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I. Ya. Poddubnyi, E. G. Erenburg, E. P. Chernova-Ivanova,

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Figure 1

Figure 1: Figure 1

Abstract

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ON THE EFFECT OF ASSOCIATION OF POLYBUTADIENE MACROMOLECULES IN VARIOUS SOLVENTS

(Presented by Academician V. A. Kargin on 18 IX 1962)

At present, a comparatively small number of works are known that are devoted to the study of the molecular weight and dimensions of polybutadiene macromolecules ($^{1-4}$). This circumstance is apparently explained by the specific difficulties of working with these polymers, associated with their insufficient stability and the irregularity of the structure of the molecular chain. We undertook a study, by the light-scattering method, of the dimensions of polybutadiene macromolecules of different structure–strongly branched potassium-butadiene rubber and linear cis-polybutadiene obtained in the presence of a complex catalyst.

In carrying out this work, however, we encountered a number of facts apparently indicating aggregation of dissolved macromolecules both in solvents close to thermodynamically ideal ($A_2 \leq 0$) and in relatively good solvents ($A_2 > 0$). The present work presents the results of an investigation of this effect. The molecular weights $\overline{M}_w$ and root-mean-square radii of polymer coils were determined on a polarization nephelometer and a photometric apparatus described by V. N. Tsvetkov and co-workers (^{5}). The polarization nephelometer was calibrated using a series of pure liquids (benzene, toluene, carbon disulfide) with known relative scattering intensity ($^{6-8}$). For all fractions studied (^{9}), the number-average molecular weight $\overline{M}_n$ was also determined by the osmotic method (^{10}) (in a benzene–isoamyl alcohol mixture, 6 : 4) and the intrinsic viscosity $[\eta]$.

Fig. 1. Dependence of Hc/R''_{90} on concentration for fraction 2a of sample B-2 in methyl ethyl ketone at different temperatures

The results obtained in measuring light scattering of fractions of potassium-butadiene polymers (samples B-1 and B-2) in methyl ethyl ketone* over a wide temperature interval preceding phase separation are presented in Fig. 1 and in Table 1.

As can be seen from the data presented, the molecular weights of the fractions increase strongly with decreasing temperature. It is obvious that at temperatures close to the θ-temperature, association of dissolved macromolecules takes place, preceding phase separation; moreover, the size of the molecular aggregates increases as the temperature is lowered. Only at a temperature of $\sim 60^\circ$ does the ratio $\overline{M}_k/\overline{M}_n$ assume values usual for the fractions obtained by us. The value of the Flory constant $\Phi' = M[\eta]/(r^2)^{3/2}$, obtained for this case, is quite satisfactory if one takes into account that the fractions studied were noticeably branched.

* According to data on the dependence of precipitation temperature on molecular weight, methyl ethyl ketone is a θ-solvent for this polymer at a temperature of 42° (^{11}).

Table 1

Dimensions and molecular weight of macromolecules of potassium-butadiene rubber at different temperatures

Fraction No.	T, °C	$M' \cdot 10^3$ (without allowance for asymmetry)	$\overline{M}_w \cdot 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$[\eta]$	$(\overline{r^2})^{1/2}$, Å	$\Phi' \cdot 10^{-21}$
B-1	46	1,660	2,260	2.3	1.53	450	32
2	48	1,060	1,390	1.4	1.56	410	31
($\overline{M}_n = 980 \cdot 10^3$)	61	890	1,100	1.1	1.73	370	43
B-2	38	2,000	2,700	3.0	–	430	–
2	48	1,000	1,240	1.4	–	370	–
($\overline{M}_n = 910 \cdot 10^3$)	60	830	1,000	1.1	–	360	–

It is interesting that when the molecular weight increases by a factor of 2–3, only a slight increase in the geometrical dimensions of the aggregates is observed. Apparently, association of molecules is accompanied by substantial compaction of the molecular coils; therefore approximation of the macromolecule by a hard-sphere model may prove to be more correct.* This is probably also connected with the fact that $A_2 = 0$ over the entire temperature range. The values of Φ' (see Table 1) at low temperatures are not indicative, since association of polymer molecules should lead to considerable polydispersity of the fractions. Introducing a correction for polydispersity would give high values of Φ', characteristic of the hard-sphere model.

Table 2

Dimensions and molecular weight of macromolecules of cis-polybutadiene in various θ-solvents

Fraction No.	Solvent	T, °C	$\overline{M}_w \cdot 10^3$	$\overline{M}_w/\overline{M}_n$	$[\eta]$	$(\overline{r^2})^{1/2}$, Å	$\Phi' \cdot 10^{-21}$	$A_2 \cdot 10^5$
D-2	Dioxane	21	1,040	2.1	1.45	430	19	2.7
1	Dioxane	25	1,050	2.1	–	430	–	4.6
($\overline{M}_n = 500 \cdot 10^3$)	Dioxane	30	1,100	2.2	–	460	–	6.7
($\overline{M}_n = 500 \cdot 10^3$)	Dioxane	40	1,100	2.2	–	460	–	10.0
D-3	Dioxane	20	1,500	3.9	1.48	570	12	0
2	Methyl butyl ketone	25	700	1.8	1.37	410	14	8.0
($\overline{M}_n = 390 \cdot 10^3$)	Methyl butyl ketone	50	750	1.9	–	450	–	15.0

