CHEMISTRY

Yu. L. SPIRIN, D. K. POLYAKOV, A. R. GANTMAKHER

1961

SovietRxiv

Abstract

Full Text

CHEMISTRY

Yu. L. SPIRIN, D. K. POLYAKOV, A. R. GANTMAKHER
and Academician S. S. MEDVEDEV

POLYMERIZATION OF STYRENE, BUTADIENE, AND ISOPRENE INITIATED BY LITHIUM ETHYL IN VARIOUS MEDIA

The present work investigated the separate and joint polymerization of styrene, butadiene, and isoprene initiated by lithium ethyl in toluene, triethylamine, diethyl ether, dioxane, and tetrahydrofuran (THF), with the aim of elucidating the dependence of the reactivity of these monomers on their structure and on the polymerization conditions. The experimental procedure was described in previous works ([1,2]).

In the polymerization of styrene, butadiene, and isoprene, the molecular weight of the polymers increased with the depth of polymerization in all the solvents studied; at the same time the dependence of the molecular weight on the concentration of the components was close to the molar ratio

$$= M/C \quad ({}^{3,4}).$$

When the investigations were carried out in the region of low initiator concentrations, $\sim 10^{-5}$ mol/l, the walls of the dilatometer were subjected to special treatment. Under these conditions, the concentration of active centers was determined from molecular-weight data. In the presence of electron-donor solvents, polymerization was carried out in all-quartz cuvette-dilatometers, and the concentration of active centers was determined spectrophotometrically at a selected wavelength.

1. **Polymerization in toluene.** In carrying out the polymerization of styrene, isoprene, and butadiene in toluene, even at comparatively low initiator concentrations, a deviation from the proportional dependence between the rate and the initiator concentration was observed. The regularities obtained were previously explained ([1]) by the formation, in hydrocarbon media, of mutually associated "living" polymers inactive in polymerization. Other authors, in studying the kinetics of polymerization of styrene ([4,5]) and isoprene ([6]), also arrived at an analogous conclusion. The presence of association of active centers was also confirmed viscosimetrically. It was found that the viscosity of solutions of "living" Li-polyisoprene in toluene decreases considerably upon deactivation of the active centers.

With increasing temperature, the equilibrium between the associates and monomeric centers active in polymerization shifts toward the latter, which causes a decrease in the activation energy of the process. Even at initiator concentrations $\sim 0.5 \cdot 10^{-4}$ mol/l, the activation energy of the styrene polymerization process decreases with increasing temperature (Table 1; Nos. 1, 2), which indicates the presence of association under these conditions. The previously obtained values of the activation energy of styrene polymerization at initiator concentrations ~ 0.01 mol/l ([1]) correspond to systems with a considerable fraction of associated active centers.

As can be seen from the data of Table 1, the change in the polymerization rate with decreasing initiator concentration is most pronounced in the polymerization of styrene (experiments Nos. 1, 3) and least pronounced in the polymerization of butadiene (Nos. 13 and 14). This indicates that the association of active centers increases in the sequence: lithiumpolystyrene $<$ lithiumpolyisoprene $<$ lithiumpolybutadiene.

Table 1

No.	Medium	Additive	Additive, vol. %	[LiR], mol/l	Temperature interval during polymerization, °C	V^1, mol/(l·sec) at +30°	E^2, kcal/mol	lg A, mol/l·sec	K, l/(mol·sec) at −40°
					Polymerization of styrene				
1	Toluene	–	–	$0.5 \cdot 10^{-4}$	+33, +47.5	$0.40 \cdot 10^{-4}$	14.0	–	
2	Toluene	–	–	$0.5 \cdot 10^{-4}$	+60, +72	$0.57 \cdot 10^{-4}$	11.6	–	
3[3]	Toluene	–	–	$3 \cdot 10^{-3}$	+7, +22	$0.7 \cdot 10^{-3}$	14.6	–	
4[3]	Toluene	–	–	$4 \cdot 10^{-2}$	–	$0.4 \cdot 10^{-2}$		–	
5	Toluene	Ether	38	$0.7 \cdot 10^{-2}$	−15, +5	–	13.3		$2.5 \cdot 10^{-4}$
6	Toluene	Ether	30	$1.15 \cdot 10^{-2}$	−2, +15	–	13.4	9.0	$2.5 \cdot 10^{-4}$

