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Polymer 48 (2007) 556–563

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Dielectric relaxation in copolymethacrylates containing side-chain nonlinear optical chromophores

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Received 11 August 2006; received in revised form 25 September 2006; accepted 30 September 2006
Available online 5 December 2006

Abstract

Molecular mobility in the films of chromophore-containing copolymethacrylates was studied by dielectric spectroscopy. Near the glass transition temperature α- and δ-relaxation processes were observed, being related to segmental mobility and the reorientation of chromophore-containing side groups, respectively. It was shown that the temperature dependences of relaxation times in the range of the δ-process are linear or curvilinear for copolymers with 20 or 50% molar fraction of chromophore-containing units, indicating that the local or cooperative character of chromophore mobility was due to the absence (presence) of inter-chromophore interactions. These data are very important for optimizing the chromophore molar content in NLO polymers since the inter-chromophore dipole–dipole interactions usually lead to the formation of centro-symmetric anti-parallel aggregates which cannot be oriented by external electric fields. It was shown that the δ-process occurs at higher temperatures than the α-process. This fact is of great importance for optimizing the poling temperature at which macroscopic non-centrosymmetric orientation of chromophore occurs under the external electric field applied across a polymer film. The poling temperature should be at least not lower than the glass transition temperature for the δ-process.

Keywords: Polymethacrylates; Nonlinear optical chromophores; Dielectric relaxation

1. Introduction

In the last decade great attention was directed to preparation and investigation of polymers with covalently attached chromophores [1–3]. Such systems are promising for applications in micro- and optoelectronics, high-speed computer systems and means of communication, for example, as low-loss optical waveguides and high bandwidth, integrated optical modulators [4]. The presence of chromophore-containing fragments in macromolecules (in the main or side chains) provides second- and/or third-order nonlinear optical (NLO) properties for these polymeric materials. For second-order NLO properties, the most widely known of which is the second harmonic generation (SHG), a macroscopically non-centrosymmetric arrangement of chromophore groups within a polymer sample is required. Such a polar ordering of chromophores is usually attained by applying strong direct electric fields across few microns thick polymer films at temperatures close to the glass transition temperature of each particular polymer. In some cases, using this poling procedure, it is possible to obtain SHG coefficients, d_{33}, and electro-optic coefficients, r_{33}, for poled chromophore-containing polymer films comparable with those obtained for typical inorganic NLO crystals like lithium niobate [5,6]. The advantages of NLO polymers are their relatively low cost, the possibility of obtaining thin films with high mechanical properties, as well as virtually unlimited possibilities of synthesizing different chemical structures.

At present, a large number of polymeric materials based on copolymers of chromophore-containing methacrylates have

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doi:10.1016/j.polymer.2006.09.063

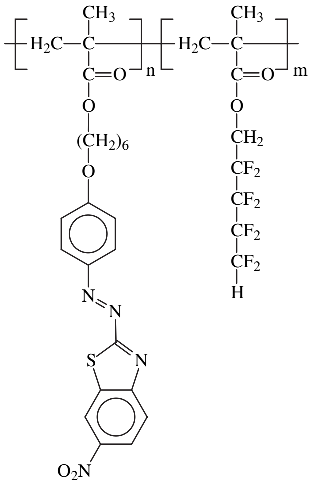
been synthesized [7–11]. Their second-order NLO properties depend on many factors, the polarizing electric field strength, the first hyperpolarizability and dipole moment of chromophore groups being among them [5,6]. Besides, it is now recognized that macroscopic polar ordering of chromophores within polymer matrices is strongly reduced due to dipole–dipole interaction between chromophores, leading to the formation of centrosymmetric anti-parallel aggregates of them (self-organization). This process is strongly affected by the shape and volume concentration of chromophore groups, being especially remarkable at high concentrations of rod-like π-conjugated chromophores [5,6,12].

It is clear that the orientation of chromophore groups in strong external fields or their self-organization in a polymer matrix is possible only during the process of their molecular reorientation. In the former case the orientation of these groups is initiated by their interaction with the external field and in the latter case by the thermal motion of kinetic units. This means that a correlation should exist between the molecular mobility of chromophore-containing polymer fragments and the possible appearance of second-order NLO properties.

One of the most suitable physical methods for the investigation of molecular mobility in polymer samples placed in an external alternating electrical field at frequency f is the dielectric method or the method of dielectric spectroscopy (DS). This method makes it possible to obtain data on the molecular mobility of a macromolecule as a whole and of its main-chain segments, bulky side groups, etc. The method is based on the study of temperature and frequency dependences of dielectric loss factor ε''. Dielectric losses in a polymer sample appear during thermal orientation of polar kinetic units when the projection of dipole moment on the direction of the measuring electric field changes.

