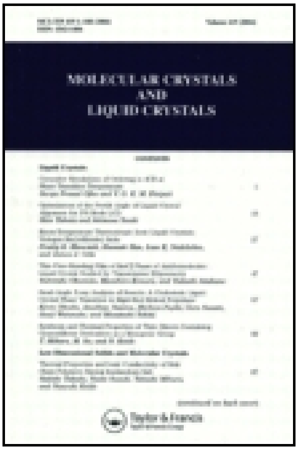

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Cooperative Forms of Molecular Mobility in Liquid-Crystalline Side-Chain Polymers

Natalia Nikonorova [a] , Tamara Borisova [a] & Valeriy Shibaev [b]

[a] Institute of Macromolecular Compounds of Russian Academy of Sciences, Bolshoy pr.31, 199004, St. Petersburg, Russia

[b] Chemical Department, Moscow State University, 119899, Moscow

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Cooperative Forms of Molecular Mobility in Liquid-Crystalline Side-Chain Polymers

NATALIA NIKONOROVA[a], TAMARA BORISOVA[a] and
VALERIY SHIBAEV[b]

[a]*Institute of Macromolecular Compounds of Russian Academy of Sciences, Bolshoy pr.31, 199004, St. Petersburg, Russia and* [b]*Chemical Department, Moscow State University, 119899, Moscow*

Dielectric behavior of LC side-chain polymers with oligomethylene spacers and mesogenic side groups with different structures has been investigated. Near T_g transition, two cooperative relaxation processes, α and δ, were observed. Relaxation times (τ), activation energies (U), and transition temperatures for the α and δ processes were determined from $\log\tau=\varphi(1/T)$ dependences. In the LC state these dependences are approximated by straight or curved lines. If the δ process is observed both in the LC and in the isotropic state, the $\log\tau=\varphi(1/T)$ dependences are approximated by two lines with a break near T_{cl}. Kinetic parameters of the α and δ processes are mainly dependent on main chain structure, while the intensities are determined by parallel and perpendicular components of the dipole moment of mesogenic group.

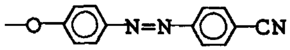
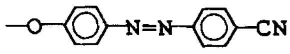
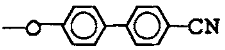
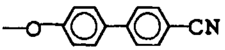
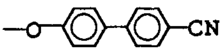
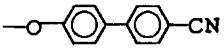
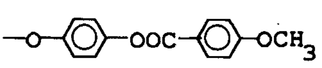
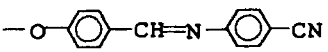
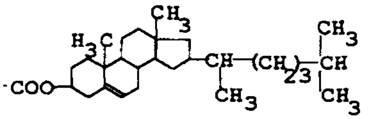
Keywords: dielectric relaxation; side-chain thermotropic polymers

INTRODUCTION

For thermotropic liquid-crystalline (LC) side-chain polymers, dielectric study manifests the specific character of molecular motion typical only for these polymers. Near T_g, two cooperative relaxation regions of dipole polarization were observed for these systems instead of one relaxation transition as in all other polymer classes[1-6].

In this work the main attention will be paid to the effect of side chain length, main chain constitution, and mesogen structure on cooperative forms of molecular mobility in thermotropic side-chain polyacrylates (PA), polymethacrylates (PM), or polysiloxanes (PS) with n methylene groups in the spacers and with cyanoazobenzene (CAB), cyanobenzene (CB), phenylbenzoate (PhB), azomethine (AM), and cholesterol (Chol) mesogenic side groups (see Table 1).

TABLE 1 Investigated side-chain polymers

Sample	n	Chemical formulae of mesogen	ref.
PA-n-CAB	3, 5, 7, 9, 11		7
PM-n-CAB	3, 5, 7, 9, 10		7
PA-n-CB	4, 5		8,9
PM-n-CB	5		9
PS-n-CB	3, 5		3
PS-m*-CB			3
PA-n-PhB	5		10
PA-n-AM	6, 11		11
PM-n-Chol	5, 10, 14		12

m*= -$(CH_2)_2$-O-$(CH_2)_2$-

RESULTS AND DISCUSSION

Dielectric measurements were carried out on the TR-9701 bridge at frequencies ranging from 60Hz to 1 MHz and at temperatures varying from 0 to 200^{0}C. As an example of dielectric behavior, the temperature dependences of tgδ for polymers with n=5 are given in Figure 1 which shows that near the glass transition temperature, two relaxation regions of dipole polarization (α and δ processes) are observed. The tgδ_m temperature of the δ process is well determined for all systems to within 0.5 -1^{0}C. As for the α process, the tgδ_m temperature can be determined precisely only for some polymers.