For the purpose of further studying the association effect, we investigated solutions of butadiene polymers of more regular structure (samples D-2 and D-3) in two θ-solvents—dioxane ($\theta = 20^\circ$) and methyl butyl ketone ($\theta = 23^\circ$). As can be seen from Table 2, the polymers studied are also associated in solution; however, in this case the association effect does not decrease with increasing temperature (despite the presence of a temperature dependence of A_2) and doubles on going from methyl butyl ketone to dioxane.**

In connection with these results it was of interest to study the behavior of the investigated polymers in solvents of different chemical nature, far from the θ-point. The solvents studied as such were oc-

* Calculation of $(\overline{r^2})^{1/2}$ according to this model for the dimensions observed in our experiment practically does not change the results.

** It is interesting to note that the molecular weights of these fractions, determined by sedimentation and diffusion in a hexane-heptane mixture (1:1), proved to be 800,000 and 875,000.

Table 3

Dimensions and molecular weight of potassium-butadiene rubber macromolecules (B-1) in various solvents

Fraction No.	$\overline{M}_n$	Solvent	$M' \cdot 10^3$	$\overline{M}_w \cdot 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$[\eta]$	$(\overline{r^2})^{1/2}$, Å	$\Phi' \cdot 10^{-21}$	$A_2 \cdot 10^{-4}$
26	708	Dichloroethane	600	1,260	1.8	2.9	690	11.3	3.5
26	708	Decane	650	1,500	2.1	3.27	775	10.6	3.6
3	720	Octane	630	1,400	1.9	3.04	755	9.9	1.6
3a	850	»	1,100	3,200	3.8	3.56	940	13.0	3.0
5a	650	»	1,100	1,700	2.6	–	610	–	3.4
6a	470	»	620	980	2.1	2.52	510	18.7	3.3
6a	470	Octane 70°	620	980	2.1	–	510	–	3.5
26	708	Chloroform	630	830	1.17	4.74	470	65	11
6a	470	»	480	580	1.23	4.0	350	47	5.0
3	720	Cyclohexane	590	900	1.25	4.6	500	32	10
3	720	Octene	590	1,060	1.47	3.76	600	17.7	1.8

octane, decane, dichloroethane, octene, cyclohexane, and chloroform (measurements were carried out at room temperature). The results are presented in Table 3 and in Figs. 2–3. As can be seen from the data given, one may distinguish a group of solvents in which the values of the molecular weights and dimensions of the dissolved particles are clearly overestimated—octane, decane, and dichloroethane. In this group the ratio $\overline{M}_w/\overline{M}_n$ varies in the range 1.8–2.6, whereas in chloroform and cyclohexane it is equal to 1.17–1.25. The ratio $(\overline{r^2}/\overline{r^2}_{\text{sv. vr}})^{1/2}$ for this group of solvents is also considerably higher (3–3.5) than for chloroform and cyclohexane (1.8–2.2).

Fig. 2. Dependence of Hc/R''_{90} on concentration for fraction 6a of sample B-1 in chloroform (a) and in octane (b –20°; v –70°)

Thus, the data presented indicate that the effect of association of macromolecules in solutions of butadiene polymers also occurs when good solvents are used. In this case association is accompanied by a strong increase in the dimensions of the aggregates, independent of temperature (see Table 3, fraction 6a), in contrast to the effect observed at a temperature close to the θ-point. Apparently, association in good solvents has a different character and is possibly connected with the presence of aggregates in the polymer mass. The phenomenon of association of macromolecules in comparatively good solvents has been observed by a number of authors for various polymer-solvent systems ($^{12-15}$). At the same time, the nature of the phenomenon in many cases remains unclear. In a number of works, the association of macromolecules is explained by the existence of specific interaction forces—the presence of hydrogen bonds, substantial dipole moments, etc. (^{13,14}). However, it is difficult to suppose that the action of such forces determines the behavior of such polymers as polyethylene (^{12}), natural rubber (^{15}), and the polybutadiene investigated by us. It seems probable that the tendency

Fig. 3. Dependence of $1/(z-1)$ on concentration for fraction 6a of sample B-1 in chloroform (a) and in octane (b –20°; v –70°)

the tendency toward association of the polymers we investigated is explained by the presence of a considerable number of strongly polarizable double bonds in the molecular chains. In any case, irrespective of the nature of the observed effect, the data we have obtained undoubtedly show that, when working with butadiene polymers, the choice of a solvent that ensures reliable data on the sizes and molecular weights of macromolecules must be approached with extreme caution.

It is possible that it is precisely the association effect that explains the fact that the equation for the dependence of intrinsic viscosity in benzene on molecular weight, obtained for polybutadienes with a high content of cis units by Cooper et al. (^{2}) on the basis of light-scattering measurements in cyclohexane, differs very substantially from the corresponding equation for the same polymers obtained by Danusso et al. (^{2}) on the basis of osmotic measurements in benzene and isobutyl acetate: at the same intrinsic viscosity, the molecular weights calculated from Danusso' s equation prove to be twice as small as those calculated from Cooper' s equation.

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