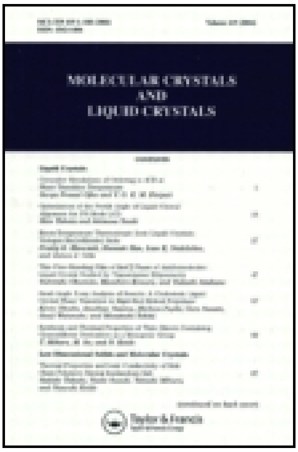

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On the Peculiar Dynamic-Mechanical Behavior of an Azobenzene-Containing Mesomorphic Polyacrylate

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ON THE PECULIAR DYNAMIC-MECHANICAL BEHAVIOR OF AN AZOBENZENE-CONTAINING MESOMORPHIC POLYACRYLATE

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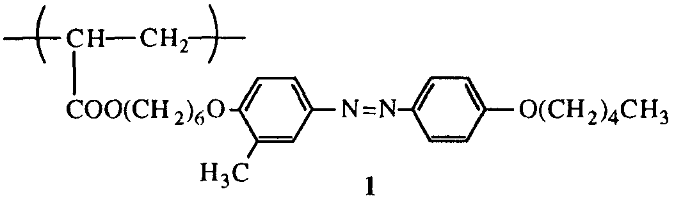
Abstract: The phenomenology of the α relaxation process in an amorphous and crystallized specimen of a side-chain LC polyacrylate, based on the azobenzene mesogenic unit, was investigated by thermal and dynamic-mechanical methods. A frequency and temperature analysis was performed. The relaxation behavior of the amorphous sample was described by the WLF equation. The α process of the semicrystalline sample was structured into two components α' and α'', both following Arrhenius type activation law. This peculiar behavior has been tentatively related to the multidomain structure of the semicrystalline sample.

Keywords: liquid crystals, azobenzene, side-chain polyacrylate, dynamic-mechanical behavior

INTRODUCTION

The physicochemical behavior of liquid crystalline (LC) side-chain polymers has become an active research area because of their potential application in data storage systems, in ferroelectric and piezoelectric devices and in systems requiring non-linear optical characteristics[1]. These polymers generally exhibit inferior or even comparable electrooptic properties with respect to the ones of conventional materials, including molecular polarization and fast response to external electric and magnetic fields, but clear superiority with respect to dimensional stability, mechanical orientability, and ease of processing. These characteristics, coupled with the great versatility of structural design at both molecular and supermolecular levels, are presently promoting more comprehensive understanding of the influence of the structural and molecular parameters on the LC behavior.

Among the various mesogenic groups that are being used in side-chain LC polymers, a particular position is held by the azobenzene group. This group, when irradiated in the π-π^* electronic transition region, undergoes a *trans-cis* configuration change that involves a local and substantially isothermal phase transition, due to the non-mesogenic character of the *cis*-form. The perturbation so generated in the matrix may be frozen in the glassy state and can be retained even if the mesogenic group relaxes back to the *trans*-form. Accordingly, this photochemically-induced isothermal phase transition process can represent the basis for a very effective erasable, photoselective image fixation technique[2-7]. In this context, the relaxation behavior of the matrix in the glassy state and the effects of aging and thermal treatments, possibly generating crystallization or densification phenomena, should be carefully assessed. Accordingly, as a part of our continuing interest[8-11] in the synthesis and physicochemical properties of azobenzene containing polymeric systems, this paper reports some preliminary results concerning a thermal and dynamic-mechanical investigation of the glass transition behavior of the azobenzene-containing polyacrylate **1**, with the following structure:



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In particular, a comparison will be made between the phenomenology of the α relaxation of an amorphous and a crystallized polymer **1** specimen.

EXPERIMENTAL

Materials

Polymer **1** was prepared, according to the procedure previously reported, by free radical polymerization of the corresponding mesogenic acrylate and is characterized by number average molecular weight of $M_n = 32000$ gmol^{-1} and first polydispersity index of $M_w/M_n = 1.8$, as determined by size exclusion chromatography.

Physicochemical Characterization

Differential scanning calorimetry (DSC) analyses were carried out under dry nitrogen flow with a Perkin-Elmer DSC 7 apparatus. Samples of 5-10 mg were employed. The temperature scale was calibrated against the melting temperatures of *n*-hexane, benzoic acid and indium. For the determination of the transition enthalpy, indium was used as a standard material. The transition temperatures were taken from the DSC traces of samples annealed by cooling from the isotropic melt, as corresponding to the maximum of the enthalpic peaks at a heating rate of 10 Kmin^{-1} (cooling 20 Kmin^{-1}).

