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# Viscoelasticity of Solutions and Blends of Narrow Molecular-mass Distribution Polymers<sup>†</sup>

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A study has been made into the initial values of viscoelasticity parameters that characterized the binary polymer systems containing 1,4-polybutadienes, produced by anionic polymerization and having a relatively narrow molecular-mass distribution ( $M_w/M_n \leq 1.1-1.2$ ). These binary systems contained polymers with  $M/M_c > 1$ . On the one hand, the latter ratio approached 2, on the other, they contained high-molecular components with  $M/M_c$  exceeding 300. The binary systems contained the high-molecular components in the amount of 0.1 to 20% which permitted determining the intrinsic characteristic values of viscosity  $[\eta]$  and elastic coefficient  $[A_G^0]$ . It has been found that from the above-mentioned sample of PB two types of the systems can be formed:

- 1) solutions of a high-molecular-mass polymer in a low-molecular one;
- 2) blends of polymer with well developed entanglement network.

In the first case the intrinsic values of the viscosity and the coefficient of elasticity are presented in the following form:

$$[\eta] \sim M_1^{-\alpha} M_2^{\beta} \quad \text{as well as} \quad [A_G^0] \sim M_1^{-\gamma} M_2^{\delta}$$

where  $M_1$  and  $M_2$  are molecular masses of the solvent and solute.

## INTRODUCTION

One of the most important problems in polymer rheology today is the description of the viscoelastic behaviour of high-molecular-mass polymers over a wide range of loading rates and compositions. It is well known<sup>1,2</sup> that

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the specific features of their viscoelastic behaviour are primarily determined by the molecular-mass (MM) and the molecular-mass distribution (MMD).

The dynamic method is particularly convenient and informative for investigation of the polymers. In this method the behaviour of a system is examined under conditions of periodic small-amplitude deformation. The use of a sufficiently wide range of frequencies makes it possible to trace the specific behaviour of the systems over a very wide range of their properties.

In the laboratory of polymer rheology of the Institute of Petrochemical Synthesis, USSR Academy of Sciences, polymer blends have been investigated since the early seventies, more specifically, 1,4-polybutadienes (PB) with a narrow molecular-mass distribution (MMD). The dynamic method was used to study PB blends in a wide range of compositions and temperatures.<sup>3,4</sup>

It has been shown that if the high-molecular component being present in an amount of up to 80% and at not very low temperatures, the blends feature a loss modulus maximum in the same frequency range where the maximum of the low-molecular component is observed. As the temperature decreases, the loss modulus-versus-frequency curve features a plateau covering the entire frequency range between the maxima of both components. Hence, as the temperature decreases, the individuality of the components in the blend becomes less manifest, which is due, primarily, to the lower activity of the high-molecular component. On the other hand, following the introduction into the blend of the low-molecular component, the loss modulus maximum of the high-molecular component degenerates, and as the content of the latter becomes relatively low (down to 20%), the transition of the high-molecular component to the high-elastic state manifests itself only in the changing trend of the  $G'(\omega)$  and  $G''(\omega)$  curves at low frequencies. In the range of frequencies corresponding to the loss modulus maximum of the high-molecular component the addition to the latter of the low-molecular component approximately to 50% results in that the values of  $G'$  and  $G''$  become less than twice as low.

As opposed to low-molecular liquids, addition of a small amount of the low-viscosity (low-molecular) component to the high-molecular one affects the rheological characteristics of the latter but slightly, while addition of the high-molecular to the low-molecular component produces a highly tangible effect.

It is precisely this finding reported elsewhere<sup>5,6</sup> that has prompted us to embark upon this research.

The other problem that we tried to solve in this work was associated with the theory proposed by Pokrovsky *et al.*<sup>7-9</sup>

It has substantiated the concept of microviscoelasticity, according to which the motion of macromolecules among other similar ones is considered to be equivalent to the movement in a viscoelastic rather than viscous medium. The characteristics of this effectiveness of a viscoelastic medium (microviscoelas-

ticity) do not coincide with those of the viscoelasticity of the system as a whole (macroviscoelasticity).

Experiments with dilute solutions of the high-molecular component make it possible to determine the intrinsic characteristic values of viscosity and high-elastic coefficient

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_2 - \eta_1}{\eta_1 \cdot C}; \quad [A_G^0] = \lim_{c \rightarrow 0} \frac{A_{G_2} - A_{G_1}}{A_{G_1} \cdot C}$$

where  $\eta_2$  and  $\eta_1$  are the viscosities of the solute and solvent, respectively;  $A_{G_2}$  and  $A_{G_1}$  are the high-elastic coefficients of the solute and solvent, respectively.

We had to determine which intrinsic characteristic values of viscosity and elastic coefficient  $[\eta]$  and  $[A_G^0]$  depend on the MM of the solvent and the added high-molecular polymer, since according to the theory,<sup>10</sup> in the case of dissolution of the high-molecular polymer in the lower-molecular one exhibiting viscoelasticity  $[\eta] \sim M_1^{-\alpha} M_2^{+\beta}$  and  $[A_G^0] \sim M_1^{-\gamma} M_2^{\delta}$  (where  $M_1$  is the MM of the solvent,  $M_2$  is the MM of the additive).

## OBJECTS AND THE METHODS OF INVESTIGATION

We have studied polybutadienes prepared by the method of anionic polymerization with relatively narrow MMD ( $M_w/M_n \leq 1.2$ ). The data for the polymers and the viscosities of the solvents used are listed in Table I. The samples contained almost the same amount of cis- and trans-isomeric structures (about 45%); the content of 1,2 units was 8–10%. The molecular masses of the samples are as follows:  $M = 10^4$ ,  $10^5$ ;  $1 \times 10^5$ ;  $5 \times 10^5$  and  $1 \times 10^6$ . The binary solutions of the indicated samples were prepared by their joint dissolution in benzene and by addition of a high-molecular-mass

TABLE I  
Characteristics of 1,4-polybutadienes

Polymer and solvent	Molecular mass	$[\eta]$ 25°C Toluene	$\eta_0$ , Pa·s	$M_w/M_n^a$
1,4-PB	$1 \times 10^4$	0.30	$2.52 \times 10^2$	1.1
	$1 \times 10^5$	1.32	$3 \times 10^6$	1.15
	$5 \times 10^5$	3.95	$1.5 \times 10^9$	1.20
	$1 \times 10^6$	7.05	$3.17 \times 10^{10}$	1.17
<i>n</i> -hexadecane	$2.26 \times 10^2$	—	$3.45 \times 10^{-2}$	—
$\alpha$ -methyl-naphthalene	$1.42 \times 10^2$	—	$2.5 \times 10^{-2}$	—

<sup>a</sup>The MMD was determined by gel permeation chromatography using a "Water-200" chromatograph on styrogel columns with permeabilities of  $3 \times 10^3$ ,  $10^4$ ,  $3 \times 10^5$  and  $10^7$  Å, the elution rate being 1 ml/mn; tetrahydrofuran was used as the solvent.

