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Abstract

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POLYMERIZATION OF BUTADIENE IN THE PRESENCE OF ALKALI METALS AND THEIR COMPOUNDS IN VARIOUS MEDIA

In carrying out polymerization in the presence of alkali metals and their compounds it was found that the structure of the polyenes formed depends substantially on the nature of the alkali metal and the medium ([1–4]). Analysis of the results for Li-, Na-, and K-initiated polymerization of dienes in hydrocarbon media indicates that under these conditions an anion-coordination mechanism of polymerization is realized, and the chain structure is determined by the participation, in the growth steps, of two catalyst centers—the metal and the alkyl. The coordination type of polymerization is realized to the greatest extent in the presence of organolithium initiators in hydrocarbon media, where the preferential formation of 1,4-structures in polyenes is observed ([5,6]). When organolithium initiators are replaced by NaR or KR, and also as the polarity of the medium increases, the fraction of structures characteristic of typically anionic polymerization increases: 3,4 for polyisoprene and 1,2 for polybutadiene, and the coordinating influence of the alkali metal decreases ([1–3]).

In a number of studies on the polymerization of dienes initiated by alkali metals and their compounds, it was noted that the fraction of structures characteristic of the anionic type of polymerization, contrary to expectation, decreased with increasing polarity of the Me*—R bond. This effect was observed in hydrocarbon media on passing from sodium- to potassium-organic compounds ([7–9]), and also in polar solvents on passing from lithium- to sodium- and potassium-organic initiators ([1,10]).

It seemed of interest to clarify the reason for this anomalous dependence. In the present work, devoted to the study of the influence of polymerization conditions on the structure of polybutadiene, considerable attention is given to this question. The purification of the monomer and solvents and the experimental procedure were described previously ([3,11–14]).

Dosing of the substances and polymerization were carried out under vacuum. The structure of polybutadiene was determined by the IR method**.

The fractions of 1,2-, 1,4-cis-, and 1,4-trans-structures were estimated from the frequencies 909, 730, and 967 cm^{-1}. The dependence of the structure of polybutadiene obtained when polymerization was initiated by organic compounds of

alkali metals on the nature of the initiator, the medium, and the temperature was studied.

The results of the investigation are given in Table 1. According to the data of Table 1 (Nos. 6, 7), the fraction of 1,2-structures in the polymerization of butadiene with metallic potassium in a hydrocarbon medium is somewhat lower, and the content of 1,4-trans-structures higher, than when polymerization is initiated by potassium-organic compounds (K. O.).

It follows from this that in the presence of metallic potassium there is simultaneous occurrence of radical and anion-coordination processes, with a considerable predominance of the latter (see [14]).

As can be seen from the data of Table 1 (Nos. 19, 20), in polymerization in the presence of polar solvents the fraction of 1,2-structures increases with decreasing temperature. From the results presented in Table 1 it follows that the sharpest dependence of the structure of polybutadiene on the nature of the alkali metal is observed in hydrocarbon media.

* Me –alkali metal.
** The method for studying structures was developed by N. V. Desyatova, F. F. Sukhov, and V. P. Basov.

Table 1

Dependence of the structure of polybutadiene on the polymerization conditions

No.	Initiator	Medium	Additive	Amount of additive, mol. %	Polymerization temperature, °C	1,2-	1,4-cis	1,4-trans
1	Ethyllithium	Hexane*	–	–	30	6.8	42.8	50.4
2	»	Toluene*	–	–	30	8.7	43.7	47.6
3	Na	Benzene	–	–	25	32.3	22.6	45.0
4	Na	Toluene**	–	–	25	31.5***	23.7	44.8
5	K	Benzene	–	–	25	35	16.5	48.5
6	K	Benzene–heptane (5 : 1)	–	–	0	38.1	12.8	49
7	K. O.****	Toluene	–	–	0	45	12	43

