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Molecular Mobility in Liquid Crystalline Side-Chain Polyacrylates and Polymethacrylates with Cyanoazobenzene Side Groups: Dielectric Spectroscopy and Thermally Stimulated Depolarization Currents

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Molecular mobility in liquid crystalline (LC) side-chain polyacrylates and polymethacrylates with cyanoazobenzene side mesogens and methylene spacers of different lengths was investigated by dielectric spectroscopy and thermally stimulated depolarization currents methods. For both series of LC polymers, near glass transition temperature (T_g), two relaxations of cooperative character related to segmental motion (α process) and reorientation of mesogens around their short axis (δ process) are observed. Cooperativity of these processes decreases with increasing length of side chains being higher for the α process. Good correlation between dielectric spectroscopy and thermally stimulated depolarization currents methods is obtained for the temperature transitions of the α and δ processes.

Keywords liquid crystaline side-chain polymers; dielectric spectroscopy; thermally stimulated depolarization currents; molecular mobility; α process; δ process

Introduction

At present, liquid crystalline side-chain polymers (LCSCps) functionalized with side mesogenic groups providing specific applications are of great interest. The introduction of mesogenic side groups into macromolecules of conventional polymers allows one to prepare materials of different types of LC structures and temperature intervals of LC phases. Such materials are promising for the creation of operating elements, for optoelectronics, holography, high speed computer systems, and communication devices.

The LCSCps containing azobenzene groups constitute a class of electro- and photocontrollable materials, with properties based on the photochemical reaction of isomerisation of azo groups, which undergo trans- and cis-isomerization under the action of UV radiation [1].

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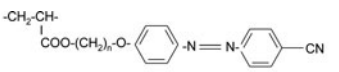
It is clear that the self-organization of mesogenic groups in a polymer matrix and the disruption of LC phase are possible only in the process of molecular reorientation of the mesogenic groups by their thermal molecular mobility. Dielectric techniques, including dielectric spectroscopy (DS) and thermally stimulated depolarization currents (TSDC) method, are the most suitable physical methods for the investigation of molecular mobility in polymer systems.

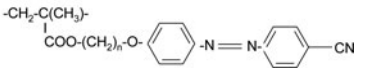
The study of molecular dynamics of LCSC polymers of various structures by DS shows a specific character of the dielectric behaviour typical of this class of polymers. In particular, two regions of dipole polarization relaxation (α and δ processes), rather than a single region (like for all other classes of polymers), were observed near the transition from the glassy to the rubberlike state, with the kinetic characteristics indicating a cooperative character of the molecular motion [2–7]. The α process has been assigned to cooperative segmental mobility, mainly connected with reorientations of the polymer backbone and spacer groups. The δ process, which is slower than the α process, is caused by rotational fluctuations of the dipole component which is parallel to the mesogenic side group around its short axis [2–7]. The use of pressure as a parameter in dielectric measurements, next to temperature, has been shown to provide additional information on the complex dynamics in LCSC polymers [8].

In this work we study molecular mobility in two series of LCSC, polyacrylates (PA-n) and polymethacrylates (PMA-n). The mesogenic groups of these materials contain fragments of azo dyes between phenyl rings and the polar cyanobiphenyl groups are bound to the main chain via aliphatic spacers with different lengths:

PA-n n=3, 5, 9, and 11



PMA-n n=5, 7, 9,and 10



(1)

These materials were synthesized in the laboratory of Prof. V.P.Shibaev (Moscow State University), details of synthesis being given elsewhere [9]. All of them exhibit the smectic phase A (S_A). Glass transition temperature (T_g) and transition temperature from S_A to the isotropic state (isotropization temperature, T_{is}), obtained by DSC, are given in Table 1 [9].

Table 1. T_g and T_{is} of the materials under investigation obtained by DSC [9]

Sample	T_g,C [9]*	T_{is},C [9]
PA-3	62	106
PA-5	39	102
PA-9	26	118
PA-11	29	114
PM-5	58	173
PM-7	50	168
PM-9	37	164
PM-10	49	161

The aim of this work is to study the molecular mobility of PA-n and PMA-n, identify the observed transitions, and reveal the effect of the main chain and of the length of the side chain on molecular mobility.