TABLE II  
The compositions of solutions of 1,4-polybutadiene

Solutions series	Molecular mass $M_w$		Additive concentration, $C$ wt %									
	solvent:	additive:	0.125	0.25	0.5	1	3	5	7	10	15	20
A	$1 \times 10^4$	$1 \times 10^5$	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	—	A <sub>5</sub>	—	A <sub>6</sub>	—	A <sub>7</sub>
B	$1 \times 10^4$	$5 \times 10^5$	—	—	B <sub>1</sub>	B <sub>2</sub>	—	B <sub>3</sub>	B <sub>4</sub>	B <sub>5</sub>	B <sub>6</sub>	—
C	$1 \times 10^4$	$1 \times 10^6$	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	—	C <sub>5</sub>	—	C <sub>6</sub>	—	C <sub>7</sub>
D	$1 \times 10^5$	$1 \times 10^6$	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>4</sub>	D <sub>5</sub>	D <sub>6</sub>	—	—	—	—
E	$1 \times 10^5$	$5 \times 10^5$	—	—	E <sub>1</sub>	E <sub>2</sub>	—	E <sub>3</sub>	—	—	—	—

component to a low-molecular-mass component. The compositions of the solutions are given in Table II.

The experiments were carried out on a "mechanical spectrometer" designed for dynamic investigations<sup>4</sup> which operates in the regime of forced nonresonance vibrations in the range of circular frequencies  $\omega$  from  $10^{-3}$  to  $3 \times 10^3$   $\text{sec}^{-1}$ . The values of the components of the complex dynamic shear modulus (the storage modulus  $G'$  and the loss modulus  $G''$ ) were determined.

## RESULTS AND DISCUSSIONS

Figures 1–3 show the frequency dependences of the storage ( $G'$ ) and loss ( $G''$ ) moduli for solutions based on polybutadiene with  $M = 1 \times 10^4$  (the solute) to which were added high-molecular mass PB with  $M = 1 \times 10^5$ ,  $5 \times 10^5$ ,  $1 \times 10^6$ . The ratio of the molecular mass of the solvent to that of the added components were 10, 50 and 100 respectively. The initial viscosities of the added components differ by  $1.2 \times 10^4$ ,  $7 \times 10^5$  and  $1.25 \times 10^7$  times. In Figure 1 the first curve refers to the solute and the curves 2–8 refer to the following concentrations of the added component: 0.125, 0.25, 1.0, 5.0, 10 and 20% by weight.

The curves of  $G'$  and  $G''$  vs.  $\omega$  in the figures for the solute of PB with  $M = 1 \times 10^4$  deserve attention in the first place. Over the entire range of frequencies studied the curves of  $G'$  and  $G''$  versus  $\omega$  increase practically monotonously (a slight inflection is observed only in the curves of  $G'$  vs.  $\omega$ ). The observed mode of variation of the dynamic characteristics is typical of polymers with a rather low molecular mass, whose rubberlike properties are very weak. It is well known that this is typical of polymers with  $MM \leq 5M_c$  where  $M_c$  is the critical value of molecular mass.<sup>11</sup> For PB the value of  $M_c$  is about 6000,<sup>12</sup> i.e., for a sample with  $M = 1 \times 10^4$  the ratio  $M/M_c$  is approximately equal to 2. Inspection of Figures 1–3 shows that depending on the molecular mass of the added component and its concentration there are

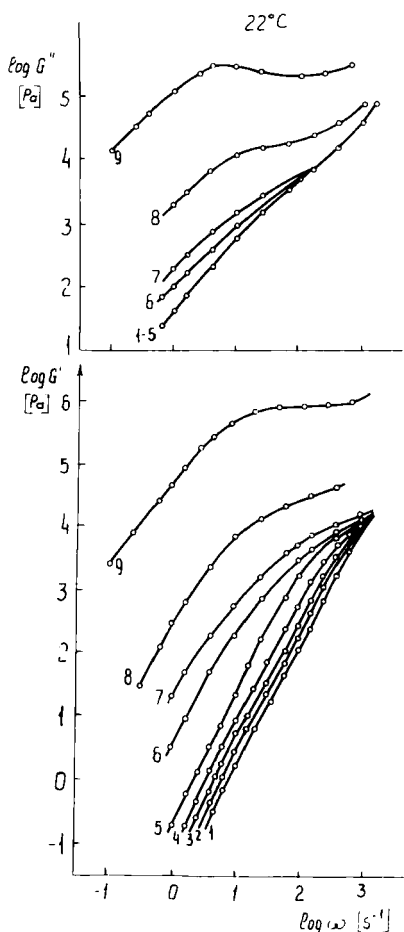


FIGURE 1 Frequency dependences of the moduli  $G'$  and  $G''$  for solutions of the series A. The curves 1–9 correspond to the following concentrations of the high-molecular-mass component, in %: 1, 0; 2, 0.125; 3, 0.25; 4, 0.5; 5, 1.0; 6, 5.0; 7, 10.0; 8, 20.0; 9, 100.

observed both qualitative and quantitative changes in the dependences shown. First, the terminal zone (the flow region) has been attained for all the dependences at low frequencies. Here the quantity  $G''$  is proportional to  $\omega$  and  $G'$  is proportional to  $\omega^2$ . In this region, one can readily calculate the values of the initial viscosity of the solutions

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega}$$

and the initial coefficient of elasticity.