The lower temperature relaxation region (α process) is caused by the segmental motion of the main chains and by the reorientation of the

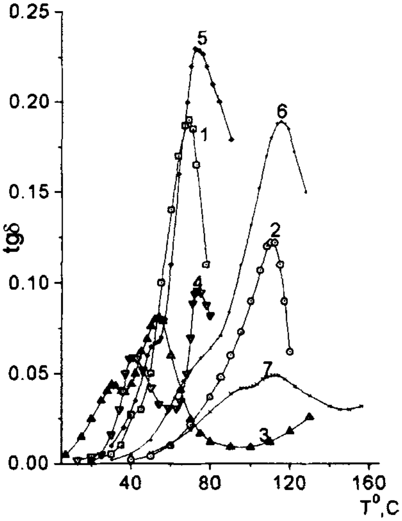


FIGURE 1 Temperature dependences of tgδ (1 kHz): PA-5-CB(1), PM-5-CB(2), PS-5-CB(3), PA-5-PhB(4), PA-5-CAB(5), PM-5-CAB(6), PM-5-Chol(7)

mesogens with respect to their long axis. The second relaxation region (δ process) is caused by the reorientation of mesogenic groups with respect to the short axis. The contributions to dielectric absorption in the α and δ processes are provided by perpendicular, $\mu_{\perp}$, and parallel, $\mu_{\parallel}$,components of the dipole moment of the mesogen[1-6].

The ratio of contributions to the α process due to segmental mobility of the main chains and to the mesogen reorientations can be evaluated from the comparison of dielectric behavior of LC side-chain polymers with that of poly-n-alkylacrylates (PA-n), poly-n-alkylmethacrylates (PMA-n), and polydimethylsiloxane (PDMS). As far as in the latter three polymer series, mesogenic groups are absent, the contribution to the α relaxation is provided only by the segmental mobility. The amplitude of the α process for PA-n[13] and PMA-n[13] are $6 - 8 \cdot 10^{-2}$ and that for PDMS[14] is $7 \cdot 10^{-3}$. Figure 1 shows that for LC side-chain polyacrylates and polymethacrylates the amplitudes of the α process are close to those for PA-n and PM-n. In contrast, for LC polysiloxanes $tg\delta_m$ in the α process is much higher than that in PDMS. This means that in LC polyacrylates and polymethacrylates the main contribution to the dielectric absorption in the α process is provided by segmental mobility. In the case of LC polysyloxane, the α process is mainly caused by mesogen reorientation.

The influence of the main chain structure on the molecular mobility of LC side-chain polymers may be shown by comparing dielectric behavior of PA-5-CB, PM-5-CB, and PS-5-CB the chemical structures of which differ only in the main chain constitution. It is known that segmental mobility and T_g values directly depend on the backbone kinetic flexibility (the lower is T_g , the higher is the kinetic backbone flexibility). Kinetic flexibility increases in the order PMMA, PMA, PDMS because their glass temperatures are 105, -7, and -123^{0}C, respectively. Figure 1 shows that the tgδ_m temperatures for the α and δ processes also decrease from PM-5-CB to PA-5-CB and to PS-5-CB. This means that the molecular mobility of the α and δ processes increases according to the increase in the main chain kinetic flexibility

Figure 1 shows also that the tgδ_m temperature of the α and δ processes for acrylate samples PA-5-CB, PA-5-CAB, and PA-5-PhB are very close. The same situation is observed for methacrylate samples: PM-5-CB, PM-5-CAB, and PM-5-Chol. This means that molecular mobility of mesogens is mainly determined by the main chain structure.

