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Anionic Polymerization and Copolymerization of Hydrocarbon Monomers Catalyzed by Organobarium Initiators

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ABSTRACT

The barium salt of the dimeric dianion of 1,1-diphenylethylene (Ba-DPhE) initiates polymerization and copolymerization of monomers capable of anionic polymerization (butadiene, isoprene, styrene) in ethereal and hydrocarbon solvents. Ba-DPhE is more stereospecific in butadiene polymerization (up to 70% of cis-1,4-units in hydrocarbon medium) than initiators based on other metals of Groups I and II. The relative reactivity of monomers in copolymerization processes in THF decreases in an order typical for anionic polymerization: styrene > butadiene > isoprene. The most interesting feature of organobarium initiators is their ability to form random butadiene-styrene copolymers with high cis-1,4-butadiene unit content when copolymerization proceeds in a hydrocarbon medium. A new phenomenon in anionic polymerization, the dependence of diene units structure on copolymer composition, was observed. Thus an increase of styrene content in butadiene-styrene copolymer leads to conversion of cis-1,4-butadiene units into trans-1,4-units (in benzene) or to conversion of

1,4-units to 1,2-units (in THF). Similarly, an increase of butadiene content in its copolymer with isoprene (in benzene) leads to conversion of cis-1,4-isoprene units into trans-1,4-units.

Spectrophotometric, conductometric, and viscometric methods were used to study organobarium active centers. Certain anomalies connected with the formation of specific aggregates due to coupling of bifunctional hydrocarbon chains with bivalent counterions were observed.

INTRODUCTION

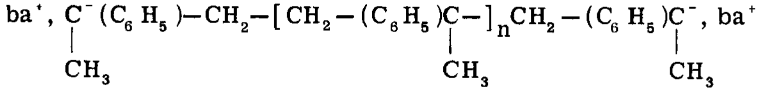
Some years ago it was found that the use of barium as an anionic polymerization initiator opened new possibilities for structure and composition control of synthetic polymers [1-3]. Thus, in hydrocarbon medium, metallic barium gives rise to polybutadiene with a higher content of cis-1,4-structure (up to 80%) than do other metals of Groups I and II [1, 2]. However, the processes of anionic polymerization of hydrocarbon monomers initiated by organobarium compounds have been studied very little because of difficulties of corresponding initiator synthesis.

The reaction of electron transfer to condensed aromatic hydrocarbons, one of the main methods of synthesis of anionic initiators containing alkali metals, with alkaline earth metals proceeds relatively smoothly only in high-polar solvents, such as HMPT [4]. In ethereal solvents the reaction proceeds with great difficulty and leads to the formation of slightly soluble compounds ineffective in polymerization processes because of the low tendency of alkaline earth metals to give up their electrons (as compared with alkali metals) [5, 6].

Recently it was found in our laboratory that active initiators of polymerization may be obtained by the reaction of metallic barium with 1,1-disubstituted vinylaromatic compounds (1,1-diphenylethylene and α-methylstyrene) in ethereal media. According to electron absorption spectra and by analogy with the same reactions of alkali metals, the compounds obtained were identified as barium salts of dianions of diphenylethylene dimer

$$\mathrm{ba^+,\ C^-(C_6H_5)_2-CH_2-CH_2-(C_6H_5)_2C^-,\ ba^+}$$

or of α-methylstyrene oligomer



$$\mathrm{ba^+,\ \underset{\underset{CH_3}{|}}{C^-}(C_6H_5)-CH_2-[CH_2-(C_6H_5)\underset{\underset{CH_3}{|}}{C}-]_nCH_2-(C_6H_5)\underset{\underset{CH_3}{|}}{C^-},\ ba^+}$$

where ba is barium equivalent, n = 2 to 4 [2]. Similar results were reported by two groups of French authors [7, 8].

In the present paper we describe our results on the polymerization and copolymerization of butadiene initiated by the barium salt of the dimeric dianion of 1,1-diphenylethylene and on the investigation of some details of structure of active centers connected with the presence of a bivalent counterion.

EXPERIMENTAL

Initiator. The barium salt of the dimeric dianion of 1,1-diphenylethylene (Ba-DPhE) was obtained by the reaction of metallic barium (in the form of a mirror obtained by sublimation in high vacuum in quartz ampules) with 1,1-diphenylethylene in tetrahydrofuran (THF) or dimethoxyethane (DME). In the polymerization processes the initiator was used either in solution as obtained or (for polymerization in hydrocarbon media) in the solid state after removal of the polar solvent by evaporation in high vacuum for an hour at room temperature and then for 20 to 40 min at 60 to 70°C.

Bistriphenylmethyl barium (Tr_2Ba) was obtained according to Ref. 9 by reaction of metallic barium with hexaphenylethane in THF or DME.

