R. V. BASOVA, A. R. GANTMAKHER, Academician S. S. MEDVEDEV

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Figure 1: Figure 1

Abstract

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R. V. BASOVA, A. R. GANTMAKHER, Academician S. S. MEDVEDEV

ON THE INFLUENCE OF THE NATURE OF ACTIVE CENTERS ON THE PROCESSES OF ANIONIC AND ANIONIC-COORDINATION POLYMERIZATION

The influence of the nature of the alkali metal and of the monomer on the structure and reactivity of active centers in anionic and anionic-coordination polymerization has been little studied. Published data on the structure of polydienes (^{1}) and on the UV absorption spectra of polyadduct metal-aromatic compounds (^{2}) indicated a substantial dependence of the state of the Me—C bond (where Me is an alkali metal) on the nature of the alkali metal and the medium. For a fuller elucidation of the dependence of the structure and reactivity of active centers based on alkali metals on various factors, knowledge of the kinetic parameters of such systems is essential. However, detailed kinetic data have been obtained only for the case of polymerization in the presence of LiR (^{3}).

Fig. 1. Polymerization of styrene (expt. No. 1) and butadiene (expt. No. 5) with KO, and of isoprene with KO (expt. No. 19) and KM (expts. No. 20, 21) in a hydrocarbon medium. For the experimental conditions, see Table 1.

In the present work we studied the influence of the nature of the monomer and the medium on the structure and properties of active centers during polymerization initiated by potassium-organic compounds (KR). The kinetics of polymerization of α-methylstyrene, styrene, isoprene, and butadiene were investigated both in a hydrocarbon medium and in the presence of additions of tetrahydrofuran (THF) at various temperatures, and the molecular weights of the corresponding polymers were determined. THF additions were varied from 0.5 to 50%. The polymerization kinetics were studied by the dilatometric method. Purification of the starting substances and the experimental procedure have been described previously (^{1}-^{3}). Various KR, synthesized both in a hydrocarbon medium (1, 2) and in THF (3, 4), were used as initiators: 1) benzylpotassium (KO); 2) low-molecular-weight dipotassium poly-α-methylstyrene (KM); 3) potassium naphthalene (KN); 4) dipotassium tetramer of α-methylstyrene (KT). In determining the rate constants of chain-growth reactions, polymerization was carried out under conditions excluding the possibility of initiation reactions and deactivation of active centers. The absence of isomerization of active centers was monitored kinetically or spectrophotometrically.

Deactivation of active centers, causing a deviation from first order in monomer during the process, was observed to some extent in the polymerization of isoprene and butadiene with KR in the presence of 35-50% THF even at low temperatures (−50°), and was absent in the polymerization of α-methylstyrene under these conditions. On going from a polar medium to a hydrocarbon one, the rate of the isomerization process decreased sharply. Only in the polymerization of isoprene at 25° was a rather considerable decrease in the number of active centers with conversion observed (Fig. 1, expt. No. 20).

As follows from the data on anionic copolymerization ([3]), the activity of monomers in chain-growth acts increases in the sequence: α-methylstyrol < isoprene < butadiene < styrene. The same sequence of monomer activities was obtained in their copolymerization in the presence of KR in a hydrocarbon medium (⌒4), which indicates a considerable polarity of the K−R bond under these conditions.

According to the data of work (⌒5), the reactivities of the α-methylstyrene and styrene carbanions, despite the sharp difference in the activities of the corresponding monomers, are close. The influence of the structure of the carbanion* in KR on its reactivity was studied by us in investigations of the initiation and chain-transfer reactions.

As follows from Fig. 1, the polymerization of styrene (expt. 1) and butadiene (expt. 5) with KO proceeded with an insignificant induction period, whereas in the polymerization of isoprene with this initiator (expt. No. 19) an increase in the rate was observed up to a considerable depth of the process. From these data it could be concluded that the rate of the reaction of initiation of polymerization of different monomers in a hydrocarbon medium at 0° in the presence of benzyl potassium increases with increasing monomer activity in the sequence isoprene < butadiene < styrene. On going from benzyl potassium to dipotassium poly-α-methylstyrene—a compound with a less stable carbanion—even the polymerization of isoprene proceeded without an induction period (Fig. 1, expt. No. 21).