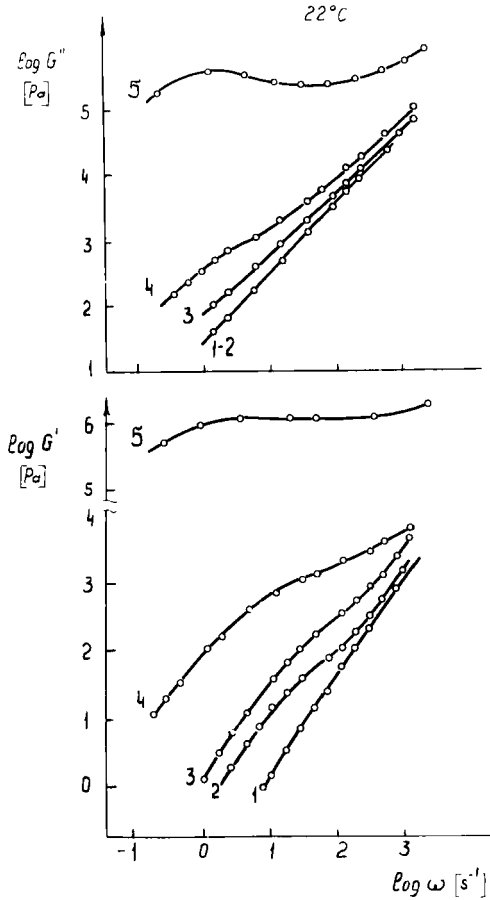


FIGURE 2 Frequency dependences of the moduli  $G'$  and  $G''$  for solutions of the series B. The curves 1-5 correspond to the following concentrations of the high-molecular-mass component, in %: 1, 0; 2, 0.5; 3, 1; 4, 5.0; 5, 100.

$$A_G^0 = \lim_{\omega \rightarrow 0} \frac{G'}{\omega^2}$$

It is well seen that the higher the ratio of the initial viscosities of the solute to the solvent, the more strongly the values of  $G'$  and  $G''$  in the terminal zone change with concentration, the most sensitive characteristic being the storage modulus. It is necessary to note that an especially sharp change in the properties is observed in the region of rather small concentrations (up to 1%) of the high-molecular-mass component added. The variations of the value of  $G'$  for solutions A, B, C with the change of the concentration from the initial value to 1% of the high-molecular-mass component added are, respectively, 1.2, 40

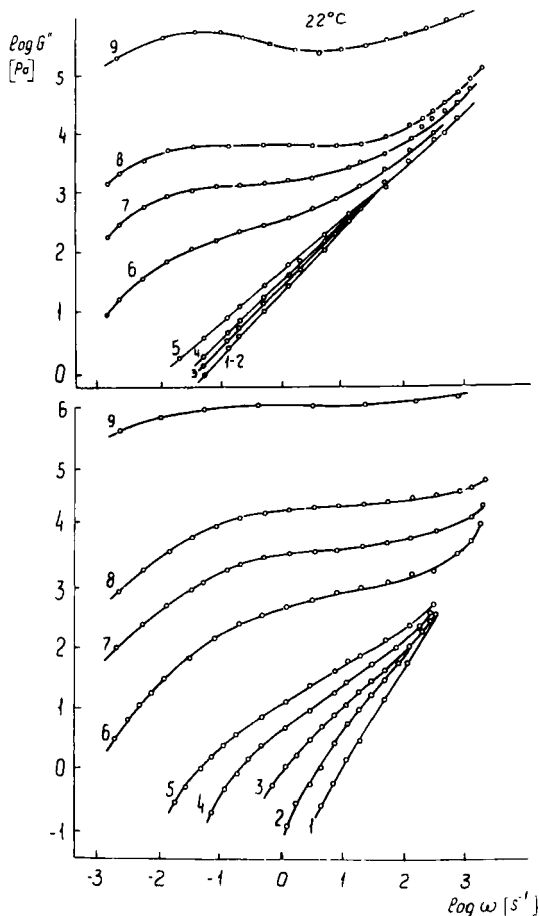


FIGURE 3 Frequency dependences of the moduli  $G'$  and  $G''$  for solutions of the series C. The curves 1–9 correspond to the following concentrations of the high-molecular-mass component, in %: 1, 0; 2, 0.125; 3, 0.25; 4, 0.5; 5, 1.0; 6, 5.0; 7, 10.0; 8, 20.0; 9, 100.

and 25,000 times. At the same time the values of  $G''$  change, respectively, by 1.2, 2.5 and 4 times, i.e., considerably less strongly.

Some typical results are presented in Figure 3. They correspond to the maximum difference in MM between the solvent and the added high-molecular component. As the concentration of the high-molecular component increases, the shape of the  $G'(\omega)$  curves changes so that in the region of concentrations above 5% the first signs of a plateau appear, while at the highest attained frequencies the beginning of a transition zone is observed. Note the sharp difference between  $G'$  and  $G''$  in the region of concentrations of up to 1%.



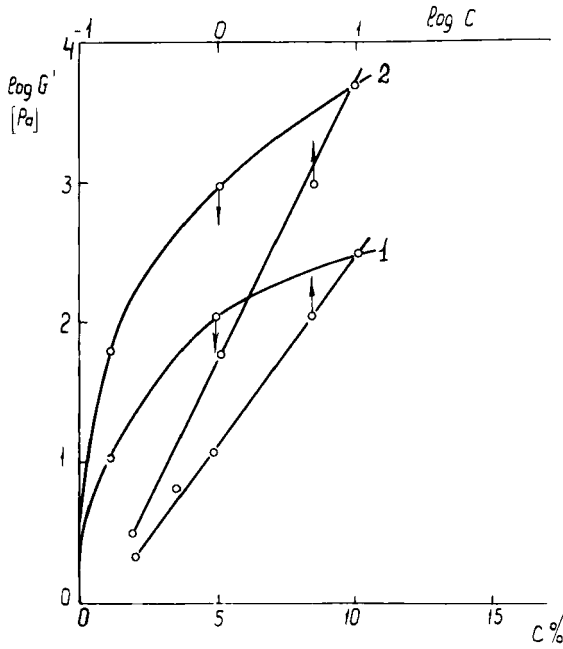


FIGURE 4 Dependence of the moduli  $G'$  on the concentration of solutions of series A(1) and series C(2) (at  $\omega = 10 \text{ s}^{-1}$ ).

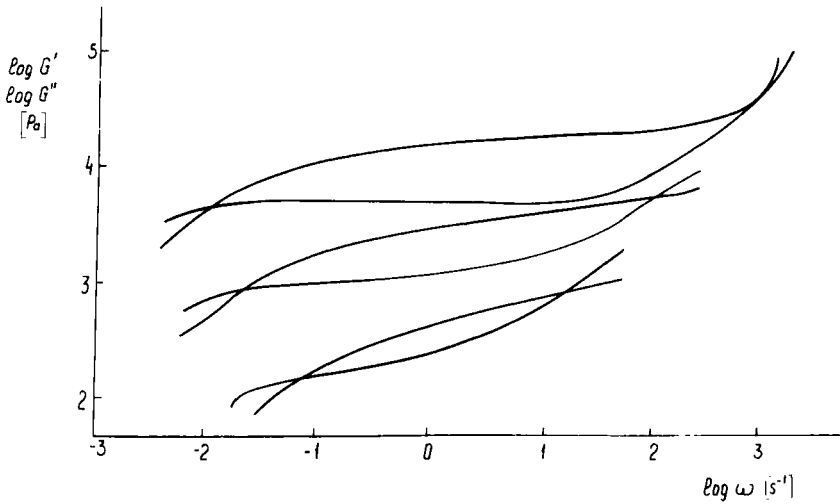


FIGURE 5 Determination of the length of the plateau for solutions of series C.