The schemes for mesogenic groups reorientation[8] demonstrate that the intensities of the α and δ processes are determined by the ratio of $\mu_{\|}$ to $\mu_{\perp}$ components of the dipole moment of the mesogenic group. The $\mu_{\|}$ and $\mu_{\perp}$ mesogen values are determined by $\mu_{\|}$ and $\mu_{\perp}$ of polar groups participating in mesogen reorientation. According to the $\mu_{\|}$ and $\mu_{\perp}$ values for these polar groups[15], we have $\mu_{\perp}<\mu_{\|}$, for CAB, CB, and AM mesogenes, and $\mu_{\perp}>\mu_{\|}$ for PhB and Chol mesogenes. Actually, for systems with $\mu_{\perp}<\mu_{\|}$ the δ process predominates, and for those with $\mu_{\perp}>\mu_{\|}$ the α process predominates (Figure 1).

The activation energies for the α (U_α) and δ (U_δ) processes were determined from the slope of the $\log\tau=\varphi(1/T)$ dependences for PA-5-CAB, PA-5-PhB, PM-5-Chol, and PS-m-CB (see Figure 2). It can be seen that in the LC state these dependences are approximated by straight or curved lines. The activation energies are typical of cooperative forms of molecular mobility, and U_α exceeds U_δ (see Table 2).

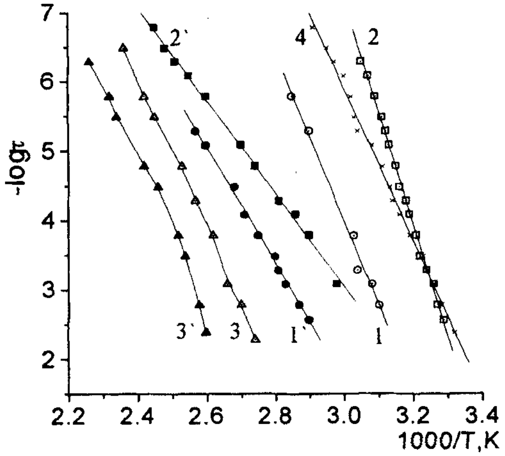


FIGURE 2 Temperature dependences of relaxation time for α(1-4) and δ(1`-3`) processes for PA-5-CAB (1,1`), PA-5-PhB (2,2`), PM-5- Chol (3,3`), and PS-m-CB(4)

This can be explained by the fact that both modes of molecular motion being cooperative processes take place under the conditions when segmental mobility is possible.

If the δ process is observed both in the liquid-crystalline and in the isotropic state, the logτ=φ(1/T) dependence is described by two lines with a break at T_{cl} corresponding to a jump-like decrease (2 -10 times) in relaxation time (see Figure 3).

It can be seen from Table 2 that the activation energies determined in the LC state, $U_{\delta,LC}$, exceed those in the isotropic state, $U_{\delta,is}$(in parentheses). The ($U_{\delta,LC}/U_{\delta,is}$) ratio ranges from 1.29 to 1.87. It means that the molecular mobility in the isotropic phase is higher than that in the LC phase. The differences in activation energies and relaxation times in the LC state as compared to those in the isotropic state are due to the interaction between mesogenic side groups, which leads to the formation of the liquid-crystalline order.

TABLE 2 Parameters of the α and δ processes, glass and clearing transition temperatures

Sample	T_{α},^{0}C	Tδ,^{0}C	U_{α},kcal/mole	Uδ,kcal/mole	T_g,^{0}C	T_{cl},^{0}C
PA-3-CAB	-	68	-	58(31)	62	106
PA-5-CAB	43	47	53	42	39	102
PA-7-CAB	28	33	57	38	31	111
PA-9-CAB	19	24	47	31	26	118
PA-11-CAB	21	25	48	34	29	114
PM-3-CAB	-	82		47(28)	93	156
PM-5-CAB	53	68	55	37	58	173
PM-7-CAB	36	47	44	31	42	168
PM-9-CAB	31	39	47	36	37	164
PM-10-CAB	31	41	50	33	41	161
PA-4-CB	53	60	59	47(27)	56	123
PA-5-CB	-	43	-	46(31)	40	70
PM-5-CB	-	65	-	43(31)	60	130
PA-5-PhB	21	33	71	35	25	122
PA-6-AM	20	23	51	29	20	154
PA-11-AM	7	12	58	29	10	160
PM-5-Chol	69	92	58	55	85	210
PM-10-Chol	33	60	40	36	60	153
PM-14-Chol	37	54	45	37	50	150
PS-3-CB	20	36	48	40	36	142
PS-5-CB	11	17	52	34	21	168
PS-m-CB	16	21	54	36(28)	21	92