No.	Medium	Additive	Additive, vol. %	[LiR], mol/l	Temperature interval during polymerization, °C	V^1, mol/(l·sec) at +30°	E^2, kcal/mol	lg A, mol/l·sec	K, l/(mol·sec) at −40°
	Toluene	Ether	30	$0.3 \cdot 10^{-2}$	−2, +15	–	13.1	8.7	$2.5 \cdot 10^{-4}$
7	Toluene	Dioxane	27	$0.8 \cdot 10^{-2}$	−17, −4	–	13.0	8.8	$3.7 \cdot 10^{-4}$
8	Toluene	Amine	30	$10^{-4} \div 3 \cdot 10^{-2}$	−40, 0	–	11.2	8.65	$1.26 \cdot 10^{-2}$
9	Toluene	THF	0.6	$5 \cdot 10^{-3}$	−25, −10	–	6.8	4.46	$1.15 \cdot 10^{-2}$
10	Toluene	THF	2.3	$4 \cdot 10^{-3}$	−55, −30	–	5.8	3.95	$3.1 \cdot 10^{-2}$
11	Toluene	THF	8	$5 \cdot 10^{-3}$	−60, −40	–	4.5	3.6	$24 \cdot 10^{-2}$
12	Toluene	THF	15	$5.4 \cdot 10^{-3}$	−70, −55	–	4.1	3.5	$44 \cdot 10^{-2}$
					Polymerization of butadiene				
13[3]	Toluene	–	–	0.005–0.02	+20, +45	$1.2 \cdot 10^{-4}$	20.5	–	–
14	Toluene	–	–	10^{-5}	−35, +55	$0.4 \cdot 10^{-4}$	16.9	–	–
15	Hexane	Amine	35	0.004	−3, +20	$4.8 \cdot 10^{-4}$	13.9	–	–
16	Hexane	Amine	35	0.011	−3, +20	$5.7 \cdot 10^{-4}$	14.4	–	–
17	Hexane	Amine	80	~ 0.0001	+15, +35	–	12.1	–	–
18	Hexane	THF	28	0.003	−38, −20	$0.19 \cdot 10^{-4}*$	10.7	–	–

No.	Medium	Additive	Additive, vol. %	[LiR], mol/l	Temperature interval during polymerization, °C	V^1, mol/(l·sec) at +30°	E^2, kcal/mol	lg A, mol/l·sec	K, l/(mol·sec) at −40°
19	Hexane	THF	80	0.0045	−60, −25	$0.25 \cdot 10^{-3}$*	7.3	–	–
	Hexane	THF	80	0.001	−40, −25	$0.7 \cdot 10^{-4}$*	6.3	–	–
					Polymerization of isoprene				
20	Toluene	–	–	$2.3 \cdot 10^{-5}$	+27, +40	$0.54 \cdot 10^{-4}$	14.7	–	–
21	Toluene	–	–	$6.0 \cdot 10^{-5}$	+27, +47	$1.0 \cdot 10^{-4}$	15.3		
22	Toluene	–	–	$1.2 \cdot 10^{-4}$	+27, +40	$1.2 \cdot 10^{-4}$	16.8		
23	Toluene	–	–	$5.0 \cdot 10^{-4}$	+27, +40	$1.6 \cdot 10^{-4}$	17.9		
24[3]	Toluene	–	–	$1.3 \cdot 10^{-3}$	+27, +44	$1.9 \cdot 10^{-4}$	18.8		
25[3]	Toluene	–	–	> 0.005	–	$2.1 \cdot 10^{-4}$	19.5		
26	Amine	–	–	0.0038	+11, +30	$5.5 \cdot 10^{-4}$	10.9		
27	Amine	–	–	0.0043	+10, +40	$6.2 \cdot 10^{-4}$	10.6		
28	Amine	–	–	0.015	+11, +30	$16 \cdot 10^{-4}$	10.9		
29	Amine	–	–	0.016	+10, +40	$16.5 \cdot 10^{-4}$	–		
30[4]	THF	–	–	–	−60, −45	–	5.5		
31[4]	THF	–	–	–	−45, −20	–	7.0		
32[4]	THF	–	–	–	−21, −10	–	8.7		

No.	Medium	Additive	Additive, vol. %	[LiR], mol/l	Temperature interval during polymerization, °C	V[1], mol/(l·sec) at +30°	E[2], kcal/mol	lg A, mol/l·sec	K, l/(mol·sec) at −40°
33[4]	THF	–	–	–	−10, +14	–	9.8		
34[4]	THF	–	–	–	+14, +27	–	13.0		

[1] Rates, referred to unit monomer concentration (V), and polymerization rate constants (K) were calculated from the rate values obtained in the temperature interval indicated in the table.