A similar dependence of the activity of the carbanion in KR on its structure was also shown in the study of chain-transfer reactions. According to the data of Table 1, the molecular weight of polybutadiene, and especially of polyisoprene, decreased sharply, whereas that of polystyrene practically did not change when benzene was replaced by toluene as solvent at 0°, i.e., in the polymerization of isoprene and butadiene a chain-transfer reaction through toluene takes place owing to the formation of the more stable benzyl carbanion. Thus, from the data presented it follows, as could have been expected from general considerations, that in anionic polymerization, as in radical polymerization, the sequence of reactivity of the active centers is the inverse of the sequence of monomer activity.

In the polymerization of α-methylstyrene with KR in a mixture of cumene or toluene with THF (THF content 50%), even at $-50°$ it was found that the molecular weight of poly-α-methylstyrene was lower than expected, which indicated the presence of a chain-transfer reaction through the monomer (possibly metalation at the CH_3 group) (Table 1, Nos. 28, 29).

Data on the rates of chain growth in the polymerization of styrene, butadiene, isoprene, and α-methylstyrene with KR in a hydrocarbon medium and in the presence of THF additives are given in Table 1. Some data obtained with LiR under the same conditions are also given there. In a number of cases the kinetics of butadiene polymerization are compared with the structure of polybutadiene.

As follows from the data of Table 1, the rate of polymerization in the presence of KR, both in a hydrocarbon medium and with 35-50% THF additives, for the monomers studied increases in the sequence α-methylstyrene $<$ isoprene $<$ butadiene $<$ styrene. Thus, the sequences of monomer activities in chain-growth reactions in separate and joint polymerization with KR, as well as with LiR in THF (^3), are parallel. These data indicate that in anionic polymerization the activity of the monomer has the determining influence on the acts of chain growth. The rate of polymerization in a hydrocarbon medium with THF additives increases in parallel with the magnitude of the THF additive.

As noted, the coordinating influence of the alkali metal on the acts of chain growth in a hydrocarbon medium increases with increasing electron-acceptor properties in the sequence Cs $<$ Rb $<$ K $<$ Na $<$ Li. However, on going from hydrocarbon solvents to polar ones this sequence changes in a number of cases (^1). According to data obtained earlier (^1), in the coordination mechanism of butadiene polymerization the predominant

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* For simplicity of presentation, the radical in the compound Me—R is conventionally called a carbanion, and the alkali metal (Me) a counterion, although in a hydrocarbon medium the Me—C bond, according to (^2), is apparently not dissociated into an ion pair.

Table 1

Polymerization of hydrocarbon monomers (M) in media of different polarity

Experiment no.	Me—R	[MeR], mol/L	Solvent	THF, vol.%	[M], mol/L	Temp., °C	Yield, %	Mol. wt $\times10^{3}$	K_p^1, L/mol·s	% 1,4-structure
M = styrene										

Experiment no.	Met –R	[MeR], mol/L	Solvent	THF, vol.%	[M], mol/L	Temp., °C	Yield, %	Mol. wt $\times10^{3}$	K_p[1], L/mol· s	% 1,4-structure
1	KO	$4.6 \cdot 10^{-4}$	toluene	–	0.7	0	100	150	4.8	
2	KM[2]	$5.7 \cdot 10^{-4}$	benzene	–	0.7	0	100	120	4.4	
3	KO	$1.4 \cdot 10^{-3}$	cumene	2.5	0.6	−50	100	41	0.32	
4	LiEt	$3.5 \cdot 10^{-3}$	ditto	2.4	0.9	−50	100	26	0.025	
					M = butadiene					
5	KO	$1.3 \cdot 10^{-3}$	benzene	–	1.4	0	100	49	0.09	55
6	ditto	$1.1 \cdot 10^{-3}$	toluene	–	1.7	0	60	24		
7	KM	$6.5 \cdot 10^{-3}$	cumene	–	1.3	−50	40	9	0.0002	44.2
8	ditto	$6.5 \cdot 10^{-3}$	ditto	–	1.3	−25	40	9	0.003	
9	KO	$2.3 \cdot 10^{-3}$	benzene	0.7	1.5	0	75	26	0.124	52.1
10	LiEt	$4.7 \cdot 10^{-3}$	ditto	0.7	1.7	0	100	19	0.075	22.4
11	ditto	$5.5 \cdot 10^{-3}$	toluene	0.6	1.8	0	100	15		
12	KO	$3.0 \cdot 10^{-3}$	cumene	2.7	1.7	−50	35	10	0.004	44.2
13	KO	$1.0 \cdot 10^{-3}$	ditto	4.7	1.1	−50	60	47	0.006	41.2
14	KH	$1.8 \cdot 10^{-3}$	ditto	15.5	1.5	−50	66	100	0.055	38.3
15	KM	$2.0 \cdot 10^{-3}$	ditto	15TEA[3]	1.5	−50	15		0.0026	42.8
16	KO	$1.14 \cdot 10^{-3}$	toluene	34	1.0	−50	75	32		
17	KO	$1.8 \cdot 10^{-3}$	cumene	44	2.0	−50	67	68	0.8[4]	34.1
18	KH		THF[3]							15.3[5]

Experiment no.	Met—R	[MeR], mol/L	Solvent	THF, vol.%	[M], mol/L	Temp., °C	Yield, %	Mol. wt $\times10^{3}$	K_p^1, L/mol·s	% 1,4-structure
					M = isoprene					
19	KO	$1.8 \cdot 10^{-3}$	benzene	—	1.3	30	30			
20	KM	$6.4 \cdot 10^{-4}$	ditto	—	1.4	25	30	58	5.7[4]	
21	ditto	$2.2 \cdot 10^{-3}$	ditto	—	1.3	0	45	34	0.033	
22	ditto	$1.6 \cdot 10^{-4}$	toluene	—	1.2	0	45	5		
23	ditto	$4.5 \cdot 10^{-4}$	ditto	—	1.6	0	55	2		
24	KT	$4.6 \cdot 10^{-3}$	cumene	2.3	1.0	−50	66	28	0.001	
25	KT	$4.0 \cdot 10^{-3}$	toluene	34.0	0.7	−50	100	13		
26	KT	$7.9 \cdot 10^{-3}$	cumene	45.0	1.3	−50	100	14	0.42[4]	
					M = α-methylstyrene					
27	KM	$1.0 \cdot 10^{-3}$	toluene	—	0.6[6]	0°	75		0.008	
28	KT	$9.0 \cdot 10^{-3}$	ditto	50	1.7	−50	60	14	0.0075	
29	KT	$8.0 \cdot 10^{-3}$	cumene	56	1.6	−50	90	27	0.0134	

[1] In the absence of association of active centers, K_p is the absolute rate constant of the chain-growth reaction. [2] KM was synthesized in the system: metallic potassium—benzene—α-methylstyrene, with $[M]$ below the limiting value. [3] Experiment no. 15 with addition of triethylamine (TEA), experiment no. 18 in THF medium. [4] From initial rates. [5] Data obtained by A. A. Arest-Yakubovich. [6] In the case of α-methylstyrene, $[M] = [M]_0 - [M]_p$, where $[M]_p$ is the equilibrium concentration of α-methylstyrene.

1,4-structures. In anionic polymerization in THF medium, the 1,2-addition form is predominantly represented.

