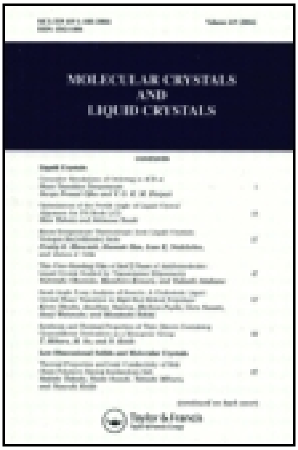

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A Trap Model Description of Enthalpy Relaxation in a Side Chain Liquid Crystal Polymethacrylate

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The enthalpy relaxation mechanism of an azobenzene side chain liquid crystal polymethacrylate is investigated by means of DSC experiments after proper annealing procedures at temperatures below the glass transition. The data are analyzed according to a recently developed trap model. The model is found to be able to describe the experimental enthalpy relaxation data fairly well, providing a means to estimate the cooperativity length of the system.

Keywords: azobenzene; differential scanning calorimetry; enthalpy relaxation; physical aging; side chain liquid crystal polymer

INTRODUCTