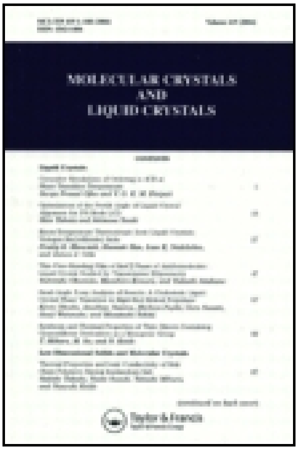

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Molecular Mobility and Phase Transitions in a Liquid Crystalline Polymer Studied by Dielectric Techniques

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Molecular Mobility and Phase Transitions in a Liquid Crystalline Polymer Studied by Dielectric Techniques

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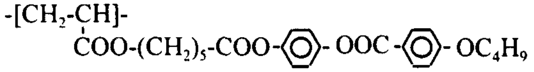
The mechanisms of molecular mobility and of phase transitions in a thermotropic, comb-shaped, side-chain liquid crystalline polymer (LCP), poly-(ε-acryloyloxycaproyloxyphenyl)-n-butoxybenzoate (PABB) were studied by dielectric techniques (dielectric relaxation spectroscopy, DRS, and thermally stimulated depolarization currents, TSDC). Two subglass secondary relaxations, β and γ, were observed in TSDC measurements, at about −100 and −150 °C, respectively. The β relaxation, as well as, the α relaxation, associated to the glass transition, were studied by DRS.

Keywords: comb-shaped LCP; dielectric relaxation; thermally stimulated depolarization; temperature derivative method

INTRODUCTION

The last few decades a close relationship between the chemical structure and the properties of the thermotropic comb-shaped LCPs has been revealed [1,2]. Comb-shaped LCPs are of interest because of their ability to form different liquid crystalline structures. Virtually all of the LC phases formed by low molecular weight compounds have been identified in LCPs. Nevertheless, not enough attention has been paid to the investigation of the physical properties of reentrant phases.

We have previously reported the synthesis of LCPs forming the reentrant nematic (RN) phase [3-5]. The chemical structure, the phase transition temperatures and molecular mass characteristics of the LCPs are as follows:



$$\begin{array}{l} -[CH_2-CH]- \\ \quad\;\; | \\ \quad COO-(CH_2)_5-COO-\langle\bigcirc\rangle-OOC-\langle\bigcirc\rangle-OC_4H_9 \end{array}$$

(I)

Glass 30 ^{0}C S_mF 76 ^{0}C RN 111 ^{0}C S_mA 127 ^{0}C N 143 ^{0}C I, Mw=31900, polydispersity 1.2 (GPC, PC standard). For the polymer (I) it is established that, with respect to the combination of optical and mechanical equilibrium characteristics, no marked differences exist between the reentrant nematic phase and the common nematic phase[4,5].

In this work broadband dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization currents (TSDC) techniques were employed to study molecular mobility and phase transitions of the fraction of the comb-shaped LC polymer (I). The studies were performed in a wide temperature and frequency range allowing to observe the temperature dependence of the local and of the segmental relaxation processes.

EXPERIMENTAL

The synthesis and the characterization of the polymer, as well as the investigation of optical and mechanical properties, have been reported previously[3-5].

All dielectric measurements were performed in the unaligned state. For the DRS measurements (10^{-2} - 10^6 Hz, -100 to 150 ^{0}C) modern equipment was used[6].

For the TSDC measurements (-185 to 30 ^{0}C) a home made apparatus was used. TSDC allows for a quick characterization of dielectric behaviour at low temperatures and low frequencies[7].

RESULTS

Figure 1 shows results of DRS measurements. At temperatures

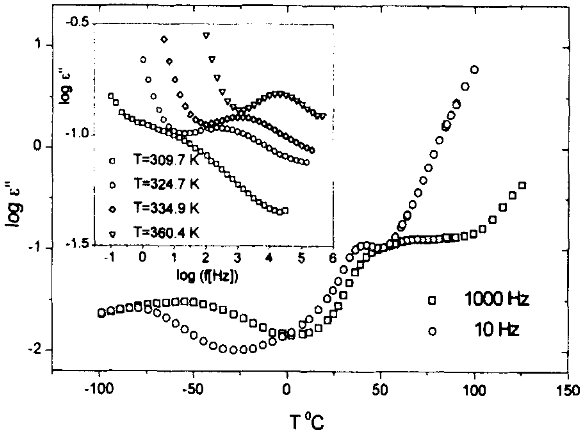


FIGURE 1 Dielectric losses versus temperature and versus frequency (inset) for polymer (I)