The samples for the dynamic-mechanical measurements were prepared as follows. The powder polymer sample was introduced into a rectangular mould. The entire assembly was placed between press plates under a nominal pressure of 5 tonncm^{-2} and let to stand at room temperature for 20 min. The temperature was then raised to 383 K and the pressure released to 0.5 tonncm^{-2}. After 30 min, the sample was quenched into cold water at 273 K and recovered as rectangular 18x5x1 mm sheet. The sample was then analyzed directly (amorphous specimen) or annealed at 303 K for 16h (crystallyzed specimen). Dynamic-mechanical measurements were performed with a dynamic-mechanical analyzer Perkin Elmer DMA-7, employing the three point bending geometry. Time-temperature scans were obtained at a scanning rate of 2 Kmin^{-1} using the following frequency values: 0.6, 1.0, 3.0, 5.0, 10, 20, 40 Hz. Frequency scans in the range 0.02-50 Hz were performed on samples equilibrated at the selected temperature for 30 min.

RESULTS AND DISCUSSION

Thermal Behavior

Figure 1 illustrates the DSC heating curves of two polymer **1** specimens subjected to different thermal treatments. The DSC curve relevant to the amorphous specimen was obtained by immediately heating a polymer **1** sample cooled at 10 K/min from the isotropic phase down to 273 K. The DSC curve relevant to the crystallyzed sample was obtained by keeping the amorphous one at 303 K for 16 h inside the DSC before collecting the DSC scan. The amorphous specimen exhibits (Figure 1A) a step at 294 K due to the glass transition and an endothermic peak at 369 K (ΔH= 1.3 Jg^{-1}) associated to the nematic-isotropic transition. On cooling both transitions are reversible and accordingly the nematic mesophase structure is frozen in the glassy state.

A further endothermic process, structured into two partly overlapping components and with a maximum at 347 K is observed for the crystallized specimen (Figure 1B). The higher temperature component of this process is attributed to the melting of crystallized portion of the material. However, the origin of the lower temperature endothermic component, whether it corresponds to the melting of less perfect crystalline regions or to a smectic-nematic transition involving smectic domains formed during annealing at 303 K should be better assessed with further investigations. In any case, it should be recognized that the structure of the solid state of the semicrystalline sample has a multidomain nature.

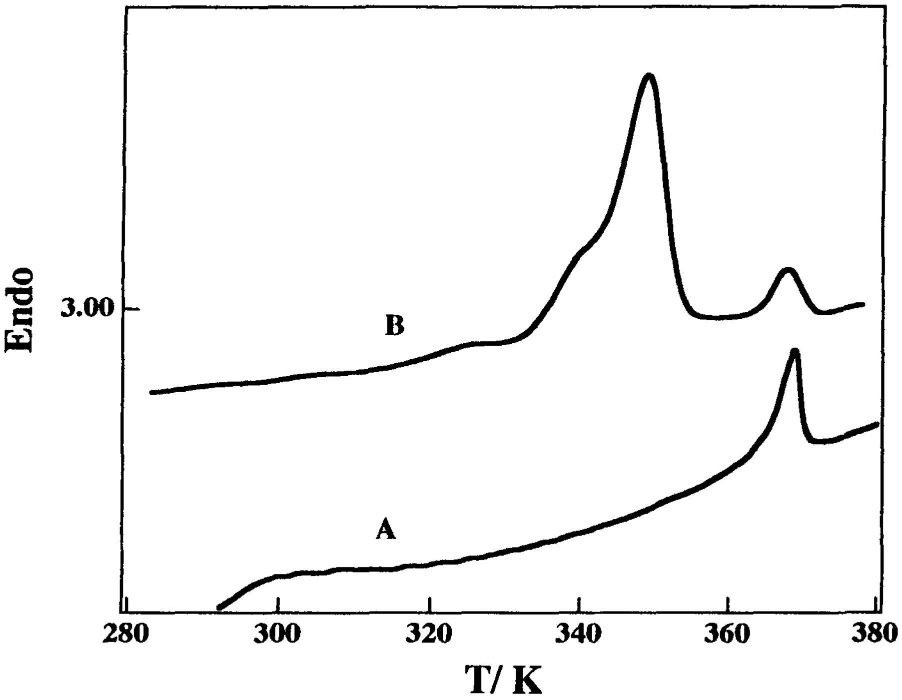

Figure 1. DSC heating curves (10 K/min) for the amorphous (A) and crystallized (B) polyacrylate **1** specimens.