No.	Initiator	Medium	Additive	Amount of additive, mol. %	Polymerization temperature, °C	1,2-	1,4-cis	1,4-trans
8	Radical ([10]) polymerization	Hydrocarbon	—	—	5	18	10	72
9	Ethyllithium	Benzene	Triethylamine	10	25	37.1	22.8	40
10	Na	»	»	10	25	43.3	17.3	39.4
11	K	»	»	10	25	37.4	16.6	46.0
12	Ethyllithium	»	Tetrahydrofuran	1	25	73.6	13.3	13.1
13	Na	»	»	1	25	44.3	12.8	42.8
14	Ethyllithium	Heptane	»	6	−50	91.5	4.1	4.4
15	N. N.*****	Cumene	»	6	−50	88	—	12
16	K. N.*****	Heptane	»	6	−50	61.6	5.1	33.3
17	K. O.	Cumene	»	5	−50	58.8	5.8	35.4
18	K. N.	»	»	15.5	−50	61.7	5	33.3
19	N. N.	Tetrahydrofuran	—	—	−50	88	—	12
20	N. N.	»	—	—	−90	92.8	0	7.2
21	K. N.	»	—	—	−50	84.7	0	15.3
22	Ethyllithium	»	—	—	−50	91	0	9

* Polymers obtained in work ([13]).

** During the polymerization of butadiene in toluene in the presence of metallic sodium and potassium, owing to chain-transfer reactions through toluene ([14]), the molecular weight of the polybutadiene was considerably lower than in benzene or heptane.

*** The possibility of obtaining polybutadiene with a relatively low content of 1,2-structures was also reported in work ([15]).

**** K. O.—potassium-organic compounds were synthesized by using a transfer reaction through solvent during the polymerization of isoprene initiated by metallic potassium in toluene ([14]). Analysis of a solution of such K. O. in

tetrahydrofuran, carried out by D. K. Polyakov by a spectrophotometric method, showed that the K. O. are a mixture of benzylpotassium (λ_{max} 335 mμ) and isomerized carbanion of low-molecular-weight polyisoprene (λ_{max} 375 mμ). The wt. % of potassium in K. O. 22.

***** N. N. and K. N.—sodium naphthalene and potassium naphthalene, respectively. The method of polymerization with these initiators is described in work ([12]).

In accordance with the mechanism proposed earlier ([3]), in hydrocarbon media the participation of the counterion in chain-growth acts, due to its interaction with the π-electrons of the monomer, is determined by the electron-acceptor properties of the alkali metal.

Accordingly, the degree of participation of the counterion* in chain-growth acts** under these conditions should increase with decreasing ionic radius and level of the free orbitals of the alkali metal, with increasing ionization potential, and with the corresponding decrease in the polarity of the Me—R bond in the sequence K < Na < Li, which is in agreement with our results (Table 1, Nos. 1, 2, 3, 4, 5).

In the presence of electron-donor solvents, their competing interaction with the counterion takes place, lowering its influence on chain-growth acts—the fraction of 1,2-structure correspondingly increases. The magnitude of this effect is determined by the strength of the complexes formed, S···MeR (S is a polar solvent), which increases with increasing electron-donor ability of the solvent and electron-acceptor properties of the counterion. Obviously, the strength of such solvates changes in the same sequence as the degree of influence of the counterion in hydrocarbon media on chain-growth acts: K < Na < Li. Accordingly, as was noted

* Here and below, for convenience of presentation, the alkali metal bound to the carbon atom is called the counterion, and the radical bound to it is called the carbanion, although in a hydrocarbon medium dissociation of the C—Me bond into an ion pair cannot be regarded as proven.

** As a parameter characterizing the degree of influence of the counterion on chain-growth acts, the fraction of 1,2-structure of polybutadiene, predominant in a typically anionic process, was chosen. Obviously, an increase in the content of 1,2-structure characterizes a decrease in the coordinating influence of the alkali metal.

earlier also in the synthesis of organoaromatic metal initiators [(17)], on going from hydrocarbon solvents to polar ones one may expect a change in the sequence characterizing the dependence of the coordinating ability of the gegenion on its nature.