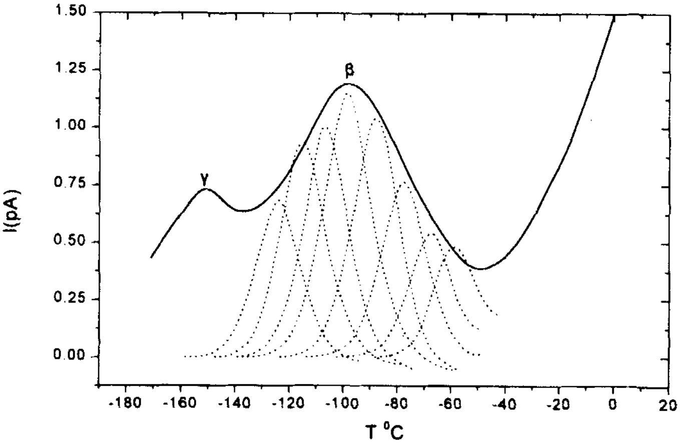


FIGURE 2 TSDC thermogram for γ and β relaxations (continous line) and thermal sampling responses (dotted line)

lower than the glass transition temperature, T_g=30 (±3) ^{0}C, we observe a broad relaxation, the β relaxation[8]. At temperatures higher than T_g the α relaxation, associated to the glass transition, is observed, followed by high ε" values, in particular at 10 Hz, due to dc conductivity. No δ relaxation[8] is observed, either masked by strong interfacial polarization or suppressed by a highly ordered F phase.

The TSDC counterpart to the DRS plot of Figure 1 is shown in Figure 2. The TSDC plot corresponds to a plot of ε"(T) at fixed low frequencies of 10^{-2} - 10^{-4} Hz [6,7]. We observe the β relaxation and a faster relaxation at lower temperatures, the γ relaxation. At high temperatures the onset of the α relaxation is observed.

The broad subglass γ and β relaxations were further analyzed by means of the TSDC thermal sampling (TS) technique[7] (Fig. 2). The activation energy E of the TS responses was calculated by the initial rise method[7].

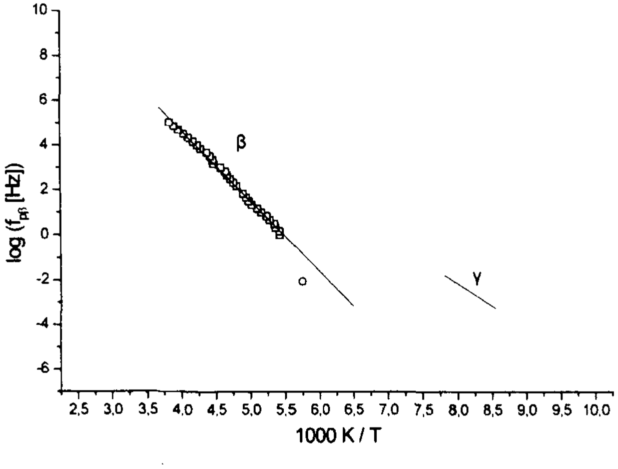


FIGURE 3 Arrhenius plot for the β relaxation (DRS, □, including one TSDC point at 10^{-2} Hz, O) and for the γ relaxation (TSDC), details in text.

Figure 3 shows the Arrhenius plot of the β relaxation measured by DRS. E is determined to 0.62 ± 0.07 eV, the pre-exponential factor in the Arrhenius equation

$$f=f_0\exp(-E/kT) \qquad (1)$$

to $\log f_0=17.2$ (Hz). Included in the plot is the TSDC point for the β relaxation, $T_m=-99$ °C (Fig. 2) at the equivalent frequency of 10^{-2} Hz [7]. The straight line for the γ relaxation corresponds to the thermal sampling response isolated in the central region of the γ relaxation ($T_m=-147$ °C, $E=0.44 \pm 0.05$ eV). The Arrhenius plot for the α relaxation, measured by DRS, is shown in Figure 4.

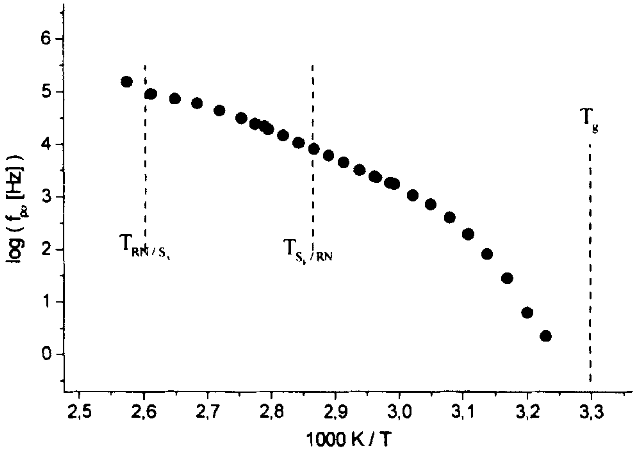


FIGURE 4 Arrhenius plot for the α relaxation.