Microstructure and composition of polymers were determined by IR spectroscopy. The composition of butadiene-isoprene copolymers was calculated by the intensity ratio of the well-defined bands at 890 cm^{-1} (3,4-isoprene unit) and at 912 cm^{-1} (1,2-butadiene unit), using calibration curves obtained for mixtures of homopolymers synthesized in the same conditions. The validity of this method is confirmed by the fact that according to the results obtained, the relative content of 3,4-isoprene and of 1,2-butadiene units is independent on copolymer composition.

Electroconductivity of organobariums and living polymers was determined in a vacuum cell with platinum coaxial electrodes at 1000 Hz [10].

The experiments were carried out in high vacuum in all-glass reaction vessels. Monomers and solvents were throughly purified according to standard procedures [2, 10] and finally were treated with dry ethyllithium or with potassium-sodium alloy.

RESULTS AND DISCUSSION

Polymerization of Butadiene in Ethereal and Hydrocarbon Media

As it was shown in preliminary communications [2, 6] Ba-DPhE solutions in THF and DME are effective initiators of polymerization of monomers capable of anionic polymerization (butadiene, isoprene, styrene, etc.). Polymerization starts without an induction period and proceeds as a pseudo-monomolecular reaction. The initiation reaction in THF at room temperature, as was shown by UV spectroscopy (the disappearance of DPhE anion maximum at 445 mμ), is completed at about 10% conversion of monomer. Polybutadiene formed in THF contains up to 80% of 1,4-units; 1,2-polymer, typical for anionic polymerization, is formed only in a considerably more strongly solvating agent—DME (Table 1). The amount of 1,2-units drops somewhat as the temperature increases, as shown previously for polymerization by alkali metals in ethereal media [11].

Dilution of the ethereal solvent with hydrocarbons (monomer as well) leads to a gradual decrease of 1,2-unit content in polymers and to an increase of the cis-1,4-unit content. This effect is especially marked in DME, where even a relatively small increase of monomer concentration leads to a significant change in polybutadiene structure (Table 2).

Of great interest is the fact that the solid initiator after removal of the polar solvent, as described in the Experimental section, may be used for initiation of homogeneous polymerization in hydrocarbon media (or in monomer bulk), producing polybutadiene with high cis-1,4-unit content. Since there are no direct methods of synthesis of organobarium compounds in hydrocarbon media, only metallic barium [1, 2, 12-14] or mixed barium-zinc and barium-aluminum compounds [3, 15-17] were used as polymerization initiators in these solvents previously. However, in the latter case the second

TABLE 1. Microstructure of Polybutadiene Catalyzed by Ba-DPhE in Ethereal Media at Various Temperatures

Solvent	Temperature (C)	Unit content (%)		
		1,2	cis-1,4	trans-1,4
THF	30	20	31	49
THF	40	19	30	51
THF	50	18	27	55
THF	70	16	26	58
DME	25	70	15	15
DME	70	74	11	15
DME	90	62	14	24

TABLE 2. Microstructure of Polybutadiene Catalyzed by Ba-DPhE in Benzene and in Ether-Benzene Mixtures at Ambient Temperature

Solvent used in initiator synthesis	Percent (vol) of polar solvent in polymerization	Unit content (%)		
		1,2	cis-1,4	trans-1,4
DME	85	71	7	22
DME	60	43	18	39
DME	10	26	37	37
DME	0[a]	8	57	35
THF	80	22	28	50
THF	9	7	36	57
THF	0[a]	10	60-70[b]	20-30[b]
Benzene[c]	0	11	76	13

[a] Polymerization on solid initiator.
[b] Depending on the conditions of THF removal.
[c] Polymerization initiated by metallic barium [2].

metal of the catalytic complex considerably changes its stereospecificity toward formation of mostly trans-1,4-polybutadiene. Polymerization of butadiene (as well as of isoprene, styrene, and their copolymerization with butadiene) by Ba-DPhE dispersed in benzene proceeds with an induction period during which the initiator is gradually transferred into solution. At conversion of 3 to 5% the system becomes homogeneous and the reaction proceeds as a first-order one. Butadiene polymerization rate in benzene at room temperature is of the same order as the polymerization rate in THF (at equal concentrations of initiator).

Polybutadiene produced on Ba-DPhE in hydrocarbon media has a higher content of cis-1,4-units than polymers produced on other metals of Groups I and II. A certain decrease in the content of cis-1,4-units (60 to 70% compared with 75 to 80% on metallic barium [1, 2]) may be explained either by the remaining strongly complexed polar solvent in the initiator or by the fact that the concentration of active centers in solution (10^{-3} g-equiv/liter) is considerably higher than in polymerization initiated by metallic barium. The dependence of polyisoprene and polybutadiene microstructure on active centers concentration, connected with association of growing polymer chains, is well known for polymerization initiated by alkali metals [18]. Traces of free 1,1-diphenylethylene which may be present in the initiator according to the synthesis procedure do not affect the polymer structure, as can be seen from data presented in the following section.

As the polymerization temperature increases, the amount of cis-1,4-units in polybutadiene slightly drops while the content of trans-1,4-units increases accordingly; the 1,2-units content in the 0 to 95°C range remains constant (Table 3). To eliminate the scatter in the data due to uncertainties in the amounts of solvent remaining in the initiator, the experiments described in Table 3 were carried out with initiators prepared in the same batch. The data presented in Table 3 show that the overall activation energy of the process is about 14 kcal/mole.

Copolymerization of Butadiene with Styrene and Isoprene

Copolymerization of butadiene with styrene initiated by Ba-DPhE in THF, as well as homopolymerization of butadiene, proceeds homogeneously without an induction period, and the polymerization rate is higher the greater is the styrene content. In the entire range of the initial monomer ratios the copolymer is enriched with styrene (Fig. 1). The values of monomer reactivity ratios obtained (Table 4) do not differ significantly from the values for copolymerization initiated by alkali metal [19] and calcium [20] compounds.

In benzene, as well as in butadiene homopolymerization, an induction period is observed during which the solution is homogenized. The initial copolymer compositions are close to the compositions of the initial monomer mixtures.

TABLE 3. Butadiene Polymerization Initiated by Ba-DPhE in Benzene at Various Temperatures[a]

Temperature (°C)	Reaction time (hr)	Polymer yield (%)	Unit content (%)		
			1,2	cis-1,4	trans-1,4
0	70	22	9	67	24
25	28	57	9	61	30
60	5	83	10	51	39
80	4	100	9	43	48
95	4	100	9	42	49

[a] Concentration of initiator, ~1 × 10^{-3} g-equiv/liter, concentration of monomer, 2.9 moles/liter.

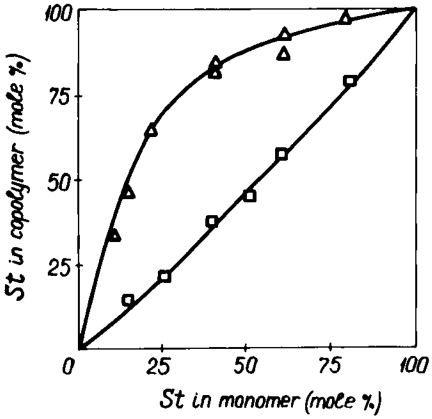


FIG. 1. Monomer-copolymer composition curve for butadiene-styrene copolymerization in THF (△) and in benzene (□) at 25°C.

TABLE 4. Monomer Reactivity Ratios in Copolymerization of Butadiene (M_1) with Other Monomers as Initiated by Ba-DPhE at 25°C

Monomer M_2	Solvent	r_1	r_2
Styrene	THF	0.13	8.5
Styrene	Benzene	1.1	0.8
Isoprene	THF	3.0	0.1
Isoprene	Benzene	2.0	0.3

Butadiene-isoprene copolymers formed both in benzene and THF are enriched with butadiene (Fig. 2); values of the monomer reactivity ratios are presented in Table 4.

Data obtained show that the relative reactivity of monomers in copolymerization initiated by organobarium compounds in THF decreases in the order styrene > butadiene > isoprene which is typical for alkali metal or calcium-initiated anionic copolymerization [19, 20]. However, in benzene the relative reactivities of styrene and butadiene are similar whereas in the case of lithium and calcium initiators the inversion of monomer reactivities takes place [19, 20].

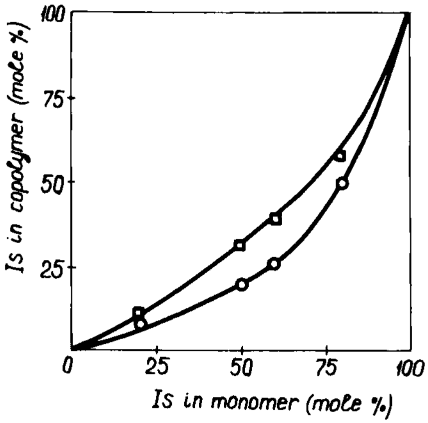


FIG. 2. Monomer-copolymer composition curve for butadiene-isoprene copolymerization in THF (○) and in benzene (□) at 25°C.

