Dynamic behaviour of nematic polymers in a magnetic field

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Dynamic properties of some polymer nematics were investigated by Freedericksz transition methods in a magnetic field. The linear aromatic polyester, comblike combined side/chain-main/chain polymer and comblike copolymers with mesogenic and functional acid groups in side chains were studied. The temperature dependencies of the effective rotation viscosity γ_1^* were obtained. At close molecular weight and temperature the γ_1^* value for linear polymer exceeds that for comblike combined polymer. Therefore the existence of side mesogenic groups decreases velocity of the orientational processes of polymer nematic. However, the highest values of effective rotation viscosity were obtained for the nematic phase of the comblike functionalised copolymers. Hence, the formation of hydrogen bonds in these copolymer leads to slowing of orientational processes. Influence of the intermolecular hydrogen bonds on dynamic properties of functionalised copolymers is stronger than that of intramolecular hydrogen bonds.

Keywords: polymer nematic, Freedericksz transitions, effective rotation viscosity, inter- and intramolecular hydrogen bonds.

1. Introduction

The distinctive feature of dynamic behaviour of polymer nematics is molecular weight dependence of viscosity coefficient. For example, theory predicts the sharp increase in rotation viscosity γ_1 with molecular weight increasing. This dependence is described by the equation

$$\gamma_1 \sim M^b \tag{1}$$

The exponent b value is determined by the rigidity of polymer chain and its conformation in a nematic melt:
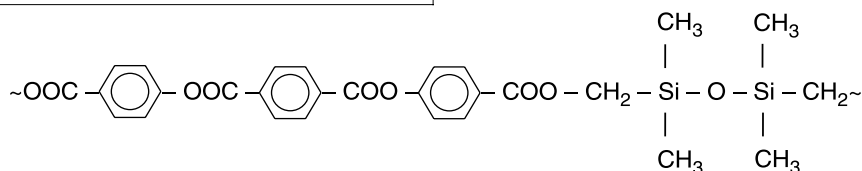
(i) $b = 6$ for rigid rod-like macromolecules, Refs. 1,2,
(ii) $b = 2$ for semi-rigid fully extended chains, Refs. 3,4,
(iii) $b = 1$ for semi-rigid macromolecules when hairpins are present, Ref. 3,
(iv) $b = 3$ for flexible polymers (for the reptation movement model), Ref. 3.

However, the number of experimental investigations devoted to analyse the molecular weight dependence of viscosity coefficient of liquid crystalline (LC) polymers is still rather restricted, that is explained by serious problems involved in these experiments. For linear aromatic polyesters (APE), the high value of the exponent $b = 4$–5 were obtained [5–7]. Correspondingly, APE macromolecules may have the conformation near the rod-like, which contradicts the flexible chain character of APE. The b values are rather less for comblike polymers. They lie in the interval from 0.7 to 2.5 and increase with temperature decreasing. In all cases, the polymer nematic viscosity is greater by several orders of magnitude than the γ_1 values for low molecular weight LC [5–10]. For LC polymer, the growth of activation energy W of reorientational processes is also observed [6,8,9].

The aim of this work is the investigation of molecular weight influence on the orientational dynamics of the nematic polymers and the hydrogen bonded blends with low molecular weight non-mesogenic dopants.
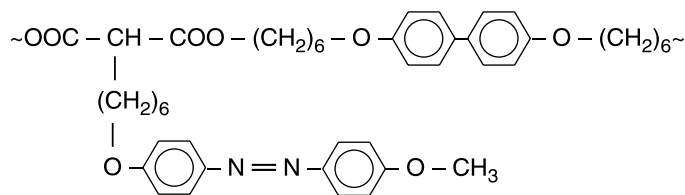
We have investigated the linear APE with flexible siloxane spacers (APE-Si)

the comblike combined side-chain/main-chain polymer (CCP-66)

