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ELECTROOPTICS OF THERMOTROPIC MESOGENIC POLYMERS IN SOLUTION AND IN BULK

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Abstract The methods of diffusion, sedimentation, viscometry and flow and electric birefringence in dilute solutions have been used for the investigation of the conformational properties of molecules of a number of thermotropic mesogenic aromatic polyesters (APE) differing in the chain structure. Elastic deformation in the nematic phase of some APE due to the action of magnetic and electric fields were investigated.

INTRODUCTION

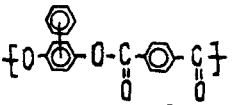
The conformational characteristics of polymer molecules (in dilute solutions) containing rigid fragments in the main chain or in the side chains determine to a large extent the possibility of **lyotropic or thermotropic mesomorphism** in a concentrated solution or in polymer bulk[1-4].

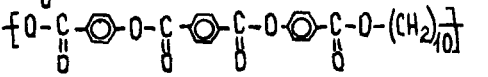
The present study carried out in dilute solutions is concerned with hydrodynamic, optical and electrooptical characteristics of molecules of aromatic polyesters differing in the chain structure and flexibility. Elastic deformations generated in the liquid crystalline melts of some of these polymers under the influence of magnetic and electric fields were also investigated.

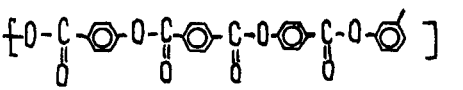
EXPERIMENTAL

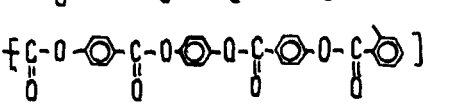
The investigations were carried out in dilute solutions on samples and fractions of aromatic poly-

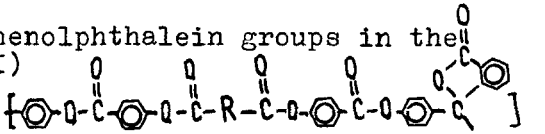
esters the molecular structures of which are given below

Para-APE (I) 

Para-alkylene APE (II) 

Para-meta-APE (III) 

Para-orto-APE (IV) 

APE containing phenolphthalein groups in the chain (V, VI, VII) 

where  is the phenyl ring incorporated into the chain in the para-  (V), meta- (VI) or orto-  (VII) positions.

The synthesis of these polymers has already been described[5]. The present study was carried out on samples of each polymer over the molecular weight ranges given in Table I.

The experimental methods used in the present paper included sedimentation-diffusion analysis of solutions, their viscometry and flow and electric birefringence[6].

RESULTS AND DISCUSSION

Hydrodynamic Properties

The molecular weight dependence of intrinsic viscosity $[\eta]$ and translational diffusion coefficient D for the polymer samples may be represented in the form of standart Mark-Kuhn relationships

$$[\eta]=K_{\eta}\cdot M^{a}\ , \quad D=K_{D}\cdot M^{-b} \qquad (I)$$

The values of the coefficients K_{η} and K_D and exponents a and b are given in Table I.

The molecular weight dependence of D and the theory of translational friction of wormlike chaine[6] are used for determination of the Kuhn's

segment length A given in Table I. The values of λ are also listed in Table I. λ is the length of the repeat unit of the polymer in the direction of the wormlike chain representing the molecule.

The length of the Kuhn segment $A=380 \cdot 10^{-8}$ cm obtained for para-APE (I) is close to the values of A known for para-aromatic polyamides[2,6]. This result is a direct evidence for and a good illustration of the structural and conformational similarity of amide and ester groups responsible for the flexibility of para-APA and para-APE, respectively.

The introduction of phenolphthalein groups, meta- or orto-phenylene rings or decamethylene "spacers" into the polymer chain drastically decreases chain rigidity as a result of distortion of its "crankshaft" structure which occurs in this case. This result is also well known for the molecules of aromatic polyamides[2,6].

Theoretical conformational analysis of molecules of the polymers investigated based on well-known chemical structures of their repeat units makes it possible to calculate the length of the Kuhn segment A_f corresponding to the unhindered rotation about the C-phenyl and O-phenyl valence bonds of the chain[6,7]. Comparison of the values of A_f obtained in this manner with those of A found experimentally permits the determination of the degree of hindrance $\sigma = (A/A_f)^{1/2}$ to intramolecular rotations about these bonds of the chain.