Experimental Part

Dielectric spectra were recorded on a Novocontrol (Germany) broad-band dielectric spectrometer integrated by a SR 830 lock-in amplifier with an ALPHA-ANB automated high-resolution frequency analyzer and an Agilent 4991 coaxial reflectometer to carry out measurements in the frequency range 10^{-2} – 3 10^6 and 10^6 – 10^9 Hz, respectively. The temperature was controlled by a nitrogen jet (QUATRO from Novocontrol) with an accuracy of ~0.1 K. Isothermal measurements were performed on molded disk-shaped samples (with the upper electrode diameter 10–20 mm) with the sample thickness controlled by 50 μm glass fibers.

TSDC curves were obtained on a TSC/RMA TherMold 9000 apparatus, using molded disks of 0.1 mm thickness and 10 mm diameter as samples. The global TSDC curves were obtained at the following experimental conditions: the sample was polarized by a dc electric field (E_p = 50 – 300 V/mm) at a polarization temperature (T_p = 50°C) and cooled down to the lowest temperature T_0 = -150°C. The field was then removed, the sample was connected to an electrometer and heated at a constant rate r = 7°C min^{-1} to the final temperature T_f = 80°C, while the depolarization current I was recorded as a function of temperature T.

Results and Discussion

For all studied samples the dielectric behaviour is qualitatively similar. As an example, the frequency dependences of dielectric loss ε'' in PM-9 in the LC and the isotropic states are given in Fig. 1.

One can see that in the LC state the curves are non symmetrical or have two ranges of ε''_{max}. In the isotropic state, i.e. at temperatures higher than 164°C the $\varepsilon'' = \phi(f)$ dependences become symmetrical and their intensities increase.

The most important characteristic of each relaxation process is the most probable relaxation time, τ_{max}, determined, according to [10], as:

$$\tau_{\max} = \tau_{HN} \left[\frac{\sin\left(\frac{\pi\alpha_{HN}\beta_{HN}}{2(\beta_{HN}+1)}\right)}{\sin\left(\frac{\pi\alpha_{HN}}{2(\beta_{HN}+1)}\right)} \right]^{1/\alpha_{HN}} \tag{2}$$

The parameters τ_{HN}, α_{HN}, and β_{HN}, in turn, are estimated from the frequency dependences of the complex permittivity, $\varepsilon^* = \varepsilon'(\omega) - i\varepsilon''(\omega)$, described by the empirical Havriliak-Negami equation [11] for one (k = 1) or a sum of two (k = 2) relaxation processes:

$$\varepsilon^*(\omega) - \varepsilon_\infty = \sum_{k=1}^{n} Im \left[\frac{\Delta\varepsilon_k}{\left\{1 + (i\omega\tau_{HN_k})^{\alpha_k}\right\}^{\beta_k}} \right] \tag{3}$$

Here, $\omega = 2\pi f$, $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ is the increment of dielectric permittivity ($\varepsilon_0 = \varepsilon'$ at $\omega \to 0$, $\varepsilon_\infty = \varepsilon'$ at $\omega \to \infty$), τ_{HN} is the Havriliak-Negami relaxation time, and α_{HN} and β_{HN} are fitting

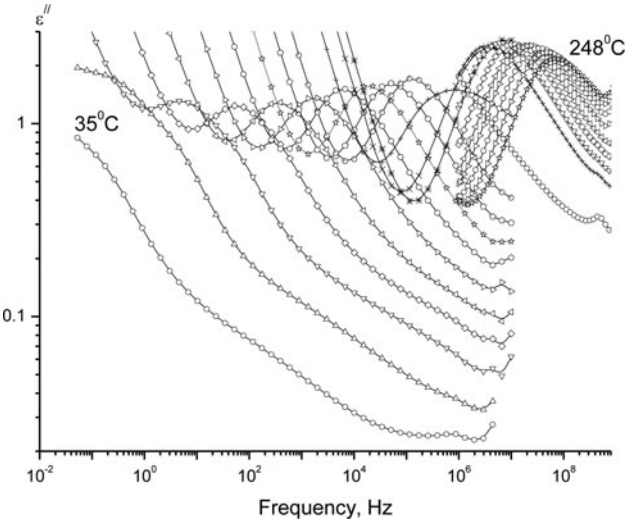


Figure 1. Frequency dependences of dielectric loss $\varepsilon^{\parallel}$ for PMA-9 at different temperatures from 35 to 248°C (step 12°C)