Dynamic-Mechanical Behavior

Polymer **1** was subjected to a dynamic-mechanical investigation in order to study his relaxation properties in the range of linear viscoelasticity. The amorphous and the crystallized specimens for the DMA analysis were prepared by replicating the thermal treatments already mentioned for the analogous samples subjected to DSC analysis. Figures 2 and 3 illustrate the trends of storage modulus G', loss modulus G" and tan δ at 1 Hz as a function of the temperature for the amorphous and crystallized specimens, respectively. In the plots of G" and tan δ vs. temperature of the amorphous specimen, two main relaxation processes are observed which, as usual, are labelled α and β in order of decreasing temperature. The α relaxation is associated to the glass-rubber transition and occurs in the temperature range from 260 to 300 K. The β relaxation, observed in the temperature range from 170 to 230 K, is believed to represent the onset of local motions of relatively short chain segments. The dynamic modulus G' at 150 K is about $1.5 \cdot 10^9$ Pa and decreases steadily with increasing temperature with

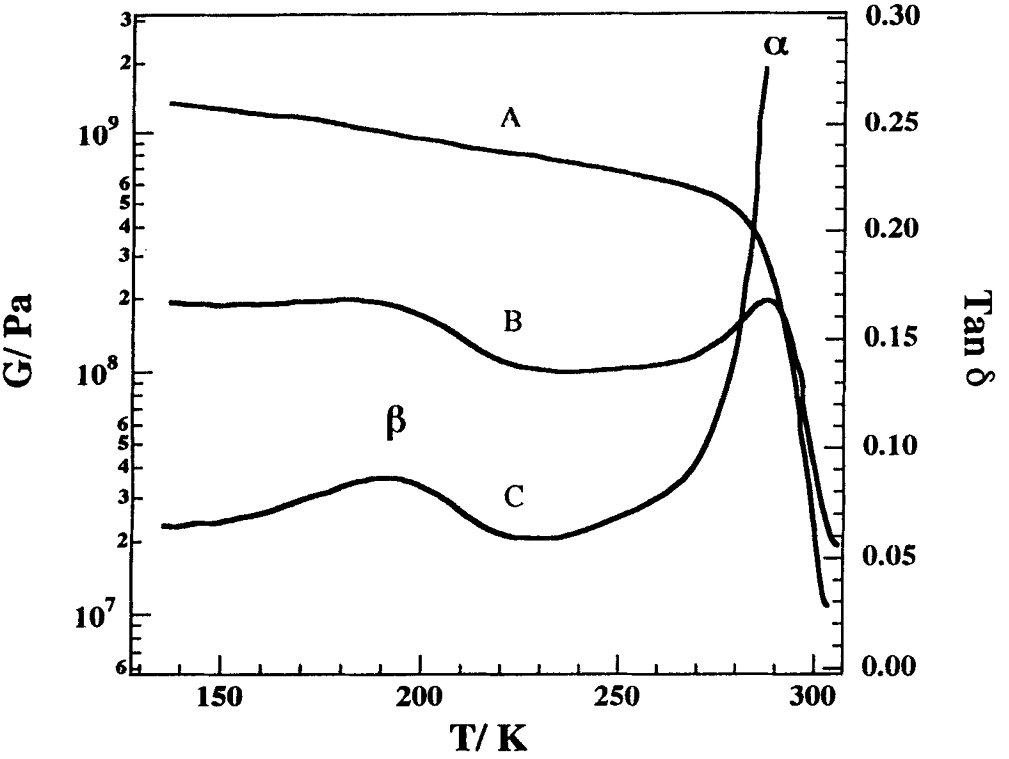

Figure 2. Plots of the dynamic storage modulus (G', A) loss modulus (G", B) and loss tangent (tan δ, C) versus temperature at 1 Hz for the amorphous polyacrylate **1**.