The data in Table I show that for para-APE(I) the rotation in the chain is close to free rotation ($\sigma = I.I$), which is characteristic of all rigid-chain polymers[6]. With increasing chain coiling (decreasing A), the degree of hindrance increases and for a chain containing orto-phenylene rings attains the value of $\sigma = 2$ close to those characteristic of flexible-chain polymers. This fact implies that the introduction of orto-phenylene rings into the chain leading to increasing compactness of its structure marcedly increases the sterical hindrances in this structure opposing the rotation of neighbouring units in the chain.

Dynamooptical Properties

For all the polymers investigated, flow birefrin-

gence, Δn, is positive and proportional to the shear stress $\Delta\tau \equiv g(\eta-\eta_0)$ where η and η_0 are the viscosities of the solution and the solvent, respectively and g is the rate gradient.

Fig.I shows the molecular weight dependence of the shear optical coefficient $[n]/[\eta] = \lim_{c\to 0}(\Delta n/\Delta\tau)$ for the aromatic polyester investigated. For samples IV and VII the molecules of which contain ortho-phenylene rings and are the most flexible, the values of $[n]/[\eta]$ are very low and do not depend on molecular weight. For polymers II and VI the molecules of which are less flexible, the values of $[n]/[\eta]$ are slightly higher but are virtually also independent of M in the molecular weight range investigated. The absence of the dependence of $[n]/[\eta]$ on M implies that the conformations of the molecules of these polymers can be described by a Gaussian coil and the shear optical coefficient is determined by the Kuhn equation

$$([n]/[\eta])_\infty = (4\pi/45kTn)(n^2+2)^2 \beta A \qquad (2)$$

where β is the anisotropy of unit length of the wormlike chain and correspondingly βA is

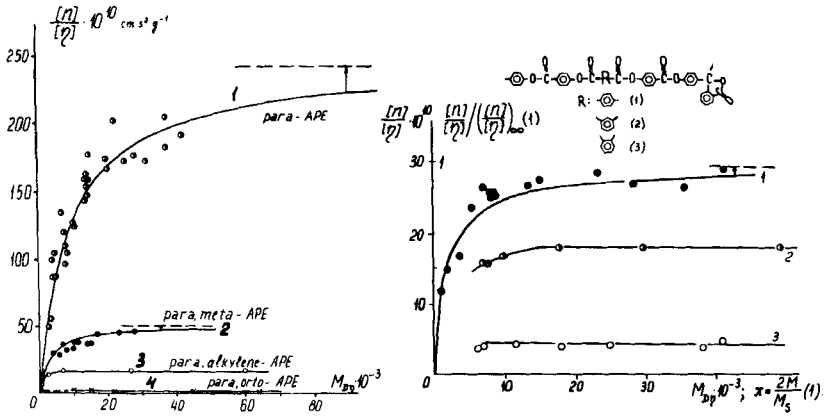


FIGURE I. Dependence of $[n]/[\eta]$ on molecular weight M for solutions of APE-I (I), APE-II (3), APE-III (2), and APE-IV (4) in DCAA (a); APE-V (I), APE-VI (2), and APE-VII (3) in TCE(b).

its segmental anisotropy.

The values of β (Table I) are calculated according to eq.(2) from the experimental values of $([n]/[\eta])_\infty$ given in Table I and the values of A obtained from the hydrodynamic data for polymers II, IV, VI and VII.

For polymers I, III and V with more rigid chains, $[n]/[\eta]$ increases with molecular weight tending to the limiting value, $([n]/[\eta])_\infty$, at high M. This increase reflects the deviation of the optical properties of the molecules from these of the Gaussian chains. For these polymers, the dependence of $[n]/[\eta]$ on M may be described by the theory of flow birefringence for wormlike chains according to which we have

$$[n]/[\eta]=([n]/[\eta])_\infty M/(M+AM_o/\lambda) \quad (3)$$

where $([n]/[\eta])_\infty$ is determind from eq. (2).

Curves I and 2 in Figure Ia and curve I in Figure Ib are the theoretical dependences corresponding to eqs.(2) and (3). They are plotted at values of A, λ, and β corresponding to the data in Table I for polymers I, III and V.