Interesting results have been obtained for the  $G'(C)$  curve at  $\log \omega = 1$  for solutions of the A and C series (Figure 4).

Assuming, in accordance with Figure 5, that the length of the plateau ( $\Delta\omega_{pl}$ ) is defined by the points of intersection of the  $G'(\omega)$  and  $G''(\omega)$  curves in the range of low ( $G''_M$ ) and higher ( $G''_H$ ) frequencies, while the value of  $G'_{pl}$  was taken at a middle point between points  $G''_M$  and  $G''_H$  we derive concentration dependences of these values, shown in Figure 6. Finally, the concentration dependence of the plateau height in the entire range of compositions (according to Refs. 3 and 4) is illustrated in Figure 7. As can be seen from Figures 4, 6 and 7 all the presented curves rise steeply in the region of low concentrations.

Consider now a series of curves (E) for a blend in which the solvent has  $MM = 1 \times 10^5$  and the added substances have  $MM = 1 \times 10^6$  (Figure 8).

Comparison of Figures 1 through 3 with Figure 8 reveals that the sensitivity of the solution properties is determined not by the ratio of MM and initial viscosities of the components but by their absolute values, the predominant role being played by the solvent properties, primarily by the value of ratio  $M/M_c$  and its initial viscosity.

From the results presented in Figures 1–3 and 8 it is seen that the variation of the viscoelastic characteristics of the polymer solutions as a function of the molecular mass of the low molecular and the added component and also of the

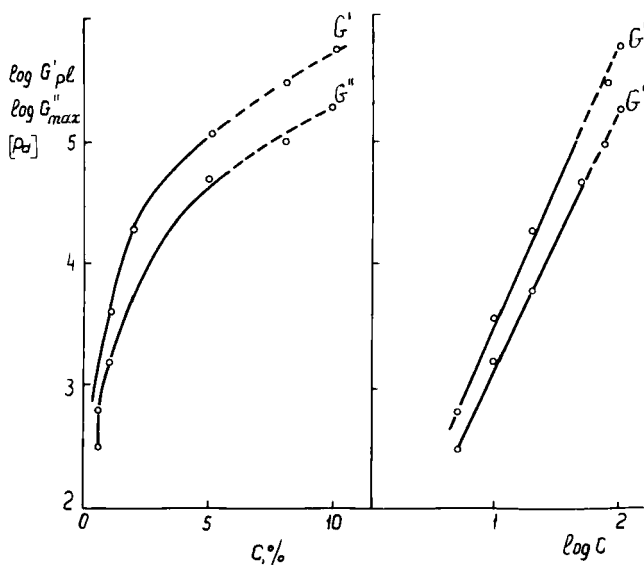


FIGURE 6 Dependence of the moduli  $G'$  and  $G''$  on the concentration of solutions of series C. Dashed line.<sup>3,4</sup>

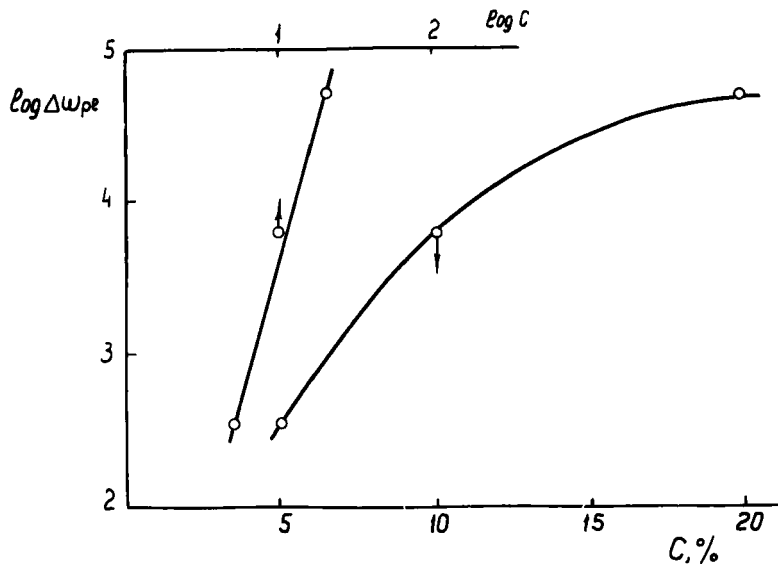


FIGURE 7 Dependence of the length of the plateau  $\Delta\omega_{pe}$  on the concentration of solutions of series C.

concentration is rather complicated. To elucidate the effect of the molecular mass of the solvent and of the molecular mass of the added component on the viscoelastic properties of solutions and to find out how the behaviour of the systems indicated differ from that of polymer solutions, we carried out measurements of the viscoelastic characteristics of solutions of polybutadienes with  $M = 1 \times 10^6$  in a good and a poor solvent, i.e.,  $\alpha$ -methylnaphthalene ( $\alpha$ -MN) and cetane, respectively (the ratio of the viscosities of these solvents is about 1.4). The results of these measurements are presented in Figure 9. It is clearly seen that the data obtained for solutions in different solvents are qualitatively similar (compare the curves 1–2 and 3–4). Quantitatively, in a poor solvent the initial viscosities are lower approximately by a factor of 3 for a 5% solution and by a factor of 10 for a 2% solution. This difference is in good agreement with the literature data,<sup>13</sup> from which it follows that for concentrated solutions the effect of the nature of solvent on the viscoelastic characteristics is practically insignificant.