Indeed, whereas in initiation of polymerization by metallic potassium the introduction of a 10% additive of triethylamine into the hydrocarbon solvent practically does not change the structure of polybutadiene (Table 1, Nos. 5, 11),

the fraction of 1,2-structures in the presence of ethyllithium or metallic sodium increases (Nos. 2, 4, 9, 10).

The degree of the coordinating influence of the gegenion under these conditions is determined by the sequence Na < Li, K, i.e., under these conditions the anionic type of polymerization is represented to the greatest extent when polymerization is initiated by metallic sodium.

The higher degree of potassium participation in chain-growth steps as compared with Na in the presence of a 10% amine additive is evidently due to the decrease in the strength of the complexes with amine on going from sodium to potassium.

The decrease in the strength of complexes with amine on going from lithium to potassium also accounts for the similar character of their coordinating influence under these conditions. When amine additives are replaced by tetrahydrofuran (THF), the solvating influence of the solvent appears more sharply, and the fraction of 1,2-structures in polybutadiene increases.

Thus, the introduction of even a 1% additive of THF into a hydrocarbon medium causes a significant change in the structure of polybutadiene when polymerization is initiated by sodium- and especially lithium-organic compounds (Table 1, Nos. 13, 12). In the presence of a 6% additive of THF, the structures of polybutadienes obtained with these initiators are close to the corresponding structures in polymerization in a medium of 100% THF (Table 1, Nos. 14, 15, 19, 22). When polymerization is initiated by metallic potassium and potassium-organic compounds, THF additives, like amine additives, change the structure of polybutadiene to a significantly smaller extent.

With this initiator, even in the presence of a 15% THF additive, the fraction of 1,2-structures in polybutadiene is considerably lower than in 100% THF (Table 1, Nos. 18, 21). The degree of the coordinating influence of the gegenion under these conditions is determined by the sequence Li < Na < K.

As follows from published data, the introduction of a THF additive into a hydrocarbon medium causes an increase in the rate of polymerization of butadiene and other monomers initiated by alkali metals and their compounds [1,3,18,4]. According to our results from the study of the kinetics of butadiene polymerization initiated by lithium-, sodium-, and potassium-orga-

Table 2

Dependence of the rate of butadiene polymerization on the nature of the alkali metal and the medium

No.	Initiator	Initiator, mol/l	Monomer, mol/l	Solvent	Additive	Amount of additive, vol. %	Polymerization temperature, °C	v^*, l/(mol·s)
1	LiEt	$1.65 \cdot 10^{-3}$	2.8	Heptane	THF	6	−50	0.003
2	K. H.	$2 \cdot 10^{-3}$	2.5	»	»	6.5	−50	0.006
3	K. H.	$2.3 \cdot 10^{-3}$	3.1	»	»	6	−50	0.005
4	LiEt	$5 \cdot 10^{-3}$	1	Toluene	—	—	0	0.0006**
5	K. O.***	$1.0 \cdot 10^{-3}$	1.35	Benzene / Heptane } 5 : 1	—	—	0	0.09
6	K. O.***	$1.5 \cdot 10^{-3}$	1.65	Toluene	—	—	0	0.08

* v is the chain-growth rate referred to unit concentration of monomer and catalyst. In the absence of association, $v = K_p$ (K_p is the chain-growth rate constant).

** Calculated from data in [13].

*** In the presence of K. O. polymerization was carried out in dilatometers with stirring. After a short induction period, polymerization proceeded under stationary conditions—the ratio $\frac{V_t}{M_t}$ (M_t is the concentration of monomer at time t) did not change during polymerization.

With this initiator, on going from benzene to toluene, the molecular weight of polybutadiene decreases by a factor of ~ 10 as a result of the chain-transfer reaction through toluene.

organic compounds in a hydrocarbon medium in the presence of THF additives; in systems with LiR initiators, despite the highest fraction of 1,2-structures, the lowest rate of the process was observed.