The deciphering of dielectric spectrum is based on the comparison of dielectric behavior of polymer systems which differ in only one element of their monomer unit chemical structure [13–16]. This makes it possible to identify the observed relaxation processes and to relate them to molecular mobility of kinetic units bearing a polar group.

In this paper random copolymers of chromophore-containing methacrylates and methacrylamides were studied. Their synthesis was described in Ref. [17]. The CP1–CP8 copolymers of the following structures were investigated:


CP1
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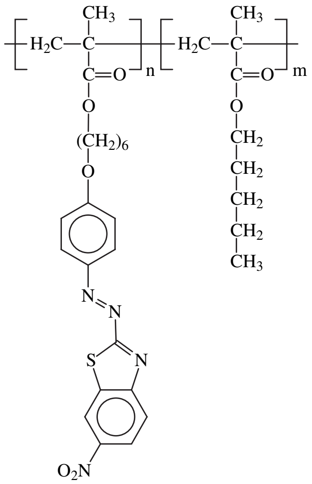
CP2
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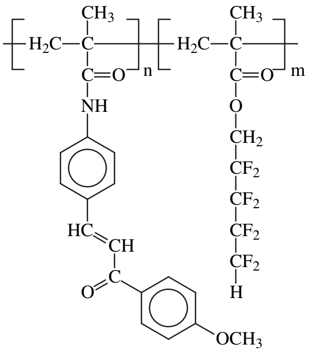
CP3
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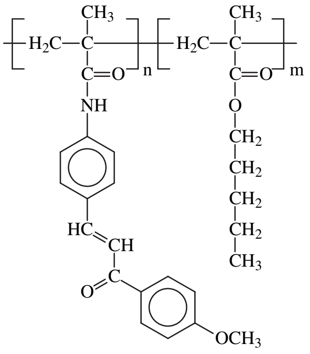
CP4
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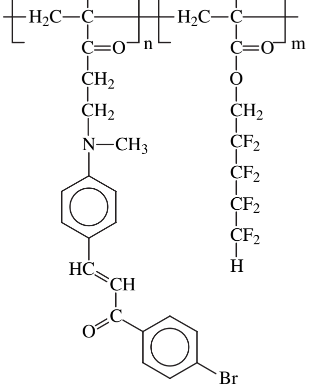
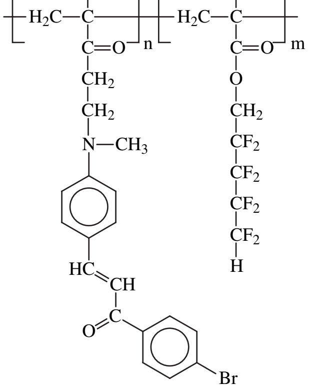

CP5
n:m 20:80


CP6
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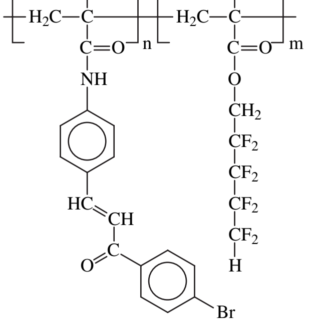
CP7
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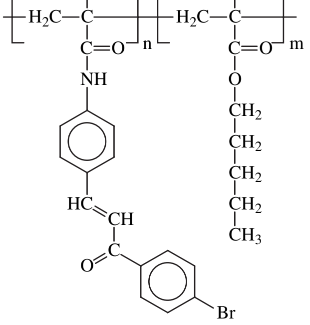
CP8
n:m 50:50

In these copolymers, long side chains are of two types: (1) rigid chromophore-containing fragments (molar fraction *n*) and (2) flexible octafluoro-amyl ($-CH_2-(CF_2)_4-H$) or amyl ($-CH_2-(CH_2)_4-H$) groups (molar fraction *m*). Besides these copolymers, two model polymers P1 and P2 without chromophore groups ($n = 0$, $m = 100$) which contain only flexible side groups $-CH_2-(CF_2)_4-H$ or $-CH_2-(CH_2)_4-H$, respectively, were investigated.

The dielectric behavior of polymethacrylates of different structures has been extensively studied [18–20]. For the present study, it is important that there are several polar groups within the chromophore-containing side chains. Therefore, their reorientation must be dielectrically active.

The chromophore-containing copolymers under investigation here are similar in their chemical structure to that of liquid crystalline (LC) side-chain polymers. In these systems, just as in LC side-chain polymers, the side functional chromophore groups could be considered as mesogenic ones. The dielectric behavior of LC side-chain polymers and, in particular, of LC polymethacrylates, was investigated in detail [20–22]. It was shown that the mesogenic groups take part in two forms of motion. The first is a local mobility at low temperatures which is related to the rotation of mesogen-containing fragments about their long axes (the β-process). The second is the cooperative mobility at temperatures higher than the glass transition temperature, T_g, which is related to the rotation of mesogenic group about their short axes (the δ-process) [13,15,20–28]. By analogy with LC side-chain polymers, it may be supposed that chromophore groups should also participate in these two forms of molecular mobility.