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$$\sim OOC - CH - COO - (CH_2)_6 - O - \bigcirc\hspace{-2pt}\bigcirc - O - (CH_2)_6\sim$$

$$|$$
$$(CH_2)_6$$
$$|$$
$$O - \bigcirc - N = N - \bigcirc - O - CH_3$$

and blends of comblike copolymer with mesogenic and functional side groups and low molecular weight dopant (PB-y), which concentration y was changed from 0 to 0.23

For all investigated LC, only homeotropic textures could be obtained. Correspondingly, we have determined the bend viscosity coefficients γ_1^* or effective rotational

$$CH_2$$
$$|$$
$$HC - COO - (CH_2)_5 - COO - \bigcirc - OOC - \bigcirc - OC_3H_7 \quad 0.7$$

$$CH_2$$
$$|$$
$$HC - COO - (CH_2)_3 - O - \bigcirc - COOH \quad x$$

$$CH_2$$
$$|$$
$$HC - COO - (CH_2)_3 - O - \bigcirc - COOH \quad \cdots \cdots \quad N\bigcirc - COOH - \bigcirc - OCH_3 \quad y$$
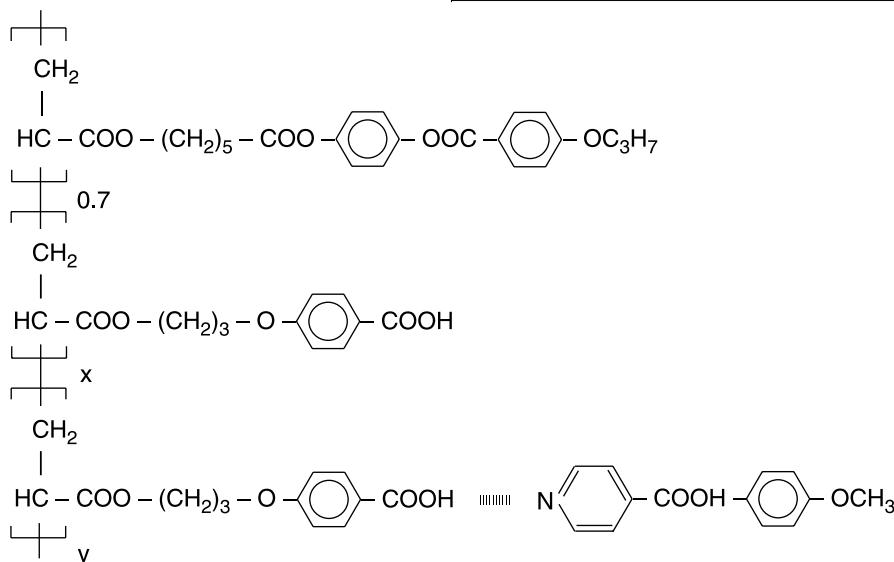
The molecular weights of polymers investigated are listed in Table 1. They were determined by GPC methods [11] and molecular hydrodynamics in dilute solutions [12]. The temperatures T_o of the phase transition from isotropic liquid (I) to nematic phase (N) were determined by polarising microscope method. The investigations of equilibrium orientational elastic characteristics of APE-Si and CCP-66 have shown that order parameter S and elastic constants K_i did not depend on molecular weight [13,14].

2. Experimental

We have used a classical method for studying Freedericksz threshold transitions in a magnetic fields [15] and dynamics of orientational processes in the nematic LC [16]. A detailed description of this method in application to dynamical investigation of the thermotropic LC polymers was given previously [17]. Wedge-shaped plane-concave nematic layers were used; the investigated LC was placed between the plane and spherical surfaces of quartz glasses. The sample was observed under a polarising microscope in parallel light beams normal to layer plane. By monitoring the interference patterns of the deformed nematic layers, one may follow the dynamics of establishing an equilibrium deformation after switching or changing of the magnetic field or observe the deformation relaxation upon turning the field off. It makes possible to determine the twist viscosity γ_1 value of the investigated polymer nematic.

Table 1. Molecular weights M, temperatures T_o, and activation energies W for investigated LC.