The considerable change in the structure of potassium polybutadiene with changing THF content (Table 1, nos. 7, 13, 14, 17, 18) indicates the presence of centers with different degrees of solvation during polymerization with KR under these conditions. According to Table 1, when small additions of THF are introduced into a hydrocarbon medium with KR ($t = -50°$), the content of 1,4-structures in the polymer changes very little and the polymerization rate increases sharply (nos. 7, 12, and 13), i.e., in this case the process proceeds mainly under the influence of less solvated centers, in the presence of which coordination polymerization occurs. With further increase in the THF content during polymerization of butadiene with KR, the content of 1,4-structures, predominant in the coordination mechanism of the process, decreases.

The formation of complexes of MeR with THF, in addition to the destruction of associates of active centers (which is especially pronounced during polymerization with

LiR*) and the corresponding increase in the effective concentration of the catalyst increases the polarity of the Me—R bond and the rate of polymerization.

With an increase in the degree of solvation of the active centers, the polarization of the Me—R bond increases and the structure of the polydienes changes. On the basis of general considerations, one may think that in the presence of THF additives the fraction of more highly solvated centers should increase in the series K<Na<Li, and also with increasing stability of the carbanion in the active center, decreasing temperature, and increasing solvating ability of the solvent. Indeed, with LiR and NaR, even at small THF additions (~6%) at −50°, the 1,2-structure of polybutadiene predominates ([1]), corresponding to polymerization in the presence of more highly solvated active centers and to the anionic type of process (active centers are ion pairs). With KR, such a high content of 1,2-structure occurs only in the polymerization of butadiene in a THF medium. Less solvated centers (analogously to KR in the presence of small THF additions) apparently have decisive importance in polymerization with Me—R in amine media (Table 1, No. 15), ether, and dioxane ([3,2,1]).

Confirmation of the formation of MeR complexes with THF of different composition, corresponding to different degrees of solvation of the organometallic compound, may be provided by data obtained for a model system, 1,1-diphenylalkyllithium, by spectrophotometry ([2]). According to ([2]), upon interaction of LiR with THF two types of complexes are formed: more highly solvated LiR compounds with THF (probably $LiR \cdot 2THF$), predominating over a broad range of THF concentrations (up to 100%), and less solvated complexes (probably $LiR \cdot THF$), predominating only at low THF concentrations.

It should be pointed out that, although the anionic type of process (active centers are ion pairs) in the presence of THF additives is represented to a greater extent in the presence of LiR than KR, the rate of polymerization under these conditions increases on going from LiR to KR (Table 1 and work ([1])). The rate of the chain-transfer reaction through toluene in the polymerization of diene hydrocarbons also increases sharply on going from LiR to KR. According to the data of Table 1 (Nos. 10, 11), even in the presence of THF additives the chain-transfer reaction through toluene in the presence of LiR during butadiene polymerization at 0°C does not take place, whereas with KR this reaction proceeds even in a hydrocarbon medium at a relatively high rate (Table 1, Nos. 5, 6).

The data presented indicate that, also for the anionic mechanism of the process, for systems in which ion pairs take the predominant part in chain-growth events, the nature of the alkali metal, determining the strength of the electrostatic interaction of the carbanion with the counterion in the ion pair, affects the kinetic parameters of the process. In this case the interaction of the carbanion with the counterion, which lowers the rate of the elementary reactions of the carbanion (for example, growth and chain-transfer reactions), at the same structure of counterion solvates, should decrease with increasing stability of the carbanion and increasing ionic radius of the counterion in the sequence Li>K.

The results obtained in the present work and in (1) confirm this dependence of the rate of the elementary reactions of the carbanion on the nature of the alkali metal.

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named after L. Ya. Karpov

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* According to data obtained by us, the activation energy of the chain-growth reaction in the polymerization of butadiene with KR (temperature interval from 0 to −50°) in a hydrocarbon medium is ~13 kcal/mole, which is significantly lower than the corresponding value with LiR, ~22 kcal/mole.

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