcal/mol), although his k_- value at 0° ($4.8 \cdot 10^4$ l/mol·sec) differs greatly from that found here*.

The enthalpy and entropy of dissociation of PBLi in THF were estimated as -0.4 ± 0.1 kcal/mol and -1.38 e.u. [11]. These low values suggest that the temperature dependence of K_d did not distort our data on E and E'.

It can be seen that the latter values are quite close. This may be due to the dominant participation of free ions in the overall process characterized by the E-value. Hence, the E-value obtained in the present work is slightly lower than that known for ion pairs, i.e. 9–10 kcal/mol [6, 13, 14].

Table 1. Influence of polymerization conditions on the microstructure of polymers obtained in the system butadiene–PBLi–THF. $m_0 \simeq 1.5$ mol/l

20°C		0°C		−16°C		−30°C		−78°C	
n_0 (mol/l)	$\frac{1,2}{1,4\text{-}trans}$	n_0 (mol/l)	$\frac{1,2}{1,4\text{-}trans}$	n_0 (mol/l)	$\frac{1,2}{1,4\text{-}trans}$	n_0 (mol/l)	$\frac{1,2}{1,4\text{-}trans}$	n_0 (mol/l)	$\frac{1,2}{1,4\text{-}trans}$
$0.64 \cdot 10^{-2}$	14.95	$1.11 \cdot 10^{-2}$	16.25	—	—	$0.79 \cdot 10^{-2}$	12.70	—	—
$0.63 \cdot 10^{-2}$	15.20	$1.14 \cdot 10^{-2}$	16.44	—	—	$0.92 \cdot 10^{-2}$	12.59	—	—
$3.10 \cdot 10^{-3}$	13.25	$2.71 \cdot 10^{-3}$	14.95	—	—	$2.03 \cdot 10^{-3}$	11.89	—	—
$3.18 \cdot 10^{-3}$	13.36	—	—	—	—	$1.98 \cdot 10^{-3}$	11.39	—	—
$3.53 \cdot 10^{-4}$	9.03	$3.44 \cdot 10^{-4}$	10.50	$4.20 \cdot 10^{-4}$	11.40	$2.29 \cdot 10^{-4}$	10.00	$4.86 \cdot 10^{-4}$	16.10
$3.53 \cdot 10^{-4}$	9.56	—	—	$4.07 \cdot 10^{-4}$	11.40	$1.50 \cdot 10^{-4}$	11.03	$3.42 \cdot 10^{-4}$	16.40

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* The cause of this discrepancy cannot yet be explained.

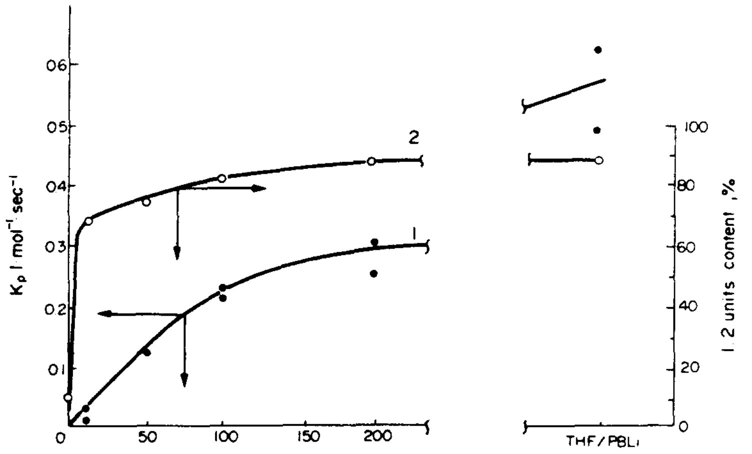

Fig. 2. Overall propagation rate constant k_p (1) and microstructure of PB (2) vs THF/PBLi ratio. Temperature 20°, $m_0 \simeq 1.5$ and $n_0 \simeq 3.10^{-3}$ mol/l, hexane used as solvent. The last point on the abscissa corresponds to pure THF.