The introduction into the polyester chain of the $-(CH_2)_{10}-$ sequences, or phenolphthalein and meta-phenylene rings preventing the coaxial direction of internal relation bonds in the chain (polymers III, V and VI) leads to an effect of decrease in β.

The chain anisotropy decreases particularly drastically when aromatic rings in the orto-position (polymers IV and VII) are incorporated into the chain. This effect results from the proportionality of the contribution provided to the chain anisotropy by each phenylene ring to the value of $3\cos^2\varphi - I$ where φ is the angle formed by the intramolecular rotation bond of this ring and the direction of the wormlike chain (direction λ). In the chain containing orto-phenylene rings, for a considerable part of para-phenylene rings contained in this chain, the angle can be more than 55°, and hence these rings can provide a negative contribution to the optical anisotropy of the chain marcedly decreasing the positive value of β.

TABLE I Hydrodynamic (K_η, K_D, a, b), conformational (λ, A, σ), optical ($([n]/[\eta])_\infty$, β) and elektrooptical (K_∞) characteristics of the molecules of aromatic polyesters in dilute solutions in dichloroacetic acid (I-IV) and in tetrachloroethane (V-VII).

Polymer	Range $M \cdot 10^{-3}$	$K_\eta \cdot 10^3$ $\frac{cm^3}{g}$	K_D $\frac{cm^2}{s}$	a	b	$\lambda \cdot 10^8$ cm	$A \cdot 10^8$ cm	σ	$\left(\frac{[n]}{[\eta]}\right)_\infty \cdot 10^{10}$ $\frac{cm\ s^2}{g}$	$\beta \cdot 10^{17}$ cm^2	$K_\infty \cdot 10^{10}$ $\frac{cm^5}{g\ stV^2}$
I	2.5-16	0.103		1.49							
			0.71		0.77	12.6	380	1.1	240	8.6	150
	16 -40	1.29		1.22							
II	5 -68	65	2.4	0.73	0.60	33	55	-	16	4.0	18
III	3.8-27	2.6	5.6	1.1	0.70	24	120	1.3	50	5.0	11
IV	10 -64	50	2.18	0.63	0.54	16	26	1.7	1.5	1.0	- 2.6
V	1.3-35	19	12	0.85	0.62	28	80	1.07	30	5.0	-
VI	7.4-49	62	9.3	0.70	0.59	29	54	1.15	18.2	4.2	-
VII	6.7-41	82	6.6	0.62	0.54	24	46	2.0	4.6	1.2	-

Electrooptical Properties

The electrooptical Kerr effect was investigated in the solutions of APE I,II,III,IV and some individual low molecular weight compounds (AE, i.e. "monomers") corresponding to different fragments of the APE chains[8] .

For the high molecular weight samples of para-APE I and for APE samples II,III and IV, the Kerr constant $K=\lim_{c\to 0}(\Delta n/cE^2)$ (E is the field strength and c - concentration) exceed these for flexible-chain polymers by three and two orders of magnetitude, respectively. This can be seen from Table I in which the values of K_∞ , the Kerr constants for the highest molecular weight samples of the polymers are given.

In the order of absolute values, the K constants for APE are close to those obtained for comb-like polymers with mesogenic side groups[4] . This similarity is due to the fact that for both these groups of polymers the Kerr effect is caused to a considerable extent by the presence of rigid mesogenic nuclei (ester-phenylene groups) in their molecules.

At the same time the data in Table I show that the values of K_∞ decrease drastically when alkyl groups or phenyl rings in the meta- or orto-positions are introduced into the chain. This decrease is particularly pronounced for para-orto-APE (IV) in which the change in the molecular structure is accomponied by a change in both the value and even the sign of the Kerr constant K_∞ . The evident reason for these marked changes is a decrease in both the chain rigidity (Kuhn segment A) and its anisotropy β on passing from the para- to the orto-structure.

However, the molecular weight dependence of the Kerr constant for these polymers (Fig.2) appears to be of the uniqul character. The K values for monomers and low molecular weight samples are negative, whereas for all polymers (except APE IV) they change their sign with increasing M and in the range of positive K values increase tending to the limit K_∞ .

The dependence of K on M for polymers I, II and III corresponds to the predictions of the theory of the Kerr effect in solutions of rigid-

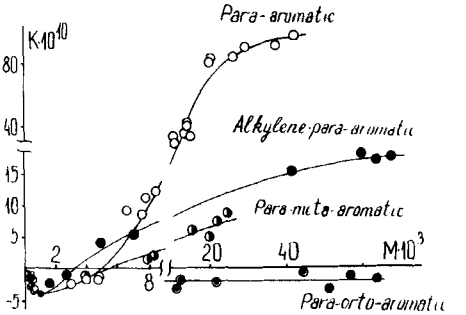


FIGURE 2. Dependence of the Kerr constant K on molecular weight M for aromatic polyester APE I, II, III and IV .

chain polymers represented by a kinetically rigid wormlike chains[9]. The dependence of K on M or on reduced chain length $x = 2L/A = 2M/M_0S$ (where S is the number of monomer units in the geometric Kuhn segment A) is described by the equation

$$\frac{K\cos^2\vartheta}{K_\infty} = \frac{3}{5}\frac{\langle h^4\rangle}{\langle h^2\rangle^2}\cdot\frac{f_1^2(x)}{f_2(x)}\cdot\left[\cos^2\vartheta - \frac{3f_1^2(\alpha x)\sin^2\vartheta}{5\alpha^2 f_1(x) f_2(\alpha x)} + \frac{6kTx\Delta b}{5\mu_0^2 S f_2(x)}\right] \quad (4)$$

$$f_1(z) = z - 1 + e^{-z};\quad f_2(z) = z^2 - 0.8 f_1(z);\quad z = x \text{ or } \alpha x$$

μ_0 and Δb are the dipole moment and the dielectric anisotropy of the monomer unit, ϑ is the angle between the dipole μ_0 and the chain direction, $\alpha = S/S_\perp$ is the parameter characterizing the ratio of the longitudinal-dipole (geometric) S to the transverse-dipole $S_\perp$ chain rigidity, h is the end-to-end distance of the chain and K_∞ is the limiting value of the Kerr constant in the range $x \to 0$:

$$K_\infty = (B\beta\lambda/M_0 kT)\,\mu_0^2 S^2 \cos^2\vartheta$$

$$B = (2\pi N_A/1215\, nkT)(n^2+2)^2(\varepsilon+2)^2 \quad (5)$$

According to eqs.4 and 5, the expression for the Kerr constant contains three terms the first of which expresses the contribution to K of the longitudinal components $\mu_0\cos\vartheta$ of monomer dipoles, the second term describes that of the normal

components $\mu_0 \sin\vartheta$ and the third determines the value of EB resulting from the dielectric anisotropy of the chain. The sign of the first term coincides with that of β, the sign of the second term is opposite to it and that of the third term is always positive.

With increasing chain length (parameter x), the importance of the second and third terms decreases and at high molecular weights, according to eq. (5), the Kerr effect is determined only by the longitudinal components of monomer dipoles. This is the principle of the "accumulation" of longitudinal dipole components in the chain with increasing chain length. At high x, according to eq.(5), the sign of K_∞ coincides with that of β and, correspondingly, with that of $([n]/[\eta])_\infty$, which is valid for all three polymers I, II and III (Table I).

In the low molecular weight range (low x), according to eqs. (4) and (5) we have

$$K_{x\to 0} = (B\beta L/M_0)[P\mu_0^2(3\cos^2\vartheta - 1)/2kT + \Delta b] \quad (6)$$

where P is the degree of polymerisation.

Under these conditions, for polymers the monomer dipole of which μ_0 is inclined to the chain by an angle $\vartheta > 55^0$, the first (dipole) term in eq. (6) is negative and, correspondingly, the Kerr constant can be negative. This is the reason for the negative K sign obtained for all the APE investigated (I - IV) at low M (Fig.2).

Both the coincidence of the signs of K_∞ and $([n]/[\eta])_\infty$ and the dependence of K on M obtained for APE I, II and III are indicative of the large-scale character of the molecular motion responsible for the Kerr effect observed in solutions of these polymers. This motion involves the orientation of the polymer molecule in the electric field by the mechanism of its rotation as a whole, which is characteristic of a cinetically rigid chain.

For polymer IV, over the entire molecular weight range investigated, the Kerr constant remains negative and virtually invariable with the changes in M. This electrooptical behaviour is characteristic of all flexible-chain polymers. This fact implies that the incorporation of the orto-phenylene rings into the polymer chain markedly decreases not only its equilibrium but al-

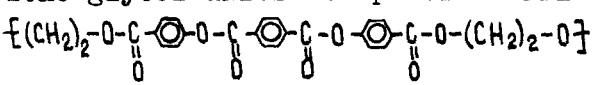
so its kinetic rigidity. As a result of this decrease, the molecules of para-orto-APE IV in the electric field are oriented by the mechanism of small-scale local motion of chain units.

Nematic Melts in Magnetic and Electric Fields

All the aromatic polyesters investigated, I - IV, when heated in bulk up to their melting point T_K form liquid-crystalline melts. However, their melting temperatures are most often above 300° and the isotropization temperatures T_o are higher than their degradation temperatures. The above mentioned facts refer not only to the most rigid para-APE I (T_K = 340°C) but also to the most flexible para-orto-APE IV (T_K = 320°C).

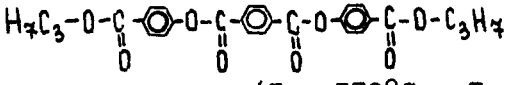
It should be noted that although the equilibrium rigidities of molecules of these two polymers differ by a factor of I5 (Table I), the temperatures of existance of their mesophases are very similar.

For the quantitative study of changes in liquid-crystalline textures in electric and magnetic fields we used a para-APE with the molecular weight $M=4\cdot10^3$ the chain of which contains diethylene glycol units as spacers - APE-VIII



(T_K =I90°C , T_o = 320°C)

For comparison, the texture changes in magnetic and electric fields of a low molecular weight nematic AE IX, a "monomer" analogue of APE VIII, were also investigated



(T_K =I70°C , T_o = 208°C)

Both AE IX and APE VIII in the nematic phase in thin layers limited by solid walls form homeotropic textures (director is normal to the wall surface). The methods developed by Freederiksz et al.[10,11] were used for the investigation of deformations of these textures in magnetic H and electric E fields. In these methods, wedge-shaped layersof the nematic, limited by planar and sphe-

rical of the quartz glasses were employed. Steady-state magnetic and sinwave (80 kHz) electric fields were applied.

For the beginning of deformation, the magnetic field should be directed parallel to the layer surface. In contrast, in the electric field, deformations in both the monomer and the polymer nematics arise if the field is parallel to the initial director orientation. This fact implies that the electric field leads to the orientation of the axes of both the monomer and the polymer normal to the field and their dielectric anisotropies $\Delta\varepsilon$ are negative.

Hence, in contrast to the case of solution, the normal component of the dipole of the monomer unit, $\mu_0 \sin\vartheta$, in the bulk of the liquid-crystalline polymer plays an active role in the orientation of the molecule in the electric field. This fact implies that the mechanism of this orientation is its small-scale motion rather than the large-scale rotation of the entire chain. In this motion, the "kinetic unit" is the monomer unit of the chain the orientation of which in the electric field is similar to that in the low molecular weight nematic.

Fig.3 shows the polarising micrographs of preparations of the polymer nematic deformed by the magnetic, H, or the electric, E, fields. In

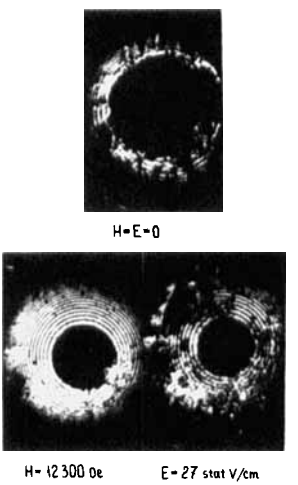


FIGURE 3. Polarizing microscopic textures of a planar-concave layer of a polymer nematic APEVIII deformed by the magnetic (H) or the electric (E) field.

crossed polaroids, the "critical boundary" separating the distorted and the undistorted parts of the nematic and illustrating the threshold character of deformation (Freederiksz transition) can be clearly seen. The interference rings, curves of equal thickness, are observed.

The pattern of the interference rings makes it possible to determine the optical anisotropy of the nematic: the difference between its two main refractive indices : $n_e - n_o$ .The values of $n_e - n_o$ obtained for the monomer and the polymer nematics are described by curve I in Fig.4 as a function of temperature T. The experimental values of $n_e - n_o$ (points) for the polymer and the monomer fall on the same curve. This fact implies that the degrees of orientational order and the values of diamagnetic anisotropies $\Delta\chi$ for the polymer and the monomer nematics in the corresponding temperature range virtually coincide. The absolute values of $\Delta\chi$ for AE IX (and correspondingly for APE VIII) can be assumed as coinciding with those for anizalaminoazobenzene described by curve 2 in Fig.4. The values of $\Delta\chi$ have

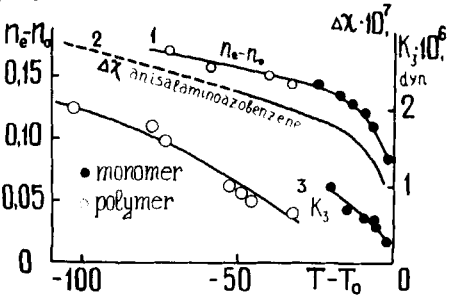


FIGURE 4. Temperature dependence of optical anisotropy $n_e - n_o$ for low molecular weight and polymer nematics (I), diamagnetic anisotropy $\Delta\chi$ for anizalaminoazobenzene (2) and the elastic bend constant K_3 for low molecular weight and polymer nematics (3).

been determined in ref.[11] in which it has been shown that these values calculated per unit volume in the corresponding temperature ranges virtually coincide for different nematics.

The measurement of critical baundaries in Fig.3 permits the determination of critical thick-

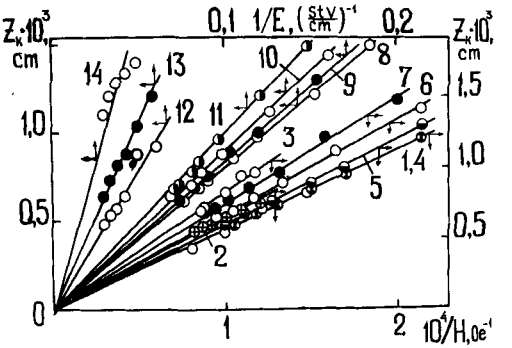


FIGURE 5. Dependence of the critical thickness Z_K for liquid-crystalline layers of the monomer (curves 4-II) and the polymer (curves I-3 and I2-I4) on the inverse strength of the magnetic, I/H, (curves I-7) and electric, I/E, (curves 8-I4) fields.
The numbers on the curves correspond to the following temperatures; 287.5 (I); 267 (2,I4); I89 (3,I2); I93 (4,II); 205.5 (5,I0); 209 (6, 9); 2I2 (7,8); 2I7 (I3)°C.

nesses Z_K on the inverse values, I/H and I/E, of magnetic and electric fields are shown in Fig.5. The experimental points obtained at a constant temperature fall on one curve passing through the origin in accordance with the threshold character of deformations predicted by the equations (7)[10,11]:

$$Z_K H = \pi \sqrt{K_3/\Delta\chi}, \quad Z_K E = 2\pi \sqrt{\pi K_3/\Delta\varepsilon} \qquad (7)$$

where K_3 is the elastic bend constant of the nematics under investigation. The slopes of the stright lines in Fig.5 determine the $K_3/\Delta\chi$ and $K_3/\Delta\varepsilon$ ratios and if the known values of $\Delta\chi$ are taken into account, they also determine the values of elastic constants K_3. The temperature dependence of K_3 for AE IX and APE VIII is described by curve 3 in Fig.4. These data show that in the corresponding temperature ranges, $T - T_0$, the values of K_3 for the polymer and the monomer are the same in the order of magnitude and close to

those for other low molecular weight nematics. By using the values of K_3 and $K_3/\Delta\varepsilon$ it is possible to determine the difference $\Delta\varepsilon$ between the two main dielectric permittivities ε_1 and ε_2 for these nematics. The values of $\Delta\varepsilon$ for the polymer and the monomer are close to each other in the order of magnitude. In the temperature range investigated they vary from -0.I to -I.0. The close values of K_3 and $\Delta\varepsilon$ for the polymer and the low molecular weight nematics reflect the factthat due to the action of magnetic and electric fields, elastic deformation in both the monomer and the polymer proceed by similar machanisms of local motion of monomer units and are virtually independent of whether these units form a part of the polymer chain or not. In this case the role of the polymer chain is manifested mainly in the kinetics of the orientation processes which are drastically retarded with increasing molecular weight and decreasing polymer temperature.

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