Due to almost equal values of the monomer reactivity ratios, the monomer units in such copolymers are randomly distributed in the polymer chain and the composition of the copolymers varies insignificantly up to high conversions. Therefore this process may be useful for the production of styrene-butadiene rubber, now obtained commercially in large quantities by radical polymerization in water emulsions.

The ability to form random butadiene-styrene copolymers with a predominant 1,4-butadiene units is, apparently, a specific property of organobarium compounds, since common initiators of anionic copolymerization form not random structures, but macro- or microblock structures [21, 22] or polymers with a high content of 1,2-units. Previously [3, 16] we have shown that bimetallic barium-zinc initiators in benzene also lead to random butadiene-styrene copolymers.

In the course of the investigation of copolymers structure a new phenomenon was observed; namely, the dependence of diene units structure on the composition of the copolymer. Thus an increase of styrene content in butadiene-styrene copolymer formed in benzene is accompanied by a gradual decrease of the relative amount of cis-1,4-butadiene units with a corresponding increase of trans-1,4-structures; the amount of 1,2-units remains practically constant (Table 5). It should be noted, however, that in the composition range required for the production of elastomeric materials (up to 25% of styrene by weight) the content of cis-1,4-butadiene units is as high

TABLE 5. Butadiene Units Structure in Butadiene-Styrene Copolymers Obtained on Ba-DPhE in Benzene at 25°C

Styrene in copolymer (mole %)	Butadiene units structure		
	1,2	cis-1,4	trans-1,4
0	12	63	25
14	11	62	27
20	14	57	29
25	14	52	34
36	14	48	38
37	10	50	40
45	10	36	54
56	10	36	54
69	12	34	54

[a] All experiments were carried out with initiators of the same batch.

as in butadiene homopolymer. In copolymers formed in THF the content of 1,2-butadiene structures is considerably higher than in the homopolymer (up to 50% instead of 20% in homopolymer) (Table 6).

A similar effect of the second monomer on the structure of diene units is observed in copolymerization of butadiene with isoprene: in copolymers prepared in benzene an increase of butadiene content leads to conversion of cis-1,4-isoprene units into trans-1,4-units while the content of 3,4-units remains constant (Table 7). However, the presence of isoprene hardly affects the structure of butadiene units in copolymers obtained both in benzene and in THF media.

Thus the monomers investigated can be arranged according to their effect on the structure of diene units in copolymers: isoprene < butadiene < styrene, where every preceeding member is affected by the following.

In general, the influence of the M_2 monomer on the microstructure of M_1 diene units in a polymer chain may be due to the following factors.

1. M_2 monomer in solution may form a complex with the counterion, thus affecting the coordination power of the counterion toward the M_1 monomer.

TABLE 6. Butadiene Units Structure in Butadiene-Styrene Copolymers Obtained on Ba-DPhE in THF at 25°C

Styrene in copolymer (mole %)	Butadiene units structure	
	1,2-	1,4-
0	22	78
16	26	74
34	49	51
47	45	55
66	51	49
83	45	55
84	51	49
87	45	55
93	61	39
97	50	50

2. The coordination power of the counterion toward the M_1 monomer may depend on the nature of the terminal unit of the growing chain (thus insertion of M_2 monomer into the chain affects the structure of the following M_1 unit).
3. Monomers M_1 and M_2 may attach themselves to different sites of diene terminal unit of allylic structure because of steric or other factors (in this case insertion of M_2 monomer into the chain affects the structure of the preceding M_1 unit).

Obviously, in Cases 1 and 2 one may expect changes in the proportion of 1,2- (3,4-) and 1,4-units as well as in the relative amount of cis- and trans-1,4-structures. In Case 3 M_2 monomer may affect only the ratio of 1,2- (3,4-) to 1,4-structures.

The solvating effect of comonomer (Case 1) can hardly play a predominant role because the basicity of monomers (styrene and butadiene) is comparable with that of benzene and much less than the basicity of THF. In order to examine this possibility more precisely, the polymerization of butadiene in the presence of some additives of various donor-acceptor power (as a model of styrene monomer) was studied. It was found that even considerable amounts of such additives (up to 1:1 to monomer) had practically no effect on polybutadiene structure (Table 8).

TABLE 7. Microstructure of Butadine-Isoprene Copolymers Catalyzed by Ba-DPhE in Benzene at 25°C[a]

Isoprene content (mole %)		Structure of butadiene units (%)			Structure of isoprene units (%)			
In monomer mixture	In copolymer	1,2-	cis-1,4	trans-1,4	1,2-	3,4-	cis-1,4	trans-1,4
0	0	12	71	17	-	-	-	-
20	10	10	66	24	not detected			
50	31	10	67	23	0	30	27	43
60	38	11	62	27	0	43	32	25
80	57	10	57	33	0	39	41	20
100	100	-	-	-	0	37	56	7

[a] All experiments were carried out with initiators of the same batch.