definite drops in correspondence of the main relaxation regions. A small decrease of G' at temperatures corresponding to the β relaxation and a drop of two orders of magnitude at temperatures corresponding to the α relaxation is observed. Above 300 K, the amorphous sample lost its dimensional stability. The dynamic-mechanical behavior of the semicrystalline specimen is definitely more complex than the one of the amorphous specimen. In the plot of G" and tan δ vs. temperature (Figure 3), four major relaxation processes are observed. The higher temperature one, which occurs above 340 K, is associated to the melting of the crystalline portion of the material. In the temperature region between 260 and 340 K two overlapping maxima of both G" and tan δ can be seen at 300 and 330 K. In the same temperature region, G' shows a marked decrease with a slope change at about 330 K. These two relaxation processes will be labelled α' and α" in order of increasing temperature. Comparing the relevant DSC curves in the corresponding temperature region, it appears that the doubling of the α relaxation process in the crystallized specimen could be associated to the glass transition of the amorphous part of the sample (α') and to the transition which occurs immediately before the melting process (α"). Finally, the β transition is also observed in the temperature range from 170 K to 230 K. To get a better view of the dynamic-mechanical behavior of polymer 1 sample, a multiplexing frequency and temperature analysis was performed. For the amorphous specimen, isothermal frequency scans in the 0.02-50 Hz range were performed in the glass transition region from 253 to 295 K. The upper

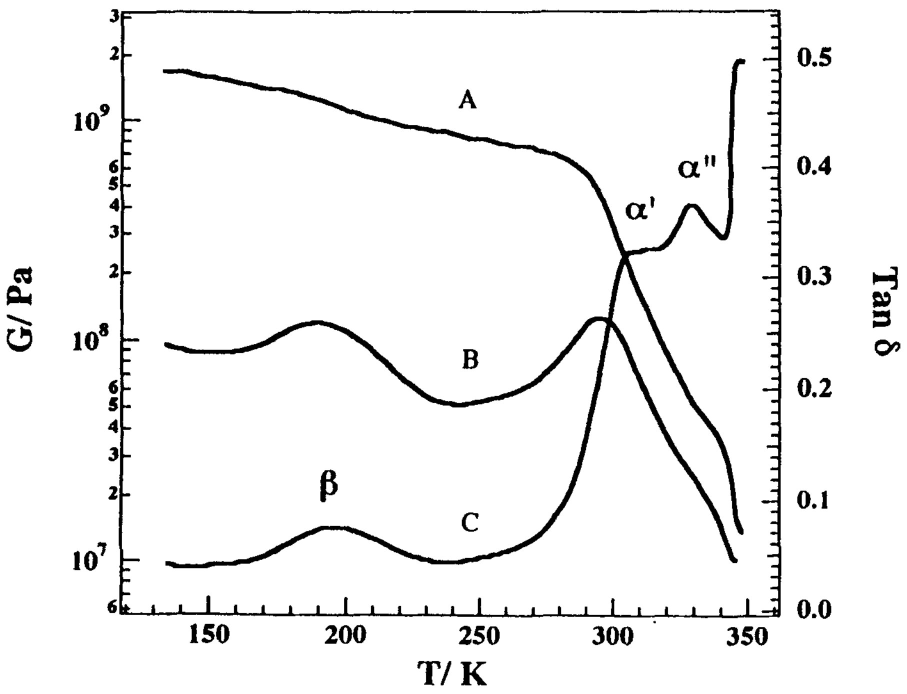

Figure 3. Plots of the dynamic storage modulus (G', A) loss modulus (G", B) and loss tangent (tan δ, C) versus temperature at 1 Hz for the crystallized polyacrylate 1.

limiting value was dictated by the onset of crystallization phenomena. In contrast, to minimize secondary crystallization processes in the crystallized specimen during the analysis, the data set relevant to the storage modulus G' as a function of the frequency was obtained from several temperature scans performed at six different frequency values in the range 0.6 to 40 Hz. The data relevant to both the amorphous and crystalline specimens were shifted to obtain the corresponding master curves. The reference curve chosen for the superposition was the one obtained at 295 K for the amorphous sample and the one at 338 K for the crystallized sample. The vertical shift density factor was not employed in both cases because it was possible to obtain the best superposition without applying it. Figure 4 illustrates the trend of the log plot ofthe reciprocal shift factor a_T as a function of the reciprocal temperature. The experimental points relevant to the amorphous sample are fitted by the WLF equation (1),