DISCUSSION

Dielectric investigation on side-chain LCPs, in particular by Kresse and co-workers[9], Haase and co-workers[10], Borisova and her team[11], Williams and his team[12], provided significant information on dynamics in relation to structure and micromorphology. Zehntel et al. [13] classified the different relaxation processes present in LCPs.

The γ relaxation was measured only by TSDC. Typical value of E, determined by TS in the central region of the peak, is 0.44 ± 0.05 eV. In the classification scheme of Zentel et al. [13] it corresponds to the β_2 process [8]. The plot in Figure 3 suggests that in the frequency region of the DRS measurements γ may overlap with β relaxation. Support for this comes from $\varepsilon''(f)$ plots which show a broadening and anomalies in the shape of the β relaxation at low temperatures. A very similar relaxation in several polyurethane systems has been shown to be due to local motions of the $(CH_2)_n$ sequences[14]. These results suggest that the γ relaxation in Figures 2 and 3 is caused by local motions in the spacer group.

The characteristics of the β relaxation (frequency and temperature position, E and f_0 values) identify that as the β_1 relaxation in the classification scheme of Zentel et al. [8,13], assigned to the rotation of the dipole moment of the central phenylbenzoate ester group. In comb-like polymethacrylates the β relaxation, with characteristics similar to those in the present study, has been shown to be a multistep cooperative process, due to the rotational fluctuation of the mesogenic unit around its long axis[6].

The change in the shape of the Arrhenius plot for the α relaxation in Figure 4 with T approaching T_g suggests that the α relaxation is related to the dynamic glass transition of the system[6]. On the other hand, on the basis of measurements on aligned systems, Williams and co-workers[12] and Borisova and co-workers[11], assigned the α relaxation to rotational fluctuations of the transversal dipole moment of the mesogenic unit, whereas Haase and co-workers[10] separated it into independent subrelaxations. To further follow this point a temperature derivative method[15] was applied for the analysis of the $f_p(T)$ dependence[6]. As an example, Figure 5 shows $(d\log f_p/dT)^{-1/2}$ against temperatures for the α relaxation. The straight line at low temperature shows that the Vogel - Tammann - Fulcher (VTF) equation is valid in this region,

$$f_p=A\exp(-B/(T-T_0)) \quad (2)$$

with temperature - independent empirical parameters A, B, T_0 [15]. On the other hand, a plot of $d\log f_p/d(1/T)$ against reciprocal temperature shows Arrhenius behaviour at higher temperatures with a reasonable values of apparent E=0.97 ± 0.05 eV. The intersection point of the two dependences gives T_c=337 ± 5 K. The ratio T_c/T_g=1.11 is in the range of values estimated for other side-chain LCPs[6].

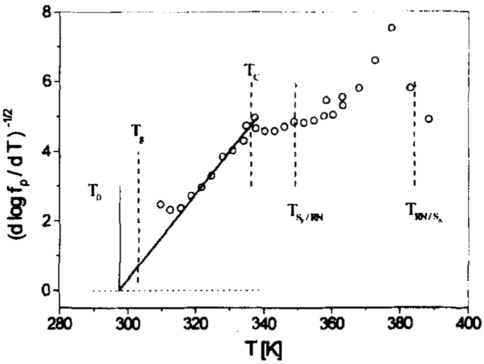


FIGURE 5 (dlogf$_p$/dT)$^{-1/2}$ versus temperature for the α Relaxation.

These results show that the α relaxation is closely related to the dynamic glass transition. As it has been stressed in[6], T_c is due to a dynamical process and has nothing to do with a phase transition. The results can be discussed in terms of cooperativity in relation to structure formation and local demixing[6].

No clear changes were observed in the plots of Figures 4 and 5 at the transition temperature $T_{S_F/RN}$. The same is true also for the plot of dielectric strength of the α relaxation against temperature (not shown) where only diffuse changes are indicated at $T_{S_F/RN}$. These results are in agreement with those of optical and mechanical measurements on the same system[5].

CONCLUSIONS

The dielectric α relaxation in PABB is associated to the dynamic glass transition of the backbone chains. A dynamic transition is observed in the temperature dependence of its relaxation rates at $T_c \approx 1.1\ T_g$, from Arrhenius-type at high temperatures to VTF-type at lower temperatures. It can be understood in terms of cooperativity in relation to microphase separation.

Acknowledgements
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