TABLE 8. Effect of Hydrocarbon Additives on Polymerization of Butadiene (M) on Ba-DPhE at 25° C

Solvent	Additive, A	Amount of additive A/(A + M) (mole %)	Polybutadiene microstructure (%) 1,2-	cis-1,4	trans-1,4	Presence of additive in polymer
Benzene	-	-	10	67-70	23-20	-
Benzene	1,1-Diphenylethylene	1.6	14	70	16	Absent
Benzene	1,1-Diphenylethylene	50	10	73	17	7%
Benzene	α-Methylstyrene	34	11	73	16	Absent
Benzene	α-Methylstyrene	56	12	71	17	Absent
Benzene	Durene	18	12	67	21	Absent
Benzene	1,4-Diphenylbutadiene-1,3	4	10	50	40	1%
Benzene	Anthracene	1[a]	12	67	21	Absent
THF	-	-	22	28	50	-
THF	1,1-Diphenylethylene	12	18	31	51	20%
THF	α-Methylstyrene	54	15	30	55	10%
THF	1,4-Diphenylbutadiene-1,3	4	31	28	41	8%

[a] Saturated solution of anthracene in benzene.

Hence, in the copolymerization in benzene, which most probably proceeds according to a coordination mechanism, the decrease of cis-1,4-diene unit content may be due to the fact that an increase of the polarity of the bond between counterion and the terminal monomer unit is in the order isoprene < butadiene < styrene, decreasing the counterion's coordination power toward diene cis-addition. (A similar explanation was proposed for copolymerization catalyzed by transition metals [23]).

It is noteworthy that the effect of styrene on the structure of butadiene units (in hydrocarbon media) takes place only in the organobarium initiators that give rise to high cis-1,4-polybutadiene. In the copolymerization initiated by mixed barium-zinc compounds which mainly form trans-1,4-polybutadiene, the diene units structure in butadiene-styrene copolymer is the same as in homopolymer in the entire composition range [16]. This fact is in good agreement with the assumption that the effect of the second monomer on copolymer microstructure is connected with the counterion's cis-coordination power.

In THF, due to the great difference in reactivities of butadiene and styrene, the butadiene part of the copolymers consists primarily of isolated monomer units. As the ratio of 1,2- to 1,4-butadiene units is determined by the site of attachment of the following monomer molecule (the first or the third carbon atom of the allylic active centre), the results obtained (50% of 1,2-units in copolymers containing 50% or more of styrene) indicate that in THF the attachment of styrene takes place with equal probability to the 1 and 3 carbon atoms while butadiene attaches itself primarily to an end atom.

However, a calculation based on a simple additive scheme (the relative content of M_1 units preceding M_2 or following immediately after it were calculated from equations of monomer unit distribution in copolymer [24]) does not adequately describe the experimental data for any of the systems investigated (butadiene-styrene-benzene, butadiene-styrene-THF, isoprene-butadiene-benzene). Apparently, for an organobarium active center, the case is complicated by the fact that the counterion is connected with two growing chains (a situation that has no analogy in active centers containing alkali metals). Thus the terminal M_2 unit may affect the addition of M_1 monomer not only to the same chain but to the geminate growing chain connected with the same counterion as well.

Some Specific Features of Structure of Active Centers with a Bivalent Counterion

The widely used theories concerning the structure of active centers in anionic polymerization were developed for systems with alkali metals as a counterion [10]. Little attention has been paid to systems with alkaline earth metals, although, as we have pointed out previously [2], the presence of a bivalent counterion may lead to some specific properties of living polymers.

To examine more precisely the effect of bivalent counterion, the properties of organobarium compounds with a bifunctional hydrocarbon part of the molecule (Ba-DPhE) were compared with properties of "common" R_2Ba compounds (bistriphenylmethyl barium, Tr_2Ba).

Electron absorption spectra of di- and triphenylmethyl barium compounds in THF and DME are similar to the spectra of corresponding alkali metal compounds, although the absorption maxima are displaced toward the shortwaves. In DME, as compared with THF, the absorption maxima are displaced toward the long-wave region and the electroconductivity of the solutions is considerably higher (Table 9). This data indicate that the metal-carbon bond in barium compounds (in ethereal media) is less polar than in alkali metal compounds and that DME solvates barium counterion much stronger than THF. Both these conclusions correlate with the data given above on the microstructure of polymers formed by organobarium initiators.

The Walden product (molar conductance × relative viscosity of solution) in both solvents shows little temperature dependence in the range from 50 to -60°C for DME and up to -90°C for THF (Fig. 3). Hence no sharp change in the solvation degree of barium cation occurs in this temperature range.