The main aim of the present work is to establish the relationship between the chemical structure of the copolymers and their molecular mobility. Particular attention will be paid to the consideration of relaxation processes due to reorientation of chromophore fragments responsible for the appearance of second-order NLO properties. In this study, the films of the chromophore-containing copolymers CP1–CP8 have not been preliminarily corona poled. Their dielectric behavior was studied in the range from room temperature to temperatures exceeding T_g by 50–100 °C. The necessity to go to such high temperatures is caused by the fact that during the corona poling of polymer films, the chromophore orientation process occurs in the highly elastic state of the polymer matrix.

2. Methods

Dielectric measurements were carried out with the aid of FRA-1260 frequency response analyzer (Novocontrol). The initial samples were the films obtained by pressing at a temperature exceeding T_g. Brass disks were used as electrodes. The diameter of the upper disks was 10–20 mm. Sample thickness was determined by 50-μm quartz fibers.

3. Results and discussion

3.1. Main features of dielectric behavior of copolymers CP1–CP8

For each of the CP1–CP8 series of copolymers, frequency dependences of dielectric permittivity ε', dielectric loss factor ε'', and conductivity in the range of frequencies 10^{-2}–10^7 Hz and temperatures 20–220 °C were obtained.

For CP1, the frequency dependence of dielectric loss factor ε'' at temperatures higher than T_g shows two ranges of dielectric absorption (Fig. 1). At the same time, for the CP2–CP8 copolymers only one relaxation process was observed on the experimental dependence $\varepsilon'' = \varphi(f)$.

As an example, Fig. 2 shows the experimental dependences $\varepsilon'' = \varphi(f)$ for CP6. It is clear that at low frequencies and high temperatures the ε'' values increase by several orders as compared to those characteristic of relaxation processes of dipole polarization. These values are typical of conductivity relaxation and of electrode polarization due to charge migration between electrode surfaces and the polymer sample [29,30]. Such dielectric behavior can be explained by the great contribution of dielectric losses caused by direct current ohmic conductivity, σ_{dc}, to the $\varepsilon'' = \varphi(f)$ dependences.

The contribution due to ohmic conductivity in polymers is determined by impurities, solvent and/or catalyst residues, and by the chemical structure of a polymer itself. For the investigated systems CP1–CP8, π-conjugated systems of chromophore groups with relatively loosely bound π-electrons predetermine the high σ_{dc} values. Moreover, for NLO polymer systems, the thermal history also affects the σ_{dc} values since double bonds within chromophore groups may break on heating [31].

The frequency dependences of alternating current conductivity, $\log \sigma_{ac} = \varphi(\log f)$, are typical for all systems

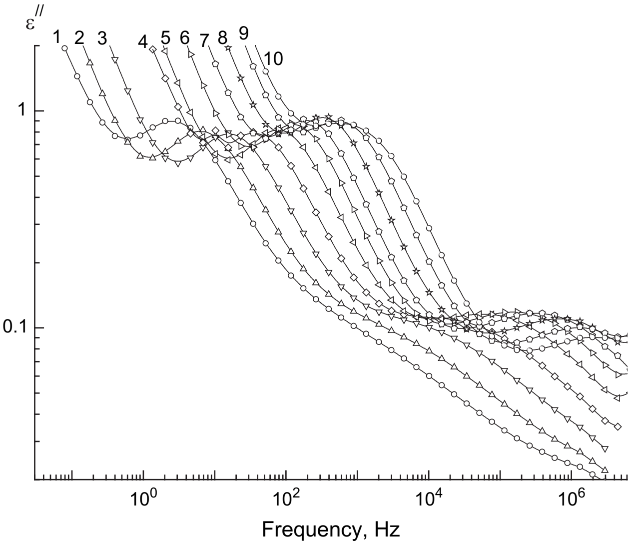

Fig. 1. Frequency dependences ε'' for CP1 at temperatures 80 (1), 90 (2), 100 (3), 110 (4), 120 (5), 130 (6), 140 (7), 150 (8), 160 (9), and 170 °C (10).