[2] The energy-activation values given are mean values based on activation-energy data determined during the process by changing the polymerization temperature at different degrees of conversion. The polymerization rates in all cases were proportional to the monomer concentration, except for the polymerization of isoprene in THF, where small deviations from proportional dependence were observed.

[3] Experiments with polymerization initiated by "living" Li-polystyrene gave higher activation-energy values (an increase in E did not exceed 1 kcal) and rates.

[4] The values of E in experiments Nos. 30–34 were obtained by successive change of temperature during one and the same process.

* At −40°.

On the basis of data on the compositions of copolymers and copolymerization constants for the butadiene–styrene system in toluene (see Table 2), and of previously obtained data for the isoprene–styrene system (1), the relative reactivity of the monomers increases in the sequence styrene < isoprene < butadiene.

2. Polymerization in the presence of electron-donor solvents. When introduced into a hydrocarbon medium···

With the introduction of ether, dioxane, triethylamine, or THF additions, the polymerization rate of styrene, isoprene, and butadiene increases and, correspondingly, the activation energies of the processes decrease (Table 1).

The sharpest effect is observed in the presence of THF, which has the strongest electron-donor properties. In the presence of a very small addition of THF, 0.6%,

Fig. 1. Dependence of the polymerization rate on initiator concentration. In amine: 1—styrene at −34°; 2—isoprene at +30°; 3—butadiene at +30°; and in THF: 4—butadiene at −39°

Figure 1: Fig. 1. Dependence of the polymerization rate on initiator concentration. In amine: 1—styrene at −34°; 2—isoprene at +30°; 3—butadiene at +30°; and in THF: 4—butadiene at −39°

the activation energy of styrene polymerization in toluene decreases from 14.5 to 6.8 kcal/mole. The activation energy of butadiene, upon going from toluene to a mixture of toluene with 30% THF, also decreases sharply (Table 1, Nos. 13, 18). In the polymerization of isoprene in THF, the activation energy determined from the course of the process increases with increasing temperature (Table 1, Nos. 30—34), which is apparently explained by the presence of pronounced chain transfer through the monomer (⁀6).

Fig. 1. Dependence of the polymerization rate on the initiator concentration. In amine: **1**—styrene at −34°; **2**—isoprene at +30°; **3**—butadiene at +30°; and in THF: **4**—butadiene at −39°.

In the presence of electron-donor solvents, as a result of the formation of their complexes with lithium, the association of "living" polymers decreases sharply. As follows from Table 1 and Fig. 1, association of lithiopolystyrene in the medium of electron-donor solvents is absent (a proportional dependence is observed between the polymerization rate and the initiator concentration), lithiopolyisoprene is associated to a slight extent in amine, and the association of lithio-polybutadiene in amine is present to a considerable extent. Even in THF, a solvent with high solvating ability, some association of lithio-polybutadiene is observed. These data confirm the dependence, obtained in hydrocarbon media, of the degree of association of active centers on their structure.

In previous studies, the features of the mechanism of polymerization of nonpolar monomers initiated by lithium ethyl in hydrocarbon media were explained by participation of the lithium component, along with the carbanionic component, in the acts of chain growth (^{7},1).

The introduction of electron-donor additions that form complexes with the lithium component of the catalyst leads to a decrease in the influence of this component on the acts of chain growth. In accordance with this, the mechanism of the process changes, approaching, in the presence of additions with high solvating ability (THF), the processes of typical anionic polymerization. With increasing THF concentration, an increase in the polymerization rate of styrene and butadiene and a corresponding decrease in the activation energy of the process are observed. It may be supposed that the decrease in activation energy with increasing THF concentration occurs both as a result of destruction of the associates formed by the active centers and as a result of changes in the structure of the complexes of THF with the active centers and an increase in the dielectric constant of the medium. However, the influence of the dielectric constant of the medium is hardly of decisive importance, since very small additions of THF cause a sharp decrease in the activation energy in styrene polymerization.