The corresponding data for a 6% THF additive are given in Table 2. As follows from the data in Table 2, a very sharp decrease in the rate of butadiene polymerization is observed on going from potassium- to lithium-organic initiators in hydrocarbon media. It may be thought that such a difference in rates is due not only to a change in the mechanism of chain-growth reactions on going from potassium- to lithium-polybutadiene, but is also the result of an increase in the

degree of association of the active centers when the alkali metal potassium in them is replaced by lithium.

On the basis of the results obtained, it may be thought that the increase in the fraction of 1,2-structures of polybutadiene and 3,4-structures of polyisoprene, observed earlier on going from potassium- to sodium-organic initiators in a hydrocarbon medium (7-9), was caused by the presence of impurities solvating the counterions.

As noted above, the strength of such solvates increases on going from potassium- to sodium-organic compounds, which also accounts for the greater polarity of the Na—R~~ bond and the higher content of 1,2- or 3,4-structures in the polymerization of dienes initiated by sodium under these conditions.

In the present work, where the monomers and solvents were subjected to thorough purification and, before polymerization, were treated with ethyllithium, the fraction of 1,2-structures of polybutadiene in hydrocarbon media increased with increasing polarity of the Me—R bond according to the series Li < Na < K.

In polar media the coordinating influence of the counterion is diminished owing to the formation of its complexes with solvent molecules, the strength of which increases according to the series K < Na < Li.

Accordingly, under these conditions the sequence characterizing the coordinating influence of the counterion changes.

In the presence of solvents with high electron-donor ability, the process will proceed by a typically anionic mechanism, in which the growth steps are determined by the interaction of the monomer with a single active center—a carbanion—and under these conditions the structure of the polydienes should not depend on the nature of the counterion.

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REFERENCES

1. A. A. Korotkov, Symposium on Macromolecular Chemistry, Prague, 1957.

2. N. Morita, A. V. Tobolsky, J. Am. Chem. Soc., **79**, 5853 (1957); A. V. Tobolsky, C. E. Rogers, J. Polym. Sci., **40**, 73 (1959).

3. Yu. L. Spirin, A. R. Gantmakher, S. S. Medvedev, *Vysokomolek. soed.*, **1**, 1258 (1959); Yu. L. Spirin et al., J. Polym. Sci., **58**, 1181 (1962).

4. Yu. L. Spirin, D. K. Polyakov et al., DAN, **139**, 898 (1961).

5. F. W. Stavely et al., Ind. and Eng. Chem., **48**, 778 (1956).

6. J. Kuntz, A. Gerber, J. Polym. Sci., **42**, 299 (1960); J. Kuntz, J. Polym. Sci., **54**, 569 (1961).

7. A. V. Meyer, R. R. Hampton, J. A. Davison, J. Am. Chem. Soc., **74**, 2294 (1952).

8. F. C. Foster, J. L. Binder, *Handling and Uses of Alkali Metals*. Advances in Chemistry, No. 19, 26 (1957).

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

10. A. Rembaum, A. V. Tobolsky, J. Polym. Sci., **61**, 155 (1962).

11. L. M. Lanovskaya, A. R. Gantmakher, S. S. Medvedev, *Vysokomolek. soed.*, **2**, 1391 (1960).

12. D. A. Solovykh, A. A. Arest-Yakubovich et al., *Vysokomolek. soed.*, **4**, 702 (1962).

13. Yu. L. Spirin, A. R. Gantmakher, S. S. Medvedev, DAN, **146**, 368 (1962).

14. R. V. Basova, A. R. Gantmakher, *Vysokomolek. soed.*, **4**, 361 (1962).

15. C. S. Marvel et al., J. Polym. Res., **1**, 275 (1960).

16. T. P. Belopolskaya, B. A. Dolgoplosk, E. I. Tinyakova, *Izv. AN SSSR, OKhN*, 1957, 63.

17. A. A. Arest-Yakubovich, A. R. Gantmakher, S. S. Medvedev, *Vysokomolek. soed.*, **3**, 1003 (1961).

18. D. J. Kelley, A. V. Tobolsky, J. Am. Chem. Soc., **81**, 1957 (1959).

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