The dependence of the overall k_p on the THF/PBLi ratio for the polymerization of butadiene in hexane is shown in Fig. 2. In contrast to systems with dimethoxy ethane [15] and 2,3-dimethoxy butane [16] as electron donor addends, the increase in k_p with the THF/PBLi ratio is not characterized by a curve with a maximum. This dependence differs also from that established for a system with *N,N,N',N'*-tetramethyl ethylene diamine (TMEDA) [13,14]; for this case, k_p becomes practically constant after the TMEDA/RLi ratio attains a value of 8.

At lower values of THF/PBLi, the dependence in Fig. 2 shows a proportionality between k_p and the THF-concentration attributable to the splitting of the $(PBLi)_4$ tetramers in the complexes PBLi·THF; the increase in k_p in this range is induced by the increase in the number of the AC. Further increase in the THF concentration causes a change in the polarity of the medium leading to the appearance of more active species i.e. carbanions. The K_d values for the THF–hexane mixtures corresponding to the THF/PBLi ratios of the former experiments were estimated from the linear dependence log K_d vs $1/\epsilon$ (where ϵ is the dielectric constant). Using known values (K_d, k_p and k_-) and Eqn (1), the $k_\pm$ values related to THF/PBLi ratios of 100 and 200 were found to be 0.17 and 0.15 l/mol·sec, respectively.

Data on the microstructure of butadiene polymers obtained in THF are given in Table 1. They show a sensitivity of the polymer structure to the concentration of PBLi and also to the polymerization temperature. This fact is in agreement with the conclusion about the simultaneous participation of various types of AC in the process, the relative role of each of the types of AC depending on the conditions.

More complete characteristics were obtained for the structure of the polymers formed in non-polar medium in the presence of various amounts of THF (Fig. 2). A considerable influence of THF is observed up to the THF/PBLi ratio of *ca.* 10. Further increase in this ratio induced relatively small changes in the PB-microstructure.

REFERENCES

1. Yu. A. Spirin and D. K. Polyakov, *Dokl. Akad. Nauk* **139**, 899 (1966).
2. M. Morton, E. Bostick, R. Livigni and L. Fetters, *J. Polym. Sci., A-1* 1735 (1963).
3. A. A. Arest-Yakubovich and S. S. Medvedev, *Vysokomolek. Soedin.* **8**, 681 (1966).
4. D. K. Polyakov, R. V. Basova, N. I. Baranov, A. R. Gantmakher and S. S. Medvedev, *Dokl. Akad. Nauk* **3**, 177 (1967).
5. A. Garton and S. Bywater, *Macromolecules* **8**, 694 (1975).
6. A. Garton and S. Bywater, *Macromolecules* **8**, 697 (1975).
7. D. J. Worsfold and S. Bywater, *Can. J. Chem.* **42**, 2884 (1964).
8. S. Bywater and D. J. Worsfold, *Can. J. Chem.* **45**, 16 (1967).
9. B. Erussalimsky, *Advances in Ionic Polymerization*, p. 13. Warszawa, (1975).
10. M. Szwarc, *Anionic Polymerization*, p. 407. Mir, Moskwa (1971).
11. L. Vinogradova, V. Sgonnik, N. Nikolaev and Kh. Tsvetanov, *Eur. Polym. J.* **15**, 545 (1979).
12. A. Siove and P. Sigwalt, *Polymer* **16**, 605 (1975).
13. A. A. Davidyan, N. I. Nikolaev, V. N. Sgonnik and K. K. Kalninsh, *Vysokomolek. Soedin.* **B17**, 586 (1975).
14. L. V. Vinogradova, N. I. Nikolaev and V. N. Sgonnik, *Vysokomolek. Soedin.* **A18**, 1756 (1975).
15. A. A. Davidyan, N. I. Nikolaev, V. N. Sgonnik and V. I. Petrova, *Vysokomolek. Soedin.* **A18**, 2004 (1976).
16. L. V. Vinogradova, K. K. Kalninsh, N. I. Nikolaev, G. V. Lyubimova and V. N. Sgonnik, *Izv. Akad. Nauk SSSR, Ser. khim.* 2724 (1977).