Figure 10 presents the dependences  $G'(\omega)$  and  $G''(\omega)$  for solutions with different solvents but with the same content of the high-molecular-mass component. The curves 1–4 refer to the 5% content of PB with  $M = 1 \times 10^6$  in  $\alpha$ -MN, cetane, PB with  $M = 1 \times 10^4$  and PB with  $M = 1 \times 10^5$ . It is clearly seen that the molecular mass of the solvent has a decisive influence on the character of the dependences given: the strongest variations of the absolute

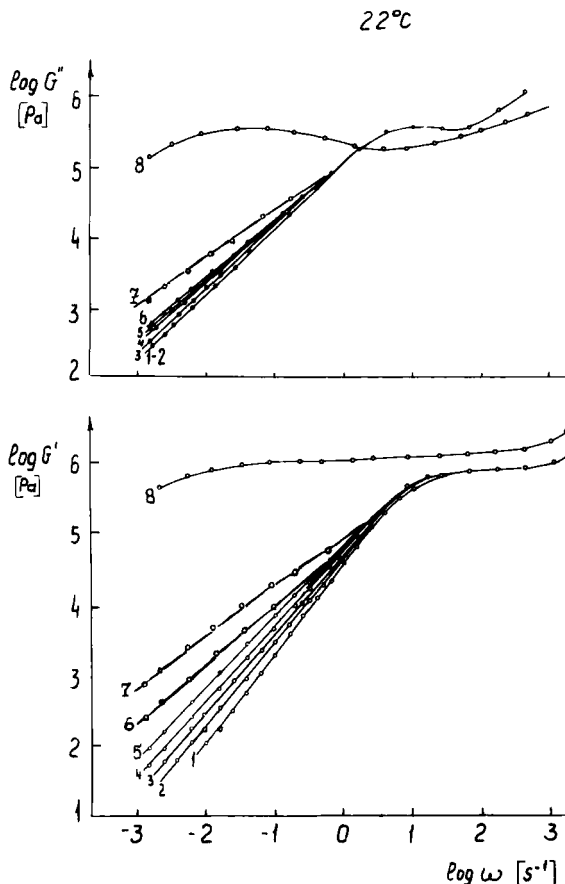


FIGURE 8 Frequency dependences of the moduli  $G'$  and  $G''$  for solutions of the series E. The curves 1–8 correspond to the following concentrations of the high-molecular-mass component, in %: 1, 0; 2, 0.125; 3, 0.25; 4, 0.5; 5, 1.0; 6, 3.0; 7, 5.0; 8, 100.

values of the dynamic characteristics are observed for the modulus of elasticity. Another important point is that the course of the curves is also changed, which is evidently associated with the nature of intermolecular interaction in these systems or with the ratio of the micro- and macroviscoelasticity, which is exactly the factor responsible for the intermolecular interaction. In the case of a purely viscous solute the curves resemble the Rouse curve.<sup>14</sup> In the case of a viscoelastic solute low molecular mass component the system behaves as a high polymer—the region of the fluid state is observed, a plateau appears and the transition to the leathery state occurs. As the molecular mass of the low molecular component increases the course of the dependences is

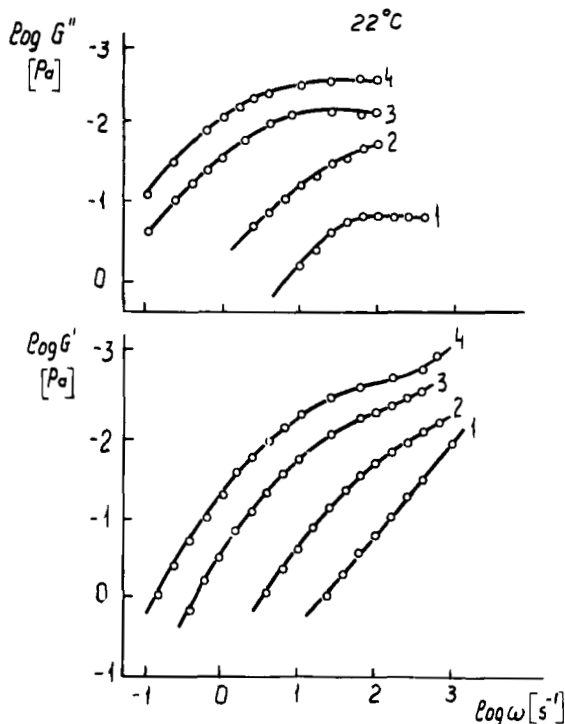


FIGURE 9 Frequency dependences of the moduli  $G'$  and  $G''$  for solutions of PB with  $MM = 1 \times 10^6$ . The curves 1-4 correspond to the following: 1, 2% in cetane; 2, 2% in  $\alpha$ -methyl-naphthalene; 3, 5% in cetane; 4, 5% in  $\alpha$ -methyl-naphthalene.

such as is observed for the polymer systems a point of inflection appears in the curves of  $G'(\omega)$  and  $G''(\omega)$  in the region of low frequencies and a maximum and a minimum occur, which coincide with the analogous minimum and maximum for PB with  $M = 1 \times 10^5$  in the region of high frequencies.

Figure 11 presents the dependences  $G'(\omega)$  and  $G''(\omega)$  for the case of PB with  $MM = 1 \times 10^4$  (the solvent, the curve 1) and 5% added amounts of PB with  $M = 1 \times 10^5$ ,  $5 \times 10^5$  and  $1 \times 10^6$  (the curves 2-4, respectively). It is seen distinctly that the largest difference in the course of the curves is observed for the dependence  $G'(\omega)$ ; this difference is the stronger, the higher the molecular mass of the added component. In the case of the added PB with  $M = 1 \times 10^6$  the dependences  $G'(\omega)$  displays a distinctly pronounced region of the rubbery state. The character of the dependences  $G''(\omega)$  in this case changes especially sharply.

Summing up the specific features of the behaviour of the above-indicated solutions of linear polymers in the region of small concentrations of one of the

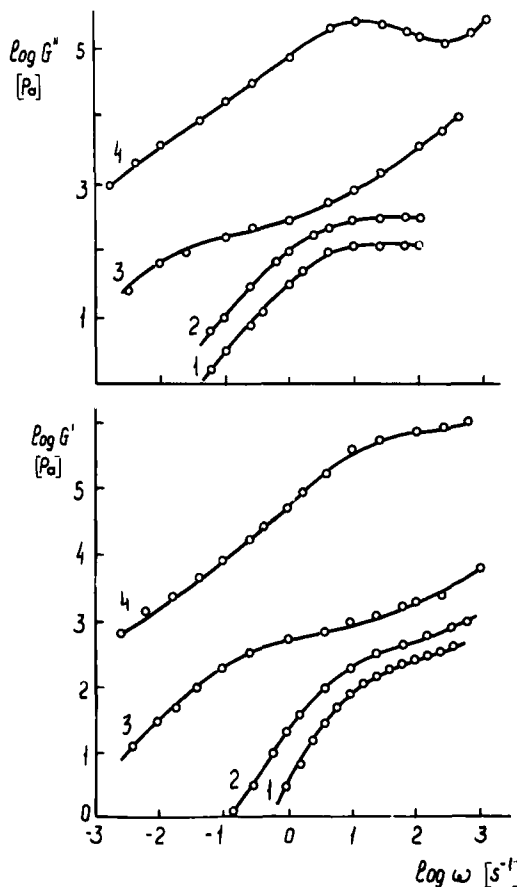


FIGURE 10 Variation of the moduli  $G'$  and  $G''$  with frequency for solutions with a 5% content of the high-molecular-mass component with  $MM = 1 \times 10^6$  as a function of the molecular mass of the matrix. The curves 1–4 correspond to: 1, cetane; 2,  $\alpha$ -methylnaphthalene; 3, PB with  $M = 1 \times 10^4$ ; 4, PB with  $MM = 1 \times 10^5$ .