TABLE 9. The Spectra and Conductancies of some Di- and Triphenylmethyl Compounds (25°C)

Compound	Solvent	λ_{max} (mμ)	Λ^a [cm^2/(ohm)(mole)]	Refs.
DPhELi	THF	490	-	25
DPhENa	THF	470	-	10
DPhEBa	THF	445	0.15	-
DPhEBa	DME	460	2.2	-
TrLi[b]	THF	500	-	26
Tr_2Ba[b]	THF	455	1.1	-
TrLi[b]	DME	500	-	27
Tr_2Ba[b]	DME	475	14	-

[a] Concentration of active centers, 1×10^{-3} mole/liter.
[b] $Tr = (C_6H_5)_3C$.

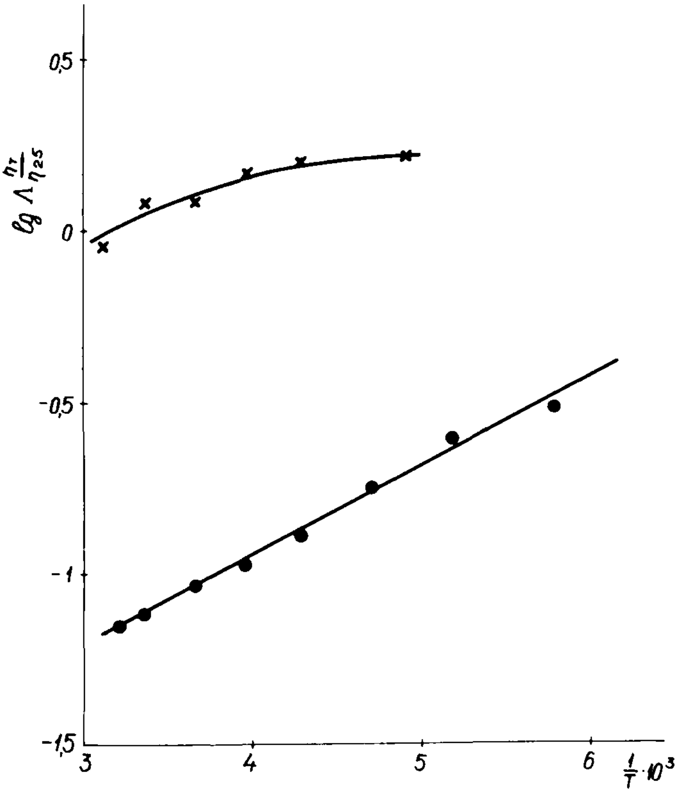


FIG. 3. Temperature dependence of conductivity of organobarium compounds in DME (×) and in THF (○).

Study of the concentration dependence of electroconductivity shows that solutions of organobariums with monofunctional anions (Tr_2Ba and bistetraphenylborate Ba) in the 10^{-4} to 10^{-5} mole/liter concentration range follow the Ostwald dilution law as expressed in terms of conductance:

$$\frac{1}{\lambda} - \frac{1}{\lambda_\infty} = \frac{c\lambda}{K_{diss}\,\lambda_\infty^{\ 2}} \qquad (1)$$

[where λ is the molar conductance in $cm^2/(ohm)(mole)$, c is the concentration in moles/liter, λ_∞ is the limiting conductance at infinite dilution] and give linear plots in $(1/\lambda)$ vs $c\lambda$ coordinates (Figs. 4 and 5).

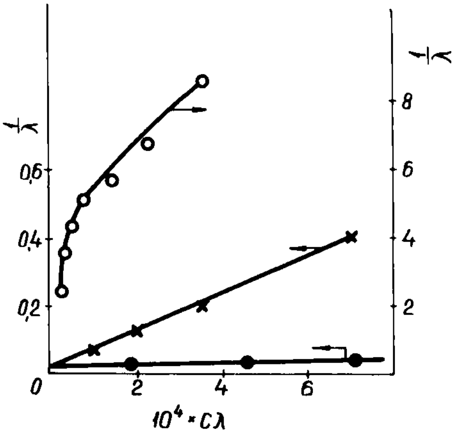


FIG. 4. $1/\lambda$ vs $c\lambda$ plots for organobariums in THF at 25° C: $[(C_6H_5)_4B]_2$ Ba (●), $[(C_6H_5)_3C]_2$ Ba (×), and Ba-DPhE (○).