parameters, corresponding to width and asymmetry of the relaxation times distribution, respectively. In the rubber state, the dc conductivity contribution to $\varepsilon^*_{(\omega)}$, appearing at low frequencies, was accounted as $\frac{\sigma_{dc}a}{\varepsilon_v\omega^s}$ [12], where $\sigma_{\rm dc}$ is the specific dc conductivity, a is a constant having dimension $[a] = [\mathrm{Hz}]^{s-1}$, s < 1, and $\varepsilon_{\rm v}$ is the permittivity of vacuum.

In the LC state the $\varepsilon'' = \phi(\mathrm{f})$ dependences are satisfactorily described by Equation 2 as a sum of two processes. As an example, in Figure 2a and 2b, the dependences $\varepsilon'' = \phi(f)$ are presented at 65°C for PMA-9 and PA-9, respectively.

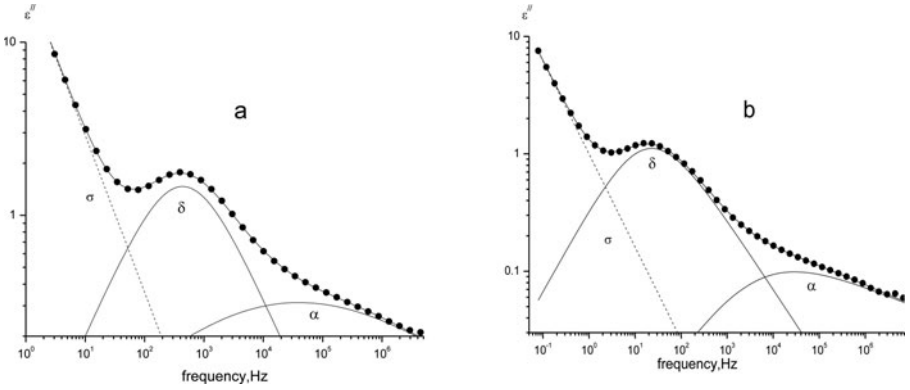


Figure 2. Frequency dependences of ε'' for PA-9 (a) and PMA-9 (b) at 65 °C described according to the HN equation (2) by the sum of the α and δ processes and a conductivity term σ. Points are experimental data, whereas the thick line gives the sum of the three contributions. HN parameters for the α and δ processes for PA-9 are: $\Delta\varepsilon = 2.11$ and 5.26, $\alpha_{\rm HN} = 0.84$ and 0.72, $\beta_{\rm HN} = 0.14$ and 1, $\tau_{\rm HN} = 9.85{\cdot}10^{-6}$ and $3.48{\cdot}10^{-4}$ s, and $-\log\tau_{\rm max} = 5.89$ and 3.46, respectively, and for PMA-9: $\Delta\varepsilon = 0.82$ and 3.87, $\alpha_{\rm HN} = 0.76$ and 0.73, $\beta_{\rm HN} = 0.14$ and 0.77, $\tau_{\rm HN} = 4.69{\cdot}10^{-6}$ and 0.00094 s, and $-\log\tau_{\rm max} = 5.35$ and 2.16, respectively.