components added, we can conclude that the viscoelastic characteristics differ strongly both qualitatively and quantitatively, especially in the terminal zone. These differences are determined in the first place by the characteristics of the solvent of the blend and, in the second place, by the molecular mass and concentration of the substances added. Note that the variation of the parameters indicated above is manifested in the first place, in the curves of the elastic modulus *vs.* frequency. From the literature it is known<sup>15</sup> that in the terminal zone (i.e., in the region of low frequencies or in the region of large relaxation times) as the molecular mass increases the elastic characteristic of the material, in particular, the initial coefficient of elasticity  $A_G^0$  varies very

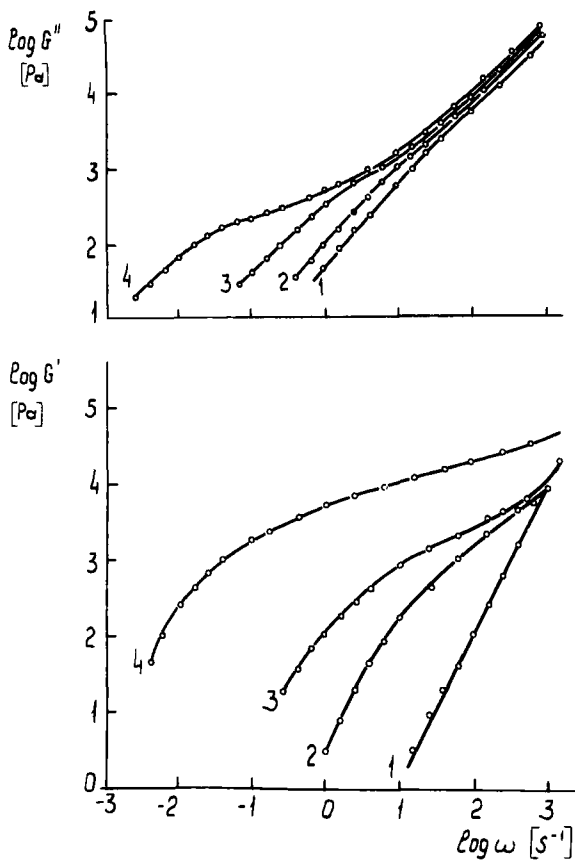


FIGURE 11 Variation of the moduli  $G'$  and  $G''$  with frequency for solutions based on PB with  $MM = 1 \times 10^4$  with a 5% content of the high-molecular-mass component as a function of the molecular mass of the added component. The curves 1–4 correspond to: 1, PB with  $MM = 1 \times 10^4$ ; 2,  $MM$  of added component  $1 \times 10^5$ ; 3,  $MM = 5 \times 10^5$ ; 4,  $MM = 1 \times 10^6$ .

sharply as a function of  $MM$ —proportionately to the seventh or eighth power,<sup>15</sup> i.e., much more sharply than does the initial viscosity. The experimental data presented here demonstrate that the elastic characteristic of the material in the terminal zone is also much more sensitive than the viscosity to the molecular composition of the system. This is especially well seen from a comparison of the curves of  $\eta_0(C)$  and  $A_G^0(C)$ .

Figure 12 presents the dependence  $\eta_0(C)$  for solutions of the polymers studied. In the case of the solutions in low viscosity solvents the initial viscosity varies proportionately to the second power of the concentration. This is in good agreement with the data obtained earlier<sup>15</sup> for solutions of PB with the

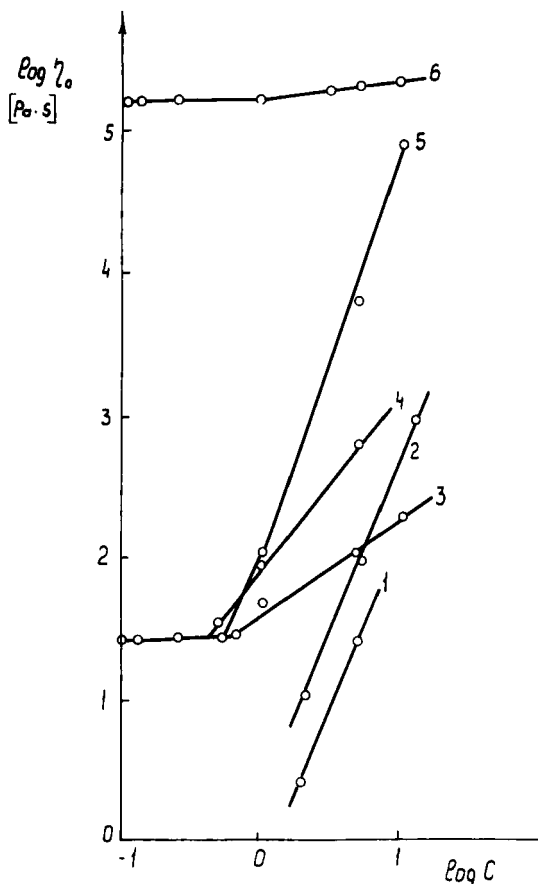


FIGURE 12 Dependence of the initial viscosity of solutions on the concentration of solutions of PB with: 1,  $MM = 1 \times 10^6$  in cetane; 2,  $\alpha$ -MN; 3, series A; 4, series B; 5, series C; 6, series E.

same  $MM$  in  $\alpha$ -MN (this is represented by two upper points in the curve 2, i.e., for the 10 and 15% concentrations). Two groups of the dependences  $\eta_0(C)$  may be differentiated for the polymer solutions.

The first group of dependences refer to solutions, for which the solvent has  $MM = 1 \times 10^4$  (the series A, B, C) and show that up to concentrations of about 0.5% the initial viscosity practically does not vary. On the other hand at  $C$  higher than 0.5% dependences of the  $MM$  added components—the slope changes from 0.7 to 3.0 depending on the initial viscosity of the added component. It should be noted that for concentrated polymer solutions the initial viscosity varies as a function of the concentration raised to the fifth power.<sup>15</sup>



The second group is given for solutions of the series E (the curve 6). In this case, the initial viscosity varies slightly with the concentration of the added component up to the values of  $C = 1\%$  and then increases in proportion to  $C^{0.3}$ .

Figure 13 shows the dependences of the initial coefficient of elasticity  $A_G^0$  as a function of the concentration of the high-molecular-mass component for solutions of types A, C and E.