LC	Fractions	M	y	T_o(K)	W(K)
APE-Si	1	12700		509	10700
	2	6200		509	9300
	3	4500		509	11600
	4	3800		509	11500
	5	3000		509	–
CCP-66	1	10200		423.5	12200
	2	9000		418	–
	3	5800		412.5	10200
	4	5400		407.5	11400
	5	4700		404	12300
	6	2000		399	11700
	7	900		374	6100
PB		5800	0	370	16700
PB-0.047			0.047	371.5	15200
PB-0.101			0.101	369	14300
PB-0.149			0.149	371	14000
PB-0.233			0.233	368	13100

viscosity coefficients [16]. The γ_1^* values are smaller than the true rotational viscosity γ_1 and depend significantly on the magnetic field strength H. The apparent decrease in viscosity of the nematic phase is related to the influence of the so-called conterflows arising during bend elastic deformation, that is to the hydrodynamic flows caused by the orientational deformation [16]. The conterflows influence shows itself the stronger the more are perturbations appearing due to external field effect, so the γ_1^* value decreases when H is increasing [16]. In the following discussion, we will consider only the γ_1^* values determined by extrapolating $\gamma_1^*(H)$ to the values corresponding to the relative magnetic field strength $H/H_c \to 1$ (H_c is critical magnetic field in Fredericksz threshold transition [15].

3. Results and discussion

In Fig. 1, the viscosity values γ_1^* for some APE-Si and CCP-66 fractions are shown depending on absolute temperature T. Firstly, we must mark that even at high temperatures near the transition I $\leftrightarrow$ N the γ_1^* values for investigated LC polymers are two orders of magnitude more than rotational viscosity of low molecular weight nematics. The γ_1^* values for APE-Si and CCP-66 (at the same M and temperature) are

comparable by order of magnitude with the γ_1 value of rotational viscosity of polymer nematics investigated before [5–10].

The coefficient γ_1^* of investigated APE-Si and CCP-66 fractions strongly depends on temperature, it decreases quickly when T is increasing (Fig. 1). Up to now, the problem of nematics viscosity coefficient dependence on the order degree S and activation energy W, so as the question about the dependence of energy W on parameter S are still debatable and there is no common model which is in good agreement with all amount of experimental data. The analysis shows that dependencies γ_1^* on T obtained for APE-Si and CCP-66 fractions are well described in the terms of Arrhenius activation model