It is interesting to note that the polymerization of styrene in ether and dioxane, despite the different dielectric constants of these solvents (4.33 and 2.28 at 20°), proceeds with similar rates and activation energies.

The compositions of copolymers of the systems styrene—isoprene and styrene—butadiene in the presence of electron-donor solvents were studied. For the solvents amine and THF, the copolymerization constants were calculated from data on the composition of the copolymers (Table 2).

In the copolymerization of the systems isoprene—styrene, butadiene—styrene, upon introduction of electron-donor solvents, the relative fraction

Table 2

Copolymerization

Experiment No.	System	Medium	Temp., °C	Copolymerization constants r_1	Copolymerization constants r_2	Amount of styrene (mol.%) in the copolymer at a ratio of 1:1 in the initial mixture
1	Styrene (1)—butadiene (2)	Toluene	25	0.1	12.5	9.0
2	Styrene (1)—butadiene (2)	Amine 40%	25	0.3	5.5	20
3	Styrene (1)—butadiene (2)	Ether 40%	25	—	—	33
4	Styrene (1)—butadiene (2)	THF	−35	8 ± 1	0.2 ± 0.1	85

Experiment No.	System	Medium	Temp., °C	Copolymerization constants r_1	Copolymerization constants r_2	Amount of styrene (mol.%) in the copolymer at a ratio of 1 1 in the initial mixture
5	Styrene (1)–isoprene (2)	Toluene	27	0.25	9.5	12
6	Styrene (1)–isoprene (2)	Amine	27	0.8	1.0	48
7	Styrene (1)–isoprene (2)	THF	27	9	0.1	82
8	Styrene (1)–isoprene (2)	»	–35	40	0	97

the styrene content in the copolymer increases. From the data obtained it is evident that the effect of solvents on separate and joint polymerization is not always similar (see, for example, the polymerization of styrene in the presence of amine and ether). In the presence of THF, the compositions of the copolymers are strongly enriched in styrene and correspond to the compositions obtained in typically anionic processes[8].

According to the data in Table 2, the relative reactivity of the monomers in THF increases in the following order: isoprene < butadiene < styrene.

The relatively small deviation from a proportional dependence of the polymerization rate of isoprene in amine and of butadiene in THF on the initiator concentration makes it possible to assume that, in separate polymerization in polar media, the reactivity of the monomers changes in the same sequence as in joint polymerization.

The effect of the solvents studied on polymerization processes depends substantially on their electron-donor ability. Relatively weak electron-donor solvents —amine, ether, dioxane—when interacting with lithium apparently change the polarization of the Li—C bond only slightly. In some cases they even increase the activation energy of chain growth, compared with hydrocarbon solvents, as occurs in the polymerization of styrene (Table 1, Nos. 2, 5, 7). However, solvents with high electron-donor ability (THF), by completely eliminating the influence of lithium, sharply increase the polarization of the Li—C bond, which correspondingly brings the process closer to the regularities of typical anionic polymerization, in which the active center is a carbanion.

Physical-Chemical Institute
named after L. Ya. Karpov

Received
24 IV 1961

REFERENCES

1. Yu. L. Spirin, D. K. Polyakov, A. R. Gantmakher, S. S. Medvedev, *Vysokomolek. soed.*, **2**, 1082 (1960).
2. L. M. Lanovskaya, A. R. Gantmakher, S. S. Medvedev, *Vysokomolek. soed.*, **2**, 1391 (1960).
3. M. Szwarc, M. Levi, R. Milkovich, *J. Am. Chem. Soc.*, **78**, 2656 (1956).
4. F. Welch, *J. Am. Chem. Soc.*, **81**, 1345 (1959).
5. D. J. Worsfold, S. Bywater, *Canad. J. Chem.*, **38**, 1891 (1960).
6. E. Bresler, A. A. Korotkov, M. I. Mosevitskii, M. Ya. Poddubnyi, *ZhTF*, ser. B, **28**, 114 (1958).
7. Yu. L. Spirin, A. R. Gantmakher, S. S. Medvedev, *Vysokomolek. soed.*, **1**, 1258 (1959).
8. D. E. Kelley, A. V. Tobolsky, *J. Am. Chem. Soc.*, **81**, 1597 (1959).

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