It is clearly seen that the dependences  $A_G^0(C)$  are different. For the solution A this is a power dependence  $A_G^0 \sim C^{1.5}$ ; for solutions C and E this dependence has the break-points at concentrations of about 0.25–0.3% and 1%. At  $C > 0.5\%$ ,  $A_G^0 \sim C^{2\beta}$  where  $\beta$  is the exponent on the dependence  $\eta_0 = f(C)$ . It

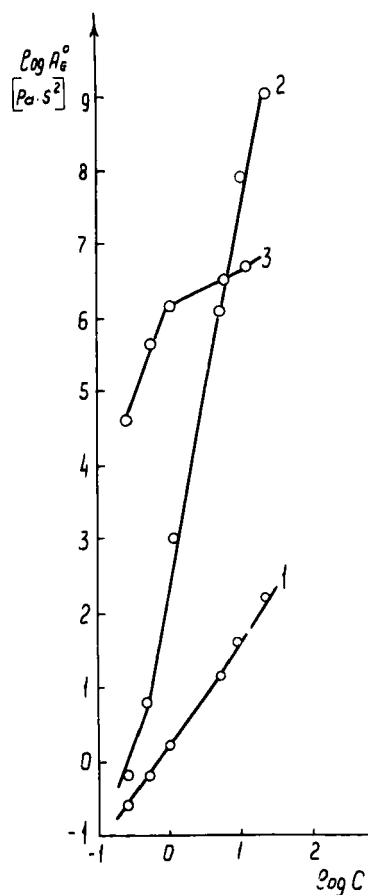


FIGURE 13 Dependence of the elasticity coefficient  $A_G^0$  on the concentration of the high-molecular-mass component added: 1, for solutions of series A; 2, series C; 3, series E.

is important that for all the solutions studied the coefficient  $A_G^0$  varies with  $C$  raised to a power two times larger than  $\eta_0 = f(C)$ . It should be noted that, according to the literature,<sup>15</sup> for concentrated polymer solutions the values of  $A_G^0 \sim C^{1.0}$ . A comparison of the curves of  $A_G^0$  and  $\eta_0$  vs. concentration shows that up to concentrations of 0.5% is practically insensitive to the variation of the concentration, while the coefficient  $A_G^0$  varies sharply in this region. The observed specific features of the variation of  $A_G^0(C)$  and  $\eta_0(C)$  may probably be accounted for by the strong (as compared with ordinary solvents) effect of the solvents, i.e., in other words, by the specificity of the interaction between the solvents and the high-molecular-mass component added.

Using the above-given data we calculated the values of the intrinsic viscosity

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_2 - \eta_1}{\eta_1 \cdot C}$$

the solutions with added polymers having different molecular masses.<sup>14</sup> It has been found that  $[\eta] = M_1^{-0.8} \cdot M_2^{0.8}$ , i.e., the macromolecular conformation of the added component is the same as in good solvent (Figure 14).

Furthermore, employing the results obtained, we calculated the intrinsic values of the initial coefficient of elasticity of the solutions (Figure 15). It has been found that  $[A_G^0] \sim M_1^{-1} M_2^2$ . This important experimental relation for polymer solutions with small concentrations of the high-molecular-mass component was obtained for the first time in the present work.

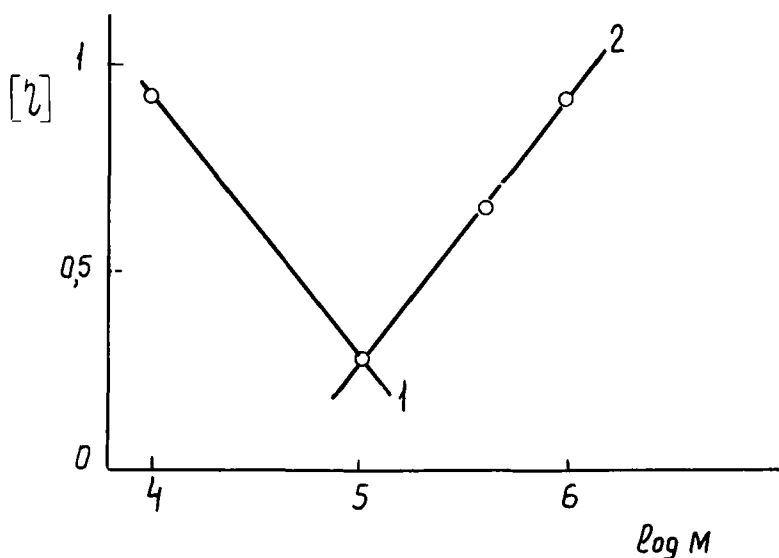


FIGURE 14 Dependence of intrinsic viscosity  $[\eta]$  on the MM solvent (1) and added component (2).

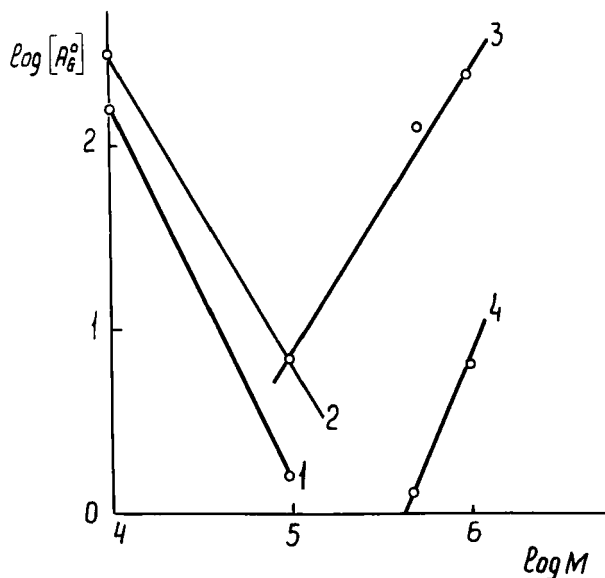


FIGURE 15 Dependence of the initial coefficient of elastic coefficient  $[A_e^0]$  on the MM of the solvent (1, 2) and added component (3, 4).

Apart from the variation of system parameters such as the initial viscosity and the coefficient of elasticity, another interesting point is the question of the ratio of these quantities for solutions which can be judged about from the variation of the equilibrium compliance of the system  $J_e = A_e^0/\eta_0^2$ . Since the time when the works of Phillipoff<sup>16</sup> and Trapeznikov<sup>17</sup> were published it has been known that diluted solutions of high polymers (polyisobutylene) are capable of undergoing very large recoverable deformations (up to 20,000%). Later, Graessley<sup>5</sup> found that solutions of high polymers give distinct maxima in the plots of the equilibrium compliance against the concentration in the region of low values of the latter.