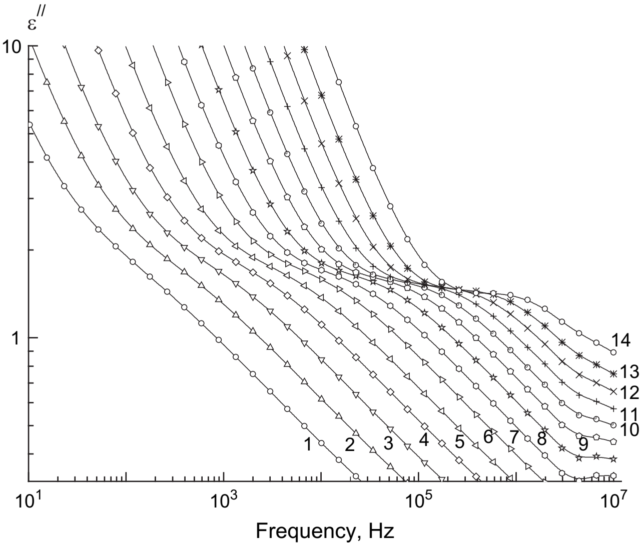

Fig. 2. Frequency dependences ε'' for CP6 at temperatures 110 (1), 116 (2), 122 (3), 128 (4), 134 (5), 140 (6), 146 (7), 153 (8), 159 (9), 165 (10), 171 (11), 176 (12), 182 (13), and 188 °C (14).

investigated in this work. As an example, they are given in Fig. 3 for CP3. At low frequencies these dependences have plateau regions caused by free motion of charges in the highly elastic state [29]. The σ_{ac} values in the plateau region correspond to direct current conductivity, σ_{dc}. In Fig. 3, the transition from the plateau region to the frequency dependence of σ_{ac} corresponds to the change of the conductivity mechanism [29,30]. In the left-hand side of dependences $\log\sigma_{ac}=\varphi(\log f)$ (plateau region) charges migrate by large distances, whereas in the right-hand side (σ_{ac} increases with frequency) the motion of charge carriers is dimensionally restricted to their potential wells.

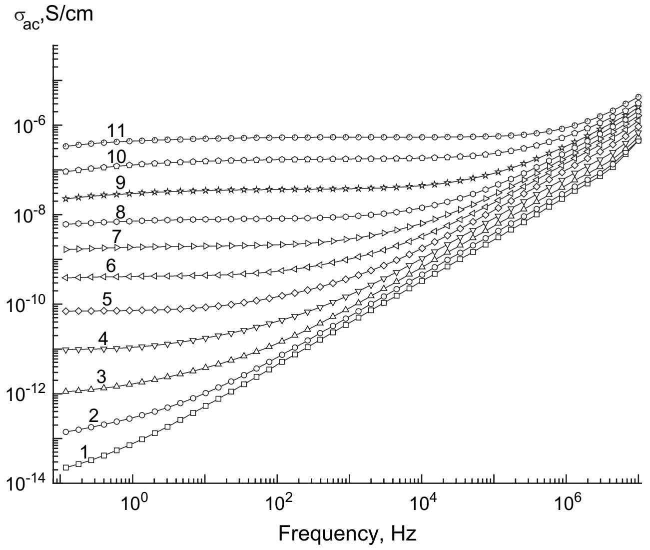

Fig. 3. Frequency dependences of conductivity on alternating current for CP3 at temperatures 60 (1), 80 (2), 100 (3), 120 (4), 140 (5), 160 (6), 180 (7), 200 (8), 220 (9), 240 (10), and 260 °C (11).

3.2. Transformations of experimental dependences $\varepsilon''=\varphi(f)$ according to Kramers–Kronig equation

Wubbenhorst and van Turnhout have proposed a way to eliminate the ohmic conductivity from dielectric loss spectra [32] using the Kramers–Kronig (KK) equations:

$$\varepsilon'(\omega)=\varepsilon_0+\frac{2}{\pi}\int_0^\infty \varepsilon''(\omega)\,\frac{\omega}{\omega^2-\omega_0^2}\,\mathrm{d}\omega$$

$$\varepsilon''(\omega)=\frac{\sigma_{\mathrm{dc}}}{\varepsilon_{\mathrm{v}}\omega_0}+\frac{2}{\pi}\int_0^\infty \varepsilon'(\omega)\,\frac{\omega_0}{\omega^2-\omega_0^2}\,\mathrm{d}\omega$$

It is clear from KK equations that ε' and ε'' are interrelated. This permits to transform the dependences $\varepsilon'=\varphi(f)$ into $\varepsilon''=\varphi(f)$. After differentiation we obtain the dependences $\varepsilon''_{\mathrm{d}}=\varphi(f)$ which are free from ohmic losses. As a result, the "resolution" of dielectric spectra is improved. Using this procedure, the frequency dependences $\varepsilon''_{\mathrm{d}}$ for CP2–CP8 were obtained.