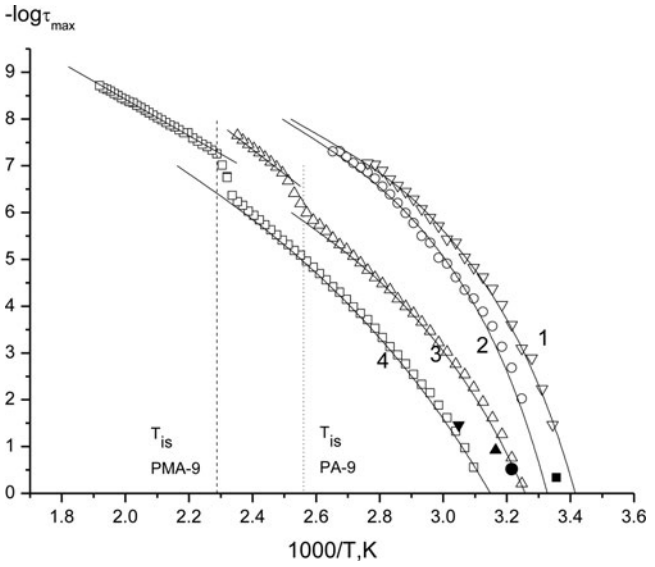


Figure 3. Dependences of -logτ_{max} on reciprocal temperature for PA-9 (1,3) and PMA-9 (2,4) in the region of α (1,2) and δ (3,4) processes; T_m at f_e for PA-9 for α (■) and δ (▲) and for PMA-9 for α (●) and δ (▼) processes, respectively.

The relaxation times τ_{max} obtained from equations (1) and (2) for these relaxation processes are presented in the coordinates $-\log\tau_{max}$ on 1/T in Fig. 3 (curves 1–4).

These dependences are curvilinear (the activation energy is temperature-dependent). This is characteristic of cooperative forms of molecular mobility. The curves 1–4 may be satisfactorily described by the empirical Vogel-Fulcher-Tammann-Hesse (VFTH) equation [13]:

$$\tau_{max} = \tau_0 \exp\left(\frac{B}{T - T_0}\right), \tag{4}$$

where τ_0, B and T_0 are temperature-independent parameters. The value τ_0 is the high-temperature-limit relaxation time, B is the activation parameter, and T_0, called the Vogel temperature or the ideal glass transition temperature, is usually a few tens of degrees below T_g. The parameters of the VFTH equation are presented in Table 2.

The comparison of the dielectric behavior of the studied PA-n and PMA-n with that for LCSC polymers of different structures [2–8] allow us to conclude that the observed processes reflect the segmental mobility (α process) and the reorientation of the cyanoazobenzene side groups relatively to their short axis (δ process). The presence of the second cooperative δ process near T_g is due to the fact that the mesogens, being rather bulky groups, are attached to the macromolecule main chain by only one of their ends through a flexible methylene spacer. This will enable them to move quite independently from the main chain in the highly elastic state above the glass transition, which cannot be expected for linear main chain liquid LC polymers.

The degree of cooperativity of the α process and the δ process can be estimated by the fragility (strength) parameter D which is obtained from Eq. 4, modified by replacing B by D^*T_0. This parameter is a measure of the fragility which determines the deviation of

Table 2. VFTH parameters of the α process and the δ process in the LC state and fragility parameter D for both processes

	α-process					δ-process in the LC state				
sample	$-\log\tau_0$, s	B, K	T_0, K	T^*_g,^{0}C	D	$-\log\tau_0$,s	B, K	T_0, K	T^*_δ,$^\circ$C,	D
PA-3	11.9	885	308	67	2.9	10.2	1085	304	76	3.5
PA-5	11.9	865	290	49	3	10.2	1285	281	62	4.6
PA-9	10.9	947	255	20	3.7	9.9	1304	249	34	5.2
PA-11	11.5	948	256.5	19	3.7	11.5	2021	227	30	8.9
PM-5	10.4	510	276	52	1.8	12.9	1535	221	67	6.9
PM-7	9.6	798	272	37	2.9	11.6	2616	231	55	11.3
PM-9	11.1	980	262	27	3.7	11.9	2783	216	44	12.9
PM-10	11.7	1247	262	16	4.8	13.2	3730	193	43	19.3

the dependence $-\log\tau_{\max} = \phi(1/T)$ from a linear Arrhenius behavior [14, 15]. The higher is the deviation of the dependence $-\log\tau_{\max} = \phi(1/T)$ from the linear one, the lower is D, the higher is fragility (the lower is strength), and the more cooperative is the process. For polymers PA-n and PMA-n, the D values for α and δ processes are given in Table 2. The results show that for both α and δ processes the parameter D increases with n, i.e. cooperativity decreases. For both series of polymers, the degree of cooperativity of the α process is higher than that of the δ process. The latter is due to the fact that the size of the mesogenic group, the reorientation of which is responsible for the appearance of the δ process, is smaller than the main chain segment, the movement of which contributes to the α process.