Figure 16 shows the dependence of the equilibrium compliance on the concentration (the curves 1–3). It is seen that in the case of the blend A there is observed a maximum in the curve of  $J_e^0(C)$ , which approximately corresponds to the 0.5% concentration. For blends B and E the maximum is diffuse, this being associated with the close molecular masses of the components blended.

The existence of different dependences of the viscoelastic behaviour of polymer systems in different regions of the concentrations of the high-molecular-mass component points to the presence of the critical values of concentrations which when exceeded will lead to a sharp change in the viscoelastic behaviour of the system. The calculation of the "critical" concentrations which correspond to the onset of the overlap of the spheres of

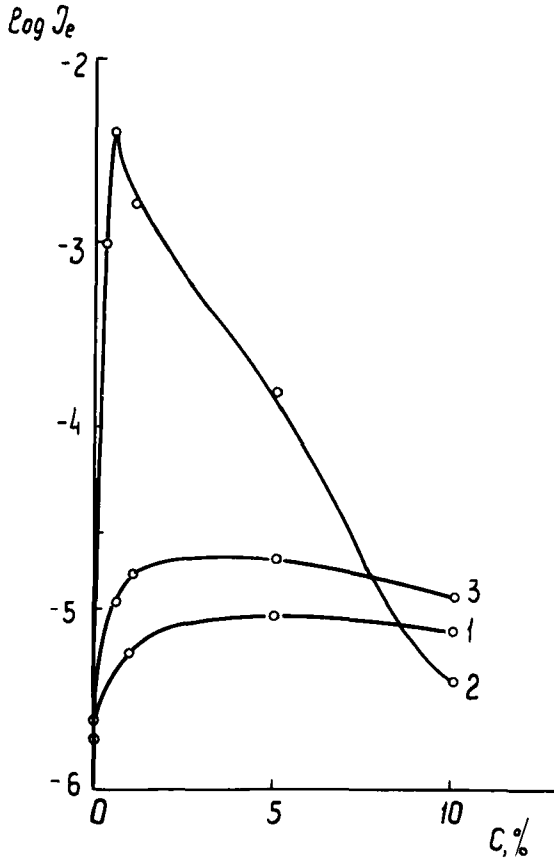


FIGURE 16 Dependence of the equilibrium compliance of solutions  $J_e^0$  on the concentration of the high-molecular-mass component. The curves 1-3 correspond to 1, series A; 2, series C; 3, series E.

polymer coils, can be carried out in an approximate manner according to Debye:

$$C_{cr} = 1.08/[\eta]$$

where  $[\eta]$  the intrinsic viscosity of the high-molecular-mass component shows that the value of  $C_{cr}$  for solutions A, B and C are equal to 0.5, 0.7 and 1%, respectively, i.e., approximately to values of the same concentrations at which a maximum is detected in the curve of the equilibrium compliance  $J_e^0$  vs. the concentration on C.

Assuming the above estimate of "critical" concentrations, we may presume that the dependences presented in Figure 1 (the curves 1-5) describe, up to

0.5% concentrations, the behaviour of noninteracting macromolecules of high-molecular-mass.

## CONCLUSIONS

A study has been made into polymer systems containing 1,4-PB produced by anionic polymerization and having a relatively narrow molecular-mass distribution ( $M_w/M_n = 1.1-1.2$ ). These binary systems contained polymers with  $M/M_c$  ( $M_c$  being the critical mass corresponding to the variation in the relationship between initial viscosity and molecular mass MM) greater than unity. On the one hand, the values of Ratio  $M/M_c$  approached 2, on the other, the binary systems contained high-molecular components with  $M/M_c$  exceeding 300. Used as the solvents were such low-molecular compounds as *n*-hexadecane and  $\alpha$ -methyl naphthalene (a mixture of isomers).

The theory<sup>9,16</sup> suggests three typical cases of binary systems:

- 1) solutions of a high-molecular polymer in a low molecular solvent or oligomer when  $M_1 < M_c$ ;
- 2) solutions of a high-molecular polymer in a viscoelastic component with  $M_1 < M'_c$  ( $M'_c$  is the critical mass corresponding to the initial values of compliance being independent of  $M_1$ ), and
- 3) a blend of polymers with matrix  $M_1 > M'_c$ .

The first case is not considered in this work. In the second,  $\eta_0$  is practically invariant, in the region of extremely low concentrations ( $< 1\%$ ), with respect to the molecular mass and concentration of the high-molecular component; at high concentrations, exponent in relation  $\eta_0 \sim C^\beta$  may increase several times with the MM of the high-molecular component ( $M_2$ ).

The characteristic values of viscosity of solutions of high-molecular polymers in a viscoelastic medium with an underdeveloped entanglement network depends both on the MM of the added high-molecular component and on the MM of the solvent. In this case, this dependence is expressed as follows:  $[\eta] = M_1^{-0.8} M_2^{0.8}$  (where  $M_1$  is the MM of the solvent). As far as the dependence of  $M_2$  is concerned, the result is close to the theory<sup>18</sup> at least in the first approximation, which states that it must equal unity.

The result for the dependence of  $[\eta]$  on  $M_2$  qualitatively agrees with Flory's theory.<sup>19</sup> It was shown that if  $M_2 > M_1^2$ , then the behaviour of the high-molecular component must be the same as in a good solvent.

In the case under consideration, the elastic coefficient perceptibly increases with concentration and can be described in terms of a relation in which exponent  $\beta$  equals six. For the first time, the intrinsic characteristic values of elastic coefficient  $[A_c^0]$  were calculated. They were found to be determined by

the following relation:  $[A_G^0] \sim M_1^{-\gamma} M_2^\delta$ . Here,  $3 > \delta > 1$ ;  $\gamma \simeq 2$ . Calculation of compliance  $I_e^0 = A_G^0/\eta_0^2$  has revealed a pronounced (about 1000-fold) increase in this value at concentrations of about 0.5% as compared to the same value at  $C = 10\%$ . This corresponds to a rapid increase in  $G'$  in the region of low concentrations.

As to the third case involving polymer blends,  $\eta_0$  at concentrations ranging from 0.1 to 10% changes only by 20%. The change in  $A_G^0$  is also peculiar; if in the region of low concentrations (0.1 to 1%) binary systems behave similarly to solutions ( $A_G^0 \sim C^4$ ), at higher concentrations the trend of this relation becomes much slower so that  $A_G^0 \sim C^{0.5}$ . Thus, the third case where both components are characterized by a highly developed network is much different from solutions, the implication being that a polymer blend is involved.

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