For CP2–CP8 copolymers, a sharp increase in $\varepsilon''_{\mathrm{d}}$ started at frequencies two or three orders lower than those for experimental dependences $\varepsilon''=\varphi(f)$. This made it possible to observe the second low frequency relaxation process, just as for the CP1 copolymer. This second low frequency process had previously been hidden by losses due to ohmic conductivity. (Only for CP2, the frequency dependences $\varepsilon''_{\mathrm{d}}$ did not show the second relaxation process but they were asymmetric. It may be assumed that they are the sum of two overlapping relaxation processes.)

Fig. 4 shows the comparison of experimental and differentiated frequency dependences ε'' for CP3 at temperatures 130

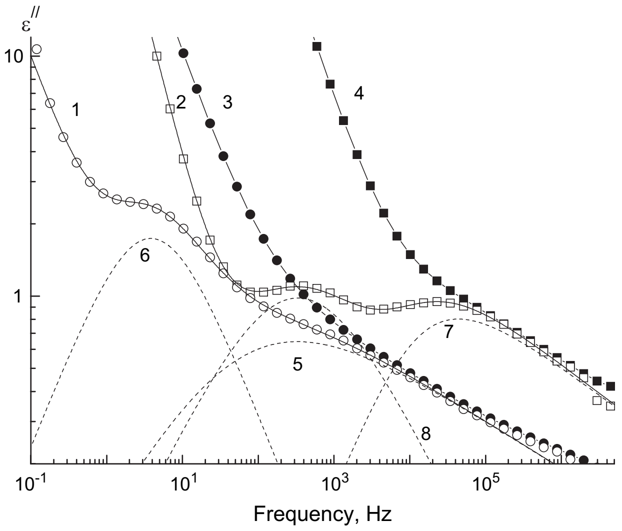

Fig. 4. Frequency dependences ε'' for CP3 at temperatures 130 (1,3) and 180 °C (2,4) for experimental (3,4) and differentiated (1,2) dependences. Dash lines are separation of curves 1 and 2 into α- (5,7) and δ- (6,8) processes according to Eq. (1). Full lines are description of curves 1–4 according to Eq. (1).

and 180 °C. Taking into account the above mentioned similarity between the chemical structures of LC side-chain polymers and chromophore-containing systems under study, it may be assumed that the high and low frequency maxima in the frequency dependences of ε'' for CP1–CP8 are caused by α- and δ-processes, respectively. For CP1–CP8 copolymers with side-chain chromophore groups, as for LC side-chain polymers, the α-process may be related to the backbone segmental mobility, whereas the δ-process reflects the reorientation of side-chain chromophore fragments about their short axes.

3.3. Analysis of the frequency dependences of ε'' with the aid of the empirical Havriliak–Negami equation

Frequency dependences $\varepsilon'' = \varphi(f)$ for CP1–CP8 copolymers were described with the aid of the empirical Havriliak–Negami (HN) equation [33]:

$$\varepsilon'' = \frac{\sigma_0 a}{\varepsilon_0 \omega^s} - \sum_{k=1}^{2} \mathrm{Im}\left[\frac{\Delta\varepsilon_k}{\{1+(\mathrm{i}\omega\tau_{\mathrm{HN}_k})^{\alpha_k}\}^{\beta_k}}\right] \qquad (1)$$

where σ_0 is the specific direct current conductivity, a is a constant having the dimensions $[a] = [\mathrm{Hz}]^{s-1}$, $s < 1$, and ε_0 is the dielectric permittivity of vacuum. The second term in Eq. (1) is the HN empirical function where $\tau = 2\pi f$ is the relaxation time, f is the frequency of alternating electric measuring field, $\Delta\varepsilon$ is the increment of dielectric permittivity, α and β are the calculated parameters corresponding to expansion and asymmetry of relaxation times distribution, respectively. In this case, the subscript k means α- or δ-process. $\tau_{\max} = 1/(2\pi f_{\max})$, $f_{\max}$ is the frequency at which ε'' passes through the maximum. The ratio between $\tau_{\max}$ and τ_{HN} is determined by the following equation [34]:

$$\tau_{\max} = \tau_{\mathrm{HN}} \left[\frac{\sin\left(\frac{\pi(1-\alpha)\beta}{2(\beta+1)}\right)}{\sin\left(\frac{\pi(1-\alpha)}{2(\beta+1)}\right)}\right]^{1/(1-\alpha)}$$

The HN equation permits to determine the contributions of the α- and δ-processes to the dependences $\varepsilon'' = \varphi(f)$. Fig. 4 shows for CP3, as an example, the separation of the $\varepsilon''_{\mathrm{d}} = \varphi(f)$ dependence (curves 1 and 2) into α- and δ-processes (dash lines) as well as the sum of these processes (full lines) obtained by calculations according to Eq. (1).