The extrapolation of the $\log\tau=\varphi(1/T)$ dependences to 1 Hz ($\tau=1/2\pi$ s.) was used to determine the transition temperatures of the α (T_{α}) and the δ (T_{δ}) processes. Figure 4 shows the T_{α} and T_{δ} values as functions of methylene groups number in the spacer. It can be seen that $T_{\alpha}=\varphi(n)$ and $T_{\delta}=\varphi(n)$ dependences are correlate to each other, and the difference between T_{δ} and T_{α} values does not exceed 20^{0}C.

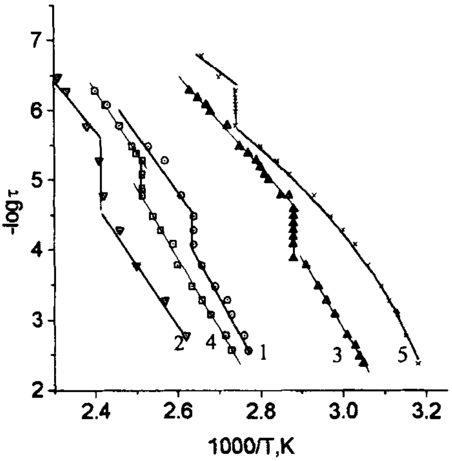


FIGURE 3 Temperature dependences of relaxation time for the δ process: PA-3-CAB(1), PM-3-CAB(2), PA-5-CB(3), PM-5-CB(4), and PS-m-CB(5)

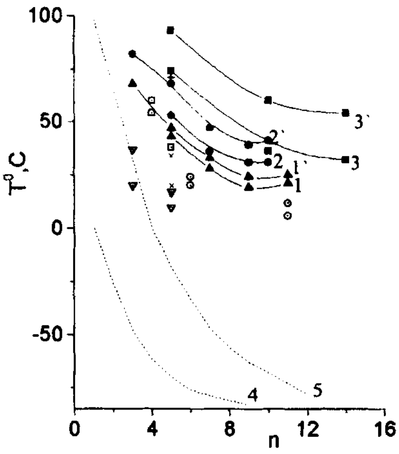


FIGURE 4 Values of T_α (1-3), T_δ (1'-3') and T_g (4,5) vs spacer length: PA-n-CAB(1,1'), PM-n-CAB(2,2'), PM-n-Chol (3,3'), PA-n (4), PM-n (5), PA-6-AM(○), PA-11-AM(○), PS-3-CB(▽), PS-5-CB(▽), PA-4-CB(□), PA-5-CB(□), PM-5-CB(+), PA-5-PhB(×)

Figure 4 also demonstrates that the values of T_α and T_δ at small n markedly decrease with increasing side chain length and then remain virtually unchanged beginning from n=9. The same character of the $T_\alpha=\varphi(n)$ dependences has been observed previously for PA-n and PM-n[7] (curves 4,5). It is likely that the shape of the $T_\alpha=\varphi(n)$ and $T_\delta=\varphi(n)$ dependences in Figure 4 is of a general character for all homologous series of side-chain polymers, and reflects the effect of internal plastification. The difference in T_α between PA-n and PM-n series and the corresponding members of the LC polymer systems increases with spaser length. Without doubt, this is the result of the interactions between mesogenic groups and of the mesomorphic order formation in LC side-chain polymers.

CONCLUSIONS

Molecular mobility investigation of thermotropic side-chain polymers shows that their dielectric behavior has common features. For all these systems two regions of dielectric absorption (α and δ processes) associated with the cooperative mobility of mesogens are observed. The $T_\alpha=\varphi(n)$ and $T_\delta=\varphi(n)$ dependences correlate to each other. This means that both these processes are related to each other, and can be observed only when the segmental mobility of the main chain exists. The parameters of mesogen molecular mobility of the α and δ processes are mainly determined by the backbone flexibility. As to the intensities of these processes, they are determined by the ratio of parallel to perpendicular components of the dipole moments of mesogenic group.

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