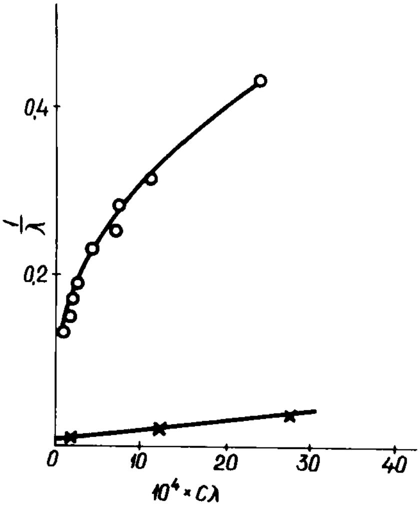


FIG. 5. $1/\lambda$ vs $c\lambda$ plots for organobariums in DME at 25° C: $[(C_6H_5)_3C]_2$ Ba (×), and Ba-DPhE (○).

The λ_∞ values for Tr_2Ba in both solvents and for $Ba[B(C_6H_5)_4]_2$ in THF are close to 70 cm^2/(ohm)(mole). The linear form of $(1/\lambda)$ vs $c\lambda$ plots and comparison of λ_∞ values with known values of λ_- {in THF, 41 cm^2/(ohm)(mole) for triphenylmethyl anion [28] and 40 cm^2/(ohm)(mole) for tetraphenylborate anion [29] } indicate that, in the concentration range mentioned above, organobarium compounds behave as 1-1 electrolytes and dissociate only by the first step:

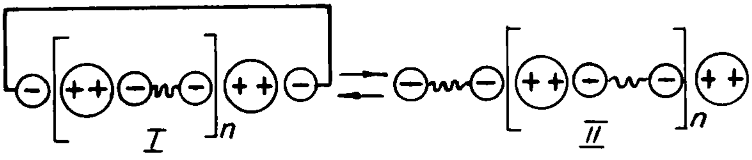
$$BaR_2 \overset{K_{diss}}{\rightleftharpoons} BaR^+ + R^- \tag{2}$$

From the results obtained, the following values of K_{diss} (at 25°C) were calculated: Tr_2Ba in THF, 3.6×10^{-7} mole/liter; in DME, 3×10^{-5} mole/liter; $Ba[B(C_6H_5)_4]_2$ in THF, 3.6×10^{-5} mole/liter.

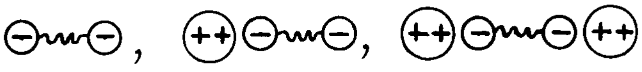
On the other hand, the concentration dependence of electroconductivity for Ba-DPhE in both solvents does not correlate with Eq. (1). The corresponding plots are not linear even at concentrations below 10^{-5} mole/liter (see Figs. 4 and 5), the conductance of Ba-DPhE solution being always considerably lower than that of Tr_2Ba.

The fact that monofunctional compounds comply with Eq. (1) indicates that the unusual behavior of Ba-DPhE cannot be explained by triple-ions formation but is due to the specific structure of bifunctional organobariums.

Indeed, as noted previously [2, 7], compounds with bifunctional anions and bivalent counterions should form in solutions a sort of cyclic aggregates (I), where the number of units n in a cycle is determined by the flexibility of the hydrocarbon part of molecule between the carbanions.



At the first stage of dissociation, aggregates I form zwitterions (II) that may disproportionate into current-carrying species, dianions and dications. These complex linear species may further dissociate down to the simplest types of particles [in accordance with Eq. (2),



free metal cations are not formed in the system]. Thus low electroconductivity of Ba-DPhE is due (1) to the fact that half of the dissociation products are zwitterions that do not contribute to the electroconductivity of the system, and, (2) to the fact that the current-carrying complex species are considerably less mobile than the corresponding monofunctional ones. The nonlinear form of $(1/\lambda)$ vs $c\lambda$ plots is explained by the fact that linear ionic aggregates dissociate into smaller species with a decrease of concentration and, consequently, the value of λ_∞ in Eq. (1) is not constant but gradually increases with dilution.

Living polymers initiated by Ba-DPhE also exhibit certain peculiarities connected with the specific structure of bifunctional organobariums. The conductometric study of butadiene polymerization in THF initiated by Ba-DPhE shows that after the monomer addition the resistance of the solution in the cell, as expected, increases rapidly due to conversion of the initiator into less dissociated polybutadiene carbanions (Fig. 6). However, then the resistance of the system starts to drop, although the viscosity gradually increases as the polymerization proceeds. It was shown by spectroscopy that the initiation step is completed when the system reaches maximum resistance, and from there on only butadienyl active centers are present in the system. Such a phenomenon is apparently due to the fact than an increase of chain length of cyclic aggregate (I) causes an increase of its dissociation constant into linear zwitterions [10, 30]. The other equilibria are displaced accordingly and the total number of current-carrying particles in the system increases.