Relaxation times, $\tau_{\max}$, obtained from Eq. (1) for all investigated NLO copolymers in the range of the α- and δ-processes are shown in Figs. 5 and 6, respectively. Moreover, Fig. 5 shows the dependences $-\log\tau_{\max} = \varphi(1/T)$ in the α-process range for the model polymethacrylates P1 and P2.

It is important from the point of view of preparing and using NLO polymers that for all systems studied here, the temperature–frequency coordinates of the δ-process are at temperatures higher by ~30 °C than those for the α-process. This is due to the fact that the reorientation of chromophores about the short axis requires rather large free volume and takes place only under the conditions of segmental mobility of the macromolecule. The fact that it is possible to observe the dielectric δ-process means that the motion of chromophore-containing fragments is relatively independent of that of the polymer backbone.

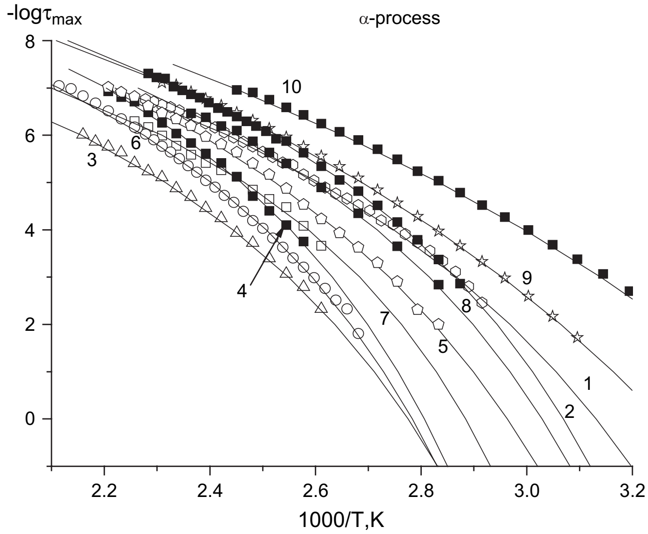

Fig. 5. Dependences of $-\log\tau_{\max}$ on inverse temperature in the range of the α-process for CP1 (1), CP2 (2), CP3 (3), CP4 (4), CP5 (5), CP6 (6), CP7 (7), CP8 (8), P1 (9), and P2 (10).

3.4. Temperature dependence of relaxation times in the range of the α-process

Temperature dependences of relaxation times, $-\log\tau_{\max} = \varphi(1/T)$, in the range of the α-process are curved for all NLO polymers. This indicates that the relaxation process considered

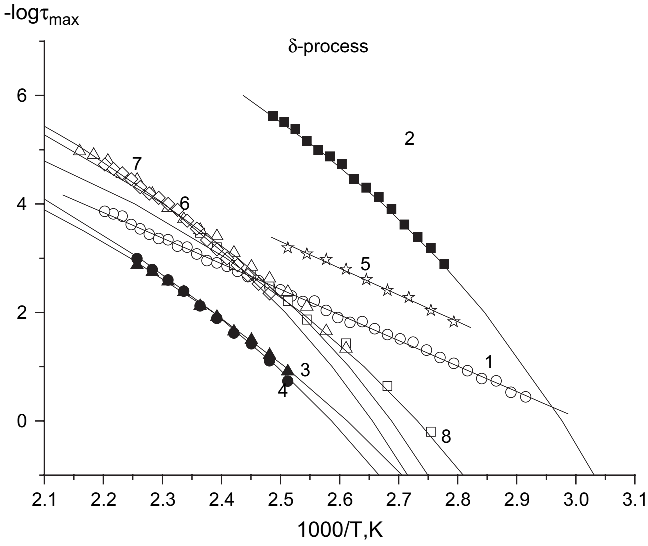

Fig. 6. Dependences of $-\log\tau_{\max}$ on inverse temperature in the range of the δ-process for CP1 (1), CP2 (2), CP3 (3), CP4 (4), CP5 (5), CP6 (6), CP7 (7), and CP8 (8).

here is cooperative. In other words, the molecular mobility of kinetic segments of polymer backbone responsible for the α-process depends on the state of their close environment and is determined to a great extent by intermolecular interactions. Cooperative forms of motion are characterized by a wide distribution of relaxation times and occur as combined correlated motion of a large number of segments belonging to neighboring macromolecules.