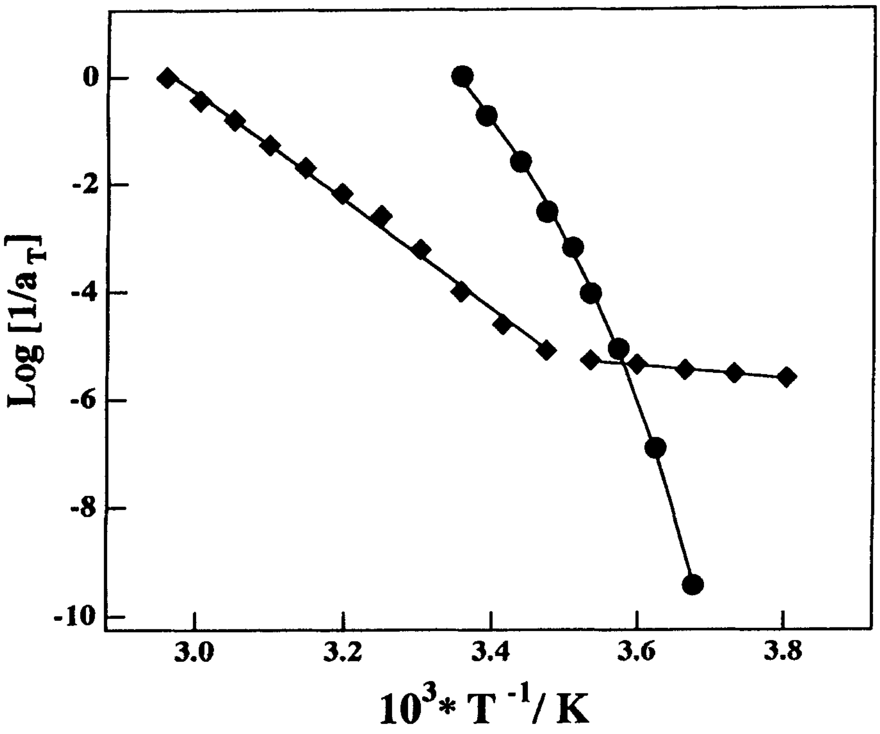

Figure 4. Trend of the logarithm of the inverse of the shift factor a_T as a function of the reciprocal temperature for the amorphous (●) and crystallized (■) polyacrylate 1 specimens.

as usual for completely amorphous polymers[12,13], for a_T:

$$a_T = A * \exp\left(\frac{B}{T - T_\infty}\right) \quad (1)$$

where A is a constant, B is the pseudo activation energy in temperature units and T_∞ is the critical temperature. The best fit parameters, as obtained using a non linear regression method, are the following: B= 1270±20 K and T_∞= 243±3 K. The T_∞ value is in good agreement with the one estimated from the general equation: T_∞= Tg-55 K. In contrast, Log($1/a_T$) as a function of the reciprocal temperature for the crystallized specimen exhibits a very unusual trend with two distinct regions above and below the critical value of 3.5 10^{-3} for 1/T which corresponds to about 294 K. In both regions, Log($1/a_T$) varies linearly with the reciprocal temperature with distinct slopes. The observed trend can be interpreted on the basis of a double activated Arrhenius type relaxation process. The equation describing the represented trend can be expressed as:

$$a_T = C * \exp\left(\frac{\Delta E}{kT}\right) \quad (2)$$

where C is a constant, ΔE is the activation energy and k is the Boltzmann constant. The dual shaped behavior is suggestive of two distinct processes occurring in the temperature region associated to the process α of the crystallized sample both following Arrhenius type activation laws. Accordingly, the activation energies relevant to the distinct processes as computed on the basis of eq. 2 result ΔE_1= 23 ± 1 kJmol^{-1} for the α' process occurring between 263 and 294 K, and ΔE_2= 190 ± 5 kJmol^{-1} for the α" process occurring between 294 and 338 K.

CONCLUSIONS

The phenomenology of the α relaxation process in an amorphous and crystallized specimen of a side-chain LC polyacrylate, based on the azobenzene mesogenic unit, was investigated by combining thermal and dynamic-mechanical techniques. The DSC analysis indicates that the actual state of the solid phase of the amorphous specimen is the frozen nematic mesophase whereas a multidomain structure is evidenced in the case of the crystallized specimen. This difference in the solid state structure reflects drammatically in the α dynamic-mechanical relaxation processes. In fact, the α relaxation behavior of the amorphous sample can be described by the WLF equation whereas the α process of the semicrystalline sample results structured into two components α' and α", both following the Arrhenius type activation law.

In general, the α relaxation process of amorphous polymers follows the WLF equation whereas for a few semicrystalline polymeric systems the α relaxation has been reported to follow the Arrhenius activation law[14]. This different behavior is connected to the local or cooperative nature of the chain motions involved in the relevant relaxation process. Relaxation processes extending over long chain distances are described by the WLF equation whereas Arrhenius-type activation laws apply to motions of shorter chain segments. Accordingly, we can tentatively explain the relaxation behavior of the semicrystalline sample by supposing the existence in the amorphous region of two different kinds of short chain segments experiencing different environments and relaxing within different temperature regions.

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