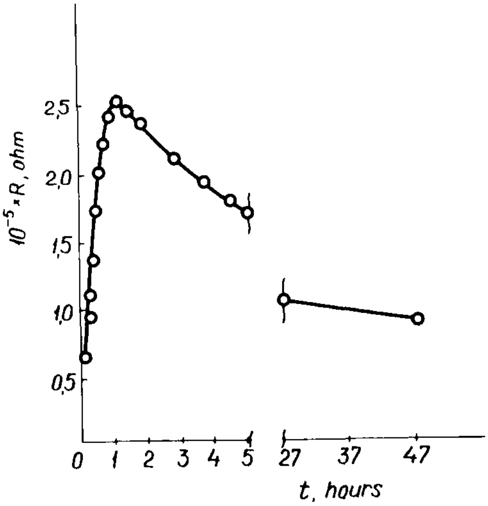


FIG. 6. The change of resistance during butadiene polymerization initiated by Ba-DPhE in THF at 25°C.

The viscosity of the system continuously grows during polymerization initiated by monofunctional Tr_2Ba (as well as by usual initiators based on alkali metals) due to the combined increase of concentration and of the molecular weight of the polymer. However, during styrene polymerization initiated by bifunctional Ba-DPhE in THF, the viscosity of the system reaches a maximum at a conversion of 90 to 95% and then noticeably drops. The specific viscosity of the living polymer at the end of the process is 2 to 3 times higher, and the maximum viscosity is 3 to 5 times higher than the viscosity of the polymer killed. Corresponding data are presented in Fig. 7, which is plotted in relative coordinates (abscissa, ratio of reaction time to the time needed to reach 90% conversion; ordinate, ratio of specific viscosity of the living polymer to maximum of specific viscosity).

The decrease of viscosity may be explained by the fact that as the size and, consequently, the flexibility of the polymer chains increases, the macromolecules are gradually redistributed between the cyclic aggregates. As a result of this process, the number of cycles in the system increases and their dimensions decrease. This effect becomes predominating at the end of the process when chain growth is nearly completed.

The estimation of molecular weights of living polymers (by viscometry) indicates that the number n of polymer chains in a macrocycle varies from 5 to 7 in the middle stage to 3 to 4 at the end of the process.

In hydrocarbon solvents the effect is much more pronounced.

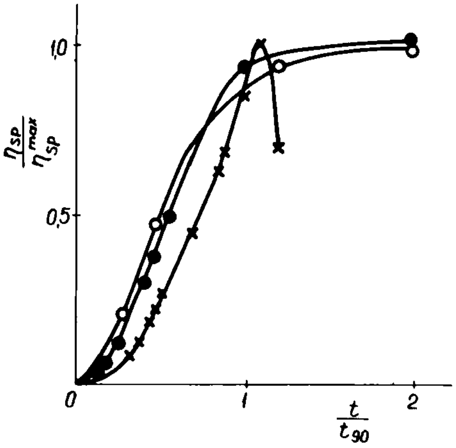


FIG. 7. The change of specific viscosity of living polystyrene in THF at 25°C initiated by Na-anthracene (●), $[(C_6H_5)_3C]_2$ Ba (o), and Ba-DPhE (×).

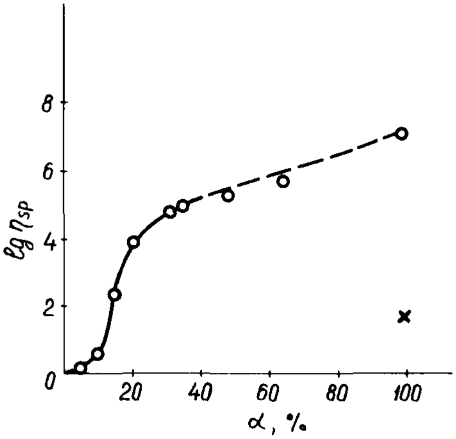


FIG. 8. The change of viscosity during butadiene polymerization by Ba-DPhE in benzene at 25°C: viscosity of deactivated polymer (×).

Thus viscosity of the system during polymerization of butadiene in benzene at room temperature increases very rapidly and the system turns into a jellylike mass by 15 to 20% conversion (polymer content, 10 to 15 g/liter). However, destruction of active centers provides a sharp drop of viscosity (by 3 to 5 orders of magnitude) and the molecular weight of the isolated polymer is near the theoretical value (Fig. 8). One should take into account, when considering the association of organobariums in benzene, that along with formation of specific aggregates of type (I) due to coupling of the bivalent counterion with two-ended hydrocarbon chains, association is possible due to formation of multicenter metal-carbon bonds (similar to association of organolithium compounds).

The results presented here lead to the conclusion that when the mechanisms of anionic polymerization processes in which alkaline earth metals take part are studied, one should bear in mind that basically new effects may appear that have no analogies in systems containing alkali metals.

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