The glass transition temperatures for polymers PA-n and PMA-n were obtained by the usual for dielectric measurements procedure: the curves 1 and 2 (Fig. 3) in the LC state described by the VFTH equation were extrapolated to $\log\tau_{\max} = 0$, i.e. to $\tau_{\max} = 1$ s. (Please note that often the T_g values are determined at $\tau = 100$ s [16]. In that case, the T_g values would be by ~5–10°C lower than those presented in Table 1). As to the transition temperature of the δ-process (T_δ), it was formally obtained by the same procedure as for the α process: extrapolation of the curves 3 and 4 (Fig. 3) to $\log\tau_{\max} = 0$. The T_g and T_δ values decrease with n that reflects the effect of internal plasticization. For all relevant homologues, PMA-n has higher T_g compared to PA-n due to the greater kinetic flexibility of the polyacrylate main chain.

The results obtained by DS can be compared with TSDC data because the phenomena studied in both methods are determined by the same dynamic behaviour of the macromolecules. The peaks displayed on the $\varepsilon'' = \phi$ (f) (DS) and $I = \phi(T)$ (TSDC) plots are due to the orientational mobility of kinetic units containing a polar group. The temperature position of depolarization current peaks T_m formally corresponds to the temperature position of tgδ or ε'' peaks observed at the equivalent frequency f_e which is determined for cooperative processes as [17, 18]:

$$f_e = \frac{E_a r}{2\pi R(T_M - T_0)^2} \tag{5}$$

$$E_a = \frac{RB}{(1 - T_0/T)^2} \tag{6}$$

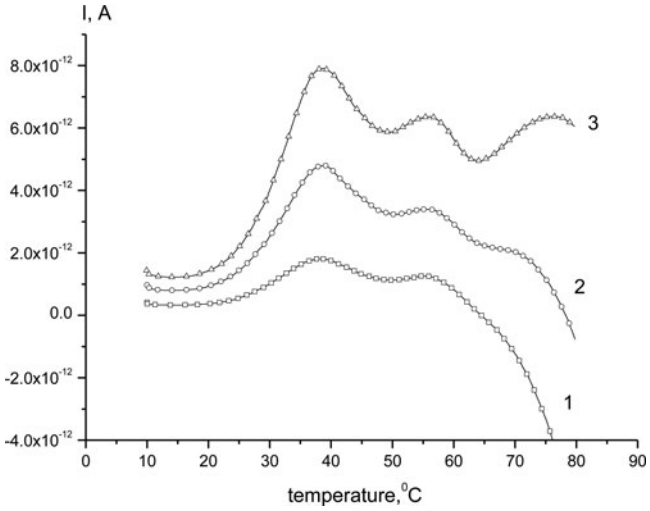


Figure 4. Global TSDC spectra for PMA-9 at $U_p = 100(1)$, 200(2), and 300(3) V/mm; $T_p = 50^\circ C$

In these equations E_a is the activation energy, T_M is the depolarization current maximum, R is the absolute gas constant and the other parameters have been defined above.

The global $I = \varphi(T)$ plots for PA-n and PMA-n are rather similar. As an example, Fig. 4 shows such plots for PMA-9.

As can be seen in Fig. 4, there are two regions corresponding to depolarization current maxima T^m in the vicinity of T^g. The intensity of depolarization current I_m shows a linear dependence on polarizing field E_p; this fact is often considered as an indication of the dipolar nature of the corresponding relaxation mechanism [17]. TSDC data have been included in Fig. 3, namely peak temperatures T_M and the corresponding equivalent frequencies f_e determined by using Eqs. (5) and (6) (see caption to Fig. 3). There is a quite good correlation between dielectric and TSDC data [19]. One can conclude that the first peak on the global curves corresponds to the α process and the second to the δ one. The third, the highest temperature peak on the global curves, generally called the ρ peak, has no analogues in DS. The depolarization current for this third peak decreases abruptly passing through zero and changing sign at about 70°C. This situation is typical for the ρ peak caused by free space charge polarization.