As to the local forms of molecular mobility, they are characterized by a jump of polar kinetic units from the one equilibrium state into another, being independent of the environment. In this case, the dependence $-\log \tau_{\max} = \varphi(1/T)$ is linear and obeys the Arrhenius equation which assumes only one relaxation time:

$$\tau_{\max} = \tau_0 \exp(U_a/RT).$$

For CP1–CP8, the dependences $-\log \tau_{\max} = \varphi(1/T)$ in the range of the α-process (similar to ordinary amorphous and semicrystalline polymers) are well described by the Vogel–Fulcher–Tammann–Hesse (VFTH) empirical equation corresponding to cooperative forms of molecular motion [35]:

$$\tau_{\max} = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \tag{2}$$

where τ_0, B, and T_0 are parameters that do not depend on temperature. T_0 is the so-called Vogel temperature which is usually lower than T_g by several tens of degrees. The B parameter is a measure of the curvature of the temperature dependence of relaxation time. The lower the B is, the higher is the cooperativity of the considered process. The parameters of Eq. (2) for CP1–CP8 in the range of the α-process are given in Table 1.

Now we will attempt to analyze in what way the chemical structure of the copolymers CP1–CP8 affects the temperature–frequency position of the dependence $-\log \tau_{\max} = \varphi(1/T)$, i.e. the molecular mobility in the range of the α-relaxation.

For CP1–CP8, a great number of structural parameters were changed: the structure of chromophore groups, the spacer, the flexible part of the copolymer, as well as the concentration (i.e. molar fraction) of chromophore groups. To identify the observed relaxation transitions, the systems differing in only one structure element will be compared below.

Table 1
Parameters of VFTH equation for the α- and δ-processes

	α-process				δ-process			
	$\log \tau_0$, s	B, K	T_0, K	T_g,[a] °C	$\log \tau_0$, s	B, K	T_0, K	$T_{g\delta}$,[a] °C
CP1	−11.4	2163	237	46	−14.2	$U = 22$ kcal/mol		
CP2	−11.6	1785	259	53	−112.6	2379	254	63
CP3	−11.0	2118	276	88	−9.8	3199	241	109
CP4	−12.2	2034	284	81	−9.9	2912	259	113
CP5	−12.1	2327	254	65	−15.8	$U = 23$ kcal/mol		
CP6	−12.2	2398	272	84	−10.7	2380	280	103
CP7	−10.5	1566	282	74	−9.7	1989	283	99
CP8	−11.4	1842	260	57	−9.4	2275	261	93
P1	−13.3	3289	200	35				
P2	−13.3	3386	176	13				

[a] At $\log \tau_{\max} = 0$.

To determine the influence of the flexible part of the copolymer on the molecular mobility of the copolymer backbone, the dependences $-\log \tau_{\max} = \varphi(1/T)$ for CP3 (3) and CP4 (4) and for CP7 (7) and CP8 (8) in the α-process range will be compared (Fig. 5). The structures of these two pairs of polymers differ only in their flexible part, octafluoro-amyl side chains for the former and amyl side chains for the latter. It is clear that the replacement of octafluoro-amyl side groups by amyl ones leads to the displacement of the dependence $-\log \tau_{\max} = \varphi(1/T)$ toward low temperatures, as well as in the case of model P1 and P2 polymers.

The effect of spacer length on segmental mobility can be seen from the comparison of the results obtained for CP6 and CP7, differing only by the presence of the spacer $-(CH_2)_2-$ between the backbone and chromophore group in CP6. Comparing curves 6 and 7 in Fig. 5, it is clear that the insertion of the spacer shifts the dependence $-\log \tau_{\max} = \varphi(1/T)$ toward higher temperatures.

The effect of the terminal substituent in the chromophore group on the dielectric behavior can be determined by comparing the pairs of copolymers CP3 vs. CP7 and CP4 vs. CP8. It is clear that going from the terminal substituent $-OCH_3$ in CP3, CP4 to $-Br$ one in CP7, CP8, the dependences $-\log \tau_{\max} = \varphi(1/T)$ shift toward low temperatures (see curves 3 vs. 7 and 4 vs. 8 in Fig. 5).

The effect of chromophore molar content in a copolymer on segmental mobility can be analyzed by comparing the data obtained for CP5 and CP6. The increase in the chromophore molar fraction from 20 to 50% leads to the increase of relaxation times by at least one order of magnitude (curves 5 and 6 in Fig. 5). At the same time, for CP1 and CP2 the temperature dependences of relaxation times in the range of the α-process are very close to each other. This is due to the fact that two structural factors (increase in the chromophore molar content from 20 to 40% and replacement of the fluorinated flexible part by the non-fluorinated one) act in opposite directions.

Hence, the analysis of dependences in Fig. 5 permits to make the following conclusions. The temperature dependences of relaxation times shift toward low temperatures, i.e. molecular mobility increases, upon: (1) going from the terminal substituent $-OCH_3$ to $-Br$ in the chromophore group, (2) substitution of the octafluoro-amyl side chains in the flexible part of the copolymers by the amyl ones, (3) decrease in the concentration of chromophore groups, and (4) insertion of a spacer between the copolymer backbone and the chromophore.