$$\gamma_1 \sim S^2 \exp(W/T) \qquad (2)$$

In Fig. 2, there are shown the dependencies of $\ln(\gamma_1^*/S^2)$ on reverse temperature $1/T$. In accordance with the Arrhenius law, the experimental points are grouping near straight lines which slope gives the activation energy W. This activation energies W determined for APE-Si and CCP-66 are listed in Table 1. The W values obtained for all fractions of investigated LC polymers are rather large. They are twice more than the typical values of energies W
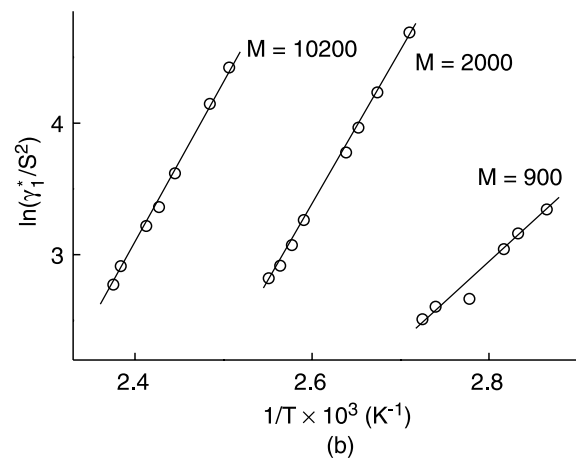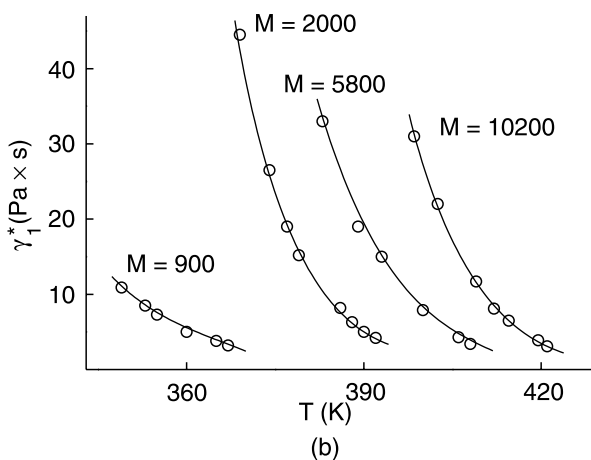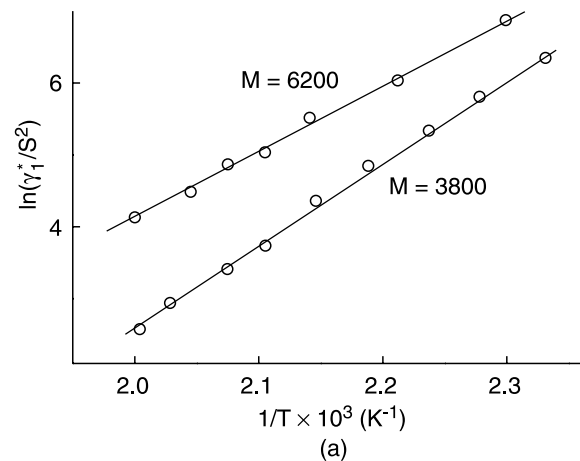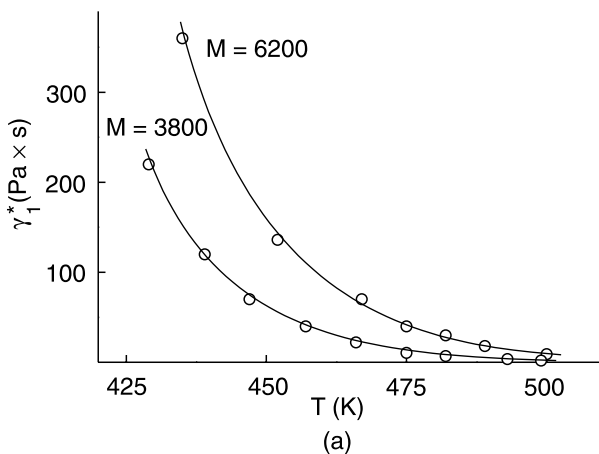

Fig. 1. Plots of the viscosity γ_1^* vs. temperature T for APE-Si (a) and CCP-66 (b).

Fig. 2. Dependencies of γ_1^*/S^2 on $1/T$ for APE-Si (a) and CCP-66 (b).

for low molecular weight nematics. From the other side, the energy values W that we got for APE-Si and CCP-66 are near to the values of activation energy for linear ($W \approx 9000$ K) [6] and comblike ($W \approx 14000$ K) [9] thermotropic LC polymers. The most important fact is that in investigated molecular weight interval the activation energy W does not depend on M (Table 1). The same result was obtained for the linear APE [6]. Thus, for comblike acrylic polymers with cyanobiphenyl mesogenic groups rather strong dependence of W on M was obtained. The activation energy for them increases 1.5 times during the polymerisation degree change from 560 to 2530 [8].

Figure 3 shows the dependencies of rotational viscosity γ_1^* on molecular weight M of the polymers. The straight lines slope determines the exponent values in Eq. (1): $b = 2.6$ for APE-Si and $b = 1.5$ for CCP-66. For the polymers investigated, the b value is much less $b = 6$ predicted for rod like molecules. The b value for linear APE-Si is more than that for the extended persistent chains. The exponent value for CCP-66 lies between the values which one may wait for the semi-rigid macromolecules in extended or partly coiled conformations.
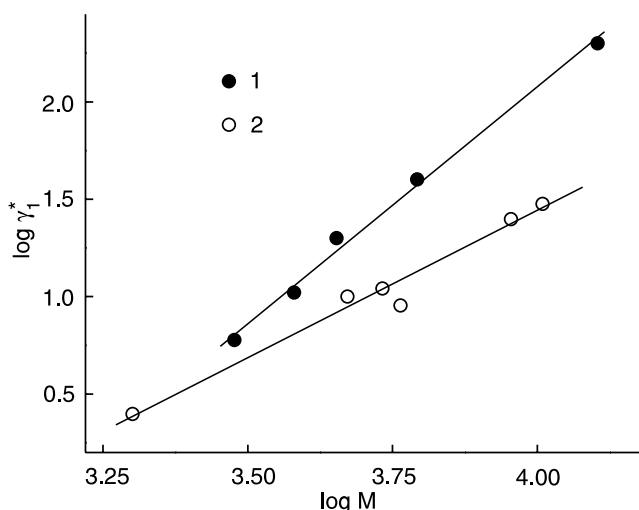

Fig. 3. Plots of log γ_1^* vs. log$M$ for APE-Si at T = 475 K (1) and CCP-66 at T = 399 K (2).

The equilibrium rigidity of polymers investigated is rather low [12]. The segment Kuhn lengths A of their macromolecules are equal approximately to 30 Å. Molecular weights of APE-Si and CCP-66 lie in interval from 2000 to 13000. Then the macromolecules of the higher molecular weight fractions contain about 20 Kuhn segments. Therefore, it may be concluded that the obtained exponent b values are reasonable. They correspond to the probable conformation of APE-Si and CCP-66 macromolecules in nematic melt. One may expect that main chain conformation of polymer investigated is slightly coiled. For combined polymer CCP-66, the complex structure of its macromolecules – the existence of long and massive side chains – promotes disturbing of the extended molecular
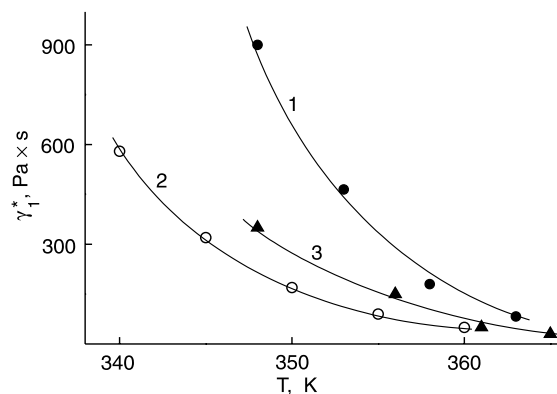

Fig. 4. The temperature dependencies of the γ_1^* values for PB (1), PA-PhB (2) (after Ref. 8) and PMS-PhB (3) (after Ref. 9).

configuration. On the other hand, the obtained b value for APE-Si is close to $b = 3$. However, it may not be assumed that the reptation movement is taking place because of the small length of macromolecules. The low molecular weight fractions consist of only 3–10 Kuhn segments. It is needed to take into account that the Kuhn segment length is determined for isolated APE-Si molecules using molecular hydrodynamic data in dilute solutions. When passing to LC melts, one may wait some growth of macromolecular rigidity and corresponding change in their conformation, increase in macromolecular longitude.

From the other side, the higher exponent b values ($b \approx 5$) were obtained before for linear APE with azoxybenzene mesogenic groups [5–7].

Comparing these results with the value $b = 2.6$ for APE-Si, it is needed to take into account the next factors:

(i) chemical nature of flexible spacer of compared polyesters is different. The siloxane chains of APE-Si are more flexible than the methylene chains in the polymers, which were studied in works [5–7].

(ii) chemical structure of mesogenic groups and their molecular characteristics are different too. For example, the absolute value and orientation of molecular dipole moment may considerably influence on the rotation viscosity coefficient.

(iii) b values were obtained at different temperatures. For APE with azoxybenzene mesogenic groups, the molecular weight dependence was obtained at 393 K [6]. It is less on 80 degrees than in the case of APE-Si. The temperature fall may lead to increase in polymer chain rigidity and to changing of macromolecular conformation. It must probably change the exponent b value in Eq. (1). The similar behaviour was observed for comblike acrylic polymers [8].

Since the hydrodynamic characteristics of LC polymer depend on the macromolecular size and conformation, the formation of hydrogen bonds may considerably change the orientational dynamics. In Fig. 4, the data obtained by us for functionalised copolymers PB and the literature data for comblike polymers in which hydrogen bonding is absent are compared. There are acrylic (PA-PhB) [8] and methyl-

siloxane (PMS-PhB) [9] polymers with phenylbenzoate mesogenic groups in the side chains. The molecular weights of PA-PhB and PMS-PhB are close to those for PB. One can see that the hydrogen bond formation leads to decrease in reorientational velocity.

The increase in viscosity of investigated polymer may be caused by formation of inter- or intramolecular hydrogen bonds. The intramolecular hydrogen bonds lead to some increase in the main chain rigidity as a result of cyclic structure formation by interaction of the acid group of functional component and the carbonyl of ester group which links a spacer and an aromatic cycles of mesogenic groups [Fig. 5(a)]. Correspondingly, the macromolecular conformation is changed; the molecular asymmetry is increased. The changes will be more than the intermolecular hydrogen bonds form [Fig. 5(b)]. The formation of only one such bond in every two macromolecules leads to supramolecular structure with double molecular weight. Correspondingly, the rotation viscosity value may strongly increase. If in every macromolecule there realises more than one intermolecular hydrogen bond then we may speak about the LC hydrogen bonded network. The viscosity coefficients will also increase in this case [8].

In order to understand the role of both mechanisms in the increase of reorientational duration, the concentration dependence of the viscosity coefficient of the hydrogen-bonded blends needs to be analysed. Indeed when the low molecular weight dopants are introduced in the copolymers, the redistribution of the matrix hydrogen bond system is taken place. The destruction of intra- and intermolecular hydrogen bonds and formation of new hydrogen-bonded mesogenic groups [Fig. 5(c)] change considerably the molecular characteristics of LC substances
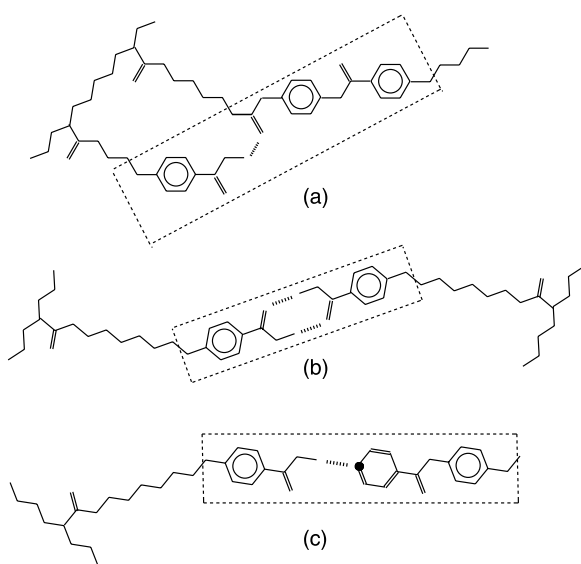
(macromolecular structure, their rigidity and conformations, molecular weight). These changes must influence the reorientational velocity and correspondingly the viscosity coefficient values.

The concentration dependencies of viscosity coefficient γ_1^* of LC blends PB-y are shown in Fig. 6. The highest values of viscosity γ_1^* and activation energy W (Table 1) were obtained for functionalised copolymer PB. The introduction of dopant molecules into the LC polymer matrix and increase in dopant concentration are accompanied by the rapid increase in the γ_1^* and W values.

The intramolecular hydrogen bonds are dominated in the investigated polymer matrix [11]. However, the destruction of these bonds cannot lead to the observed change in rotation viscosity. In fact, the change of the bond between acid group and carbon atom of ester group to the bond between acid group and dopant molecule practically does not influence the polymer chain rigidity (destruction of intramolecular cycles decreases rigidity and massive hydrogen bonded groups formation increases it), but it leads to the growth of molecular weight. It means that during intramolecular hydrogen bonds destruction one may wait that rotational viscosity γ_1^* of the blend will be rather increasing [see Eq. (1)].

The destruction of the matrix intermolecular hydrogen bonds on the contrary must be accompanied by viscosity decrease. In such case when the bonds number is not large (the situation takes place for copolymer investigated by us), their destruction leads to the rapid decrease in molecular weight M. Hence, the viscosity γ_1^* will increase during the decrease in low molecular weight dopant concentration y.

In the other case when the number of intermolecular hydrogen bonds in the system is large and LC hydrogen-bonded network is forming then the hydrogen bonds destruction leads to the growth of the distance between the network knots and to quick decrease of viscosity coefficient. We must mark that qualitatively such changes were found during investigation of the comblike nematic polymers when the formation of the supramolecular network

Fig. 5. Hydrogen bonds and hydrogen-bonded mesogenic groups existing in LC copolymers BP and LC blends BP-y: (a) intramolecular hydrogen bonds, (b) intermolecular hydrogen bonds, and (c) hydrogen bonds between dopant molecule with acid group of copolymer BP.
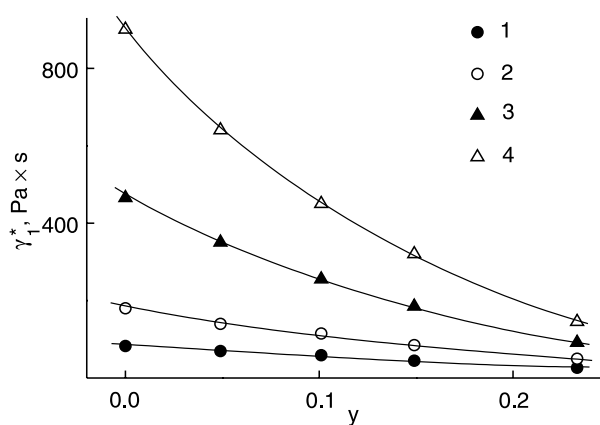

Fig. 6. Plots of the viscosity γ_1^* vs. dopant concentration y for hydrogen-bonded LC blends BP-y at the temperatures $T = 363$ K (1), 358 K (2), 353 K (3), and 348 K (4).

structures was going on due to γ-radiation [8]. In such LC systems, the reorientational processes are strongly slowing with network formation. The γ-radiation doze increase leads to the growth of the knot number. This process is accompanied by the increasing in the rotational viscosity values γ_1^* and activation energy W.

4. Conclusions

Investigation of the dynamics of Freedericksz transition methods makes it possible to conclude that the main physical processes, which govern the twist viscosity in the polymer LC, are probably the same as in low molecular weight nematics. The monomer units play the leading role in the mechanism of macromolecular reorientation. This assumption is suggested by the experimental fact that the temperature dependencies of polymer viscosity γ_1^* have the same character and the close quantitative parameters (the activation energy W) for all samples and fractions of each investigated LC polymer. The polymer character is manifested in the increase of absolute values of viscosity γ_1^* and energy W. These changes are caused by the correlation in the mesogenic group movement due to the flexible spacer connecting these groups.

The features of dynamics of investigated nematic polymers are related sufficiently to their flexible nature. The higher flexibility provides the relativity movement freedom of mesogenic groups and promotes the conformational transitions in the polymer nematic melt. Because the polymer spacers are flexible, each mesogenic group interacts primarily with its lateral neighbours, as in usual low molecular weight nematics. However this interaction in the LC polymers is realised partially through the spacer. The chemical bonding of mesogenic groups reduces the orientational fluctuations and increases the duration of the reorientational processes.

In the nematic hydrogen-bonded polymer systems, the reorientational velocity depends mainly on the existence of the intermolecular hydrogen bonds. The formation of these bonds leads to the sharp change in the dynamical characteristics of high molecular weight LC. Its rotation viscosity γ_1^* and activation energy W are increased. The decisive importance of the intermolecular hydrogen bonds is preserved also for the functionalised LC copolymers in which the intramolecular hydrogen bonds are prevailed.

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