For the δ process, in the isotropic state, the $-\log\tau = \phi(1/T)$ dependences in Fig. 3 become linear and have an Arrhenius character:

$$\tau(T)_{\max} = \tau_0 \exp\left(\frac{E_a}{RT}\right) \tag{7}$$

where $\tau_0 = \tau_{max}$ at $T \to \infty$ and E_a is the activation energy. Values of $-\log \tau_0$ and E_a for the δ process in the isotropic state are presented in Table 3.

For both series of polymers, a jump in relaxation times (about 1-2 orders of magnitude) at the transition from the mesophase to the isotropic state was observed. This jump, related with the increase in mesogen mobility, is a clear indication of the order disappearance and of the decrease in intermolecular interactions. A linear dependence $-\log\tau_{max} = \phi(1/T)$ is characteristic of local forms of mobility. For local forms of mobility, τ_0 and

Table 3. Parameters of the Arrhenius equation (7) for the δ process in the isotropic state

Sample	$-\log\tau_0$,s	E_a, kcal/mole
PA-3	22.1	31.3
PA-5	21.8	28
PA-9	21.3	26.6
PA-11	21.3	26
PM-5	18.2	23.4
PM-7	15.2	16
PM-9	16.2	17.9
PM-10	15.2	15.4

E_a are about 10^{-11}– 10^{-13} s and 4–12 kcal/mole, respectively. For local relaxation processes observed, as a rule, in the glassy state, and caused by the motion of individual polar atoms or small groups, the mobility is mainly determined by intramolecular interactions and the reorientation of polar kinetic units is virtually non-correlated with the neighboring chains. The data of Table 3 show that (absolute) τ_0 and E_a values exceed those for typical local processes. This may be due to the fact that the mesogenic groups are fairly bulky, so their motion relative to the short axis requires a sufficient free volume that leads to an increase in the cooperativity of the process. This is indicated by a comparison of the data in Table 3 for PA-n and PMA-n. It is evident that the parameters τ_0 and E_a for polyacrylates are higher than those for polymethacrylates due to the higher packing density of polyacrylates.

Conclusions

Molecular mobility in two series of LCSC polyacrylates (PA-n) and polymethacrylates (PMA-n) with cyanoazobenzene side mesogens and methylene spacers of different length was investigated by DS and TSDC methods. Following the overall behavior of LCSC polymers with various structures of the backbone and the mesogen, the PMA-n and PA-n studied here exhibit two relaxations of cooperative character near T_g, related to segmental motion (α process) and reorientation relative to the mesogenic short axis (δ process), respectively. The characteristic temperatures of the α and δ processes, T_g and T_δ, respectively, were determined by extrapolation of the $-\log \iota_{max} = \phi(1/T)$ dependences described by VFTH equation to $\log \iota_{max} = 0$. The T_g and T_δ values, as well as the cooperativity of the α and δ processes, decrease with increasing length of the side chain, this behaviour being related with the effect of internal plasticization. For all relevant homologues, PMA-n has higher T_g compared to PA-n due to the greater kinetic flexibility of the polyacrylate main chain.

The relaxation times for the δ process exhibit a jump at the transition S_A/T_{is}, related with the increase in mesogen mobility at disappearance of the liquid crystalline structure and with the decrease of intermolecular interactions. In the isotropic state, the dependences $-\log \tau_{max} = \varphi(1/T)$ become linear, which is characteristic of local forms of mobility. However, the parameters of the Arrhenius equation, τ_0 and E_a, exceed those for typical local processes, because the mesogenic group motion requires a sufficient free volume that leads to an increase in the cooperativity of the δ process.

The global TSDC curves show three peaks of depolarization current. The comparison of the two methods at the equivalent frequency allows us to attribute the first and second

peak on the global thermogram to the α and δ process, respectively, and the third peak at higher temperatures, having no analogue in the dielectric spectra, to the ρ peak caused by free space charge polarization.

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