For the studied copolymers CP1–CP8, relaxation times in the range of the α-process vary over two to three orders of magnitude (from curve 3 to curve 2 in Fig. 5). The T_g values for the copolymers CP1–CP8 were obtained by extrapolation of the dependences $-\log \tau_{\max} = \varphi(1/T)$ to $\log \tau_{\max} = 0$, i.e. to the relaxation time $\tau = 1$ s. For CP1–CP8, the obtained glass transition temperatures differ by not more than 42 °C (Table 1).

3.5. Temperature dependence of relaxation times in the range of the δ-process

As has been shown for LC side-chain polymers, the temperature dependence of relaxation times in the range of the δ-process can be described either by the Arrhenius equation [21,36] or by the VFTH one [22,37,38]. For CP1 and CP5, the dependences $-\log \tau_{\max} = \varphi(1/T)$ in the range of the δ-process are straight lines, i.e. they obey the Arrhenius equation. In the case of CP2–CP4 and CP6–CP8, these dependences could be described by the VFTH equation.

As for the relationship between the chemical structure and chromophore mobility, the analysis of data in Fig. 6 makes it possible to draw the following conclusions. For copolymers CP3 vs. CP4 (curves 3, 4 in Fig. 6) and CP6 vs. CP7 vs. CP8 (curves 6–8 in Fig. 6), having similar chromophores and chromophore molar content of 50%, the relaxation time values of the δ-process are very close to each other. This means that the molecular mobility of chromophore groups in the range of the δ-process depends mainly on the chromophore chemical structure. For the CP3, CP4 and CP6–CP8 systems, the temperature–frequency coordinates of the δ-process are curvilinear, being adequately described by the VFTH equation. It means that this process corresponds to a cooperative form of molecular mobility for which intermolecular interactions are important. It is evident that in NLO copolymers intermolecular interaction are mainly determined by the presence of chromophore groups. The parameters of the VFTH equation and the transition temperature of the δ-process, $T_{g\delta}$, for CP2–CP4 and CP6–CP8 are given in Table 1. (Formally, the $T_{g\delta}$ values, as well as in the case of the α-process, are determined by extrapolation of the dependences $-\log \tau_{\max} = \varphi(1/T)$ to $-\log \tau_{\max} = 0$.)

For copolymers CP1 and CP5 with lower molar content of chromophore-containing units (20%), the dependences $-\log \tau_{\max} = \varphi(1/T)$ are linear. The parameter values of the Arrhenius equation (τ_0 and activation energy, see Table 1) are typical for local form of molecular mobility for polymethacrylates of different structures [18,39]. It means that in CP1 and CP5, in contrast to CP3, CP4 and CP6–CP8, there are no intermolecular interactions between chromophore groups.

4. Conclusions

For the first time, molecular mobility in the films of chromophore-containing copolymethacrylates was studied by dielectric spectroscopy. Dielectric spectra of NLO systems considered here were analyzed similarly to those of LC side-chain polymers.

The investigated copolymers exhibit near the glass transition temperature two ranges of dipole polarization relaxation: α- and δ-relaxation processes which are related to the segmental mobility and the reorientation of chromophore-containing side groups, respectively.

It seems that the existence of the α- and δ-transitions for NLO polymers with side-chain chromophore groups is a general phenomenon, indicating that the motion of chromophore side groups is relatively independent from that of the polymer backbone.

The cooperative character of chromophore mobility for copolymers with relatively high molar fraction of chromophore-containing units (50%) is a consequence of intermolecular interactions between chromophores. For copolymers with lower chromophore molar fraction (20%), there are no intermolecular interactions between chromophore groups, their reorientation being of local character. These data are very important for optimizing the chromophore molar content in NLO polymers since the inter-chromophore dipole–dipole interactions usually lead to the formation of centrosymmetric anti-parallel aggregates which cannot be oriented by external electric fields [5,6,12].

The fact that the δ-process appears at higher temperatures than that of the α-process is of great importance for optimizing the poling temperature at which macroscopic non-centrosymmetric orientation of chromophore occurs under the external electric field applied across a polymer film. To align chromophore dipoles along the external field direction, the chromophores should be able to rotate about their short axes, because that is the motion which changes the direction of the chromophore dipoles. Hence, the poling temperature should be at least not lower than the glass transition temperature for the δ-process.

Thus, the study of the dielectric behavior of polymers with side-chain chromophores can be regarded as one of the steps necessary to the preparation of materials with predetermined NLO properties. Up to the present, although NLO polymer systems are in great demand, their dielectric investigations were not given much attention.

Acknowledgements

This research was supported by RFBR (04-03-32464 and 04-03-33011) and by grant of Ministry of Education and Science of Spain (SAB2004-0119, resolution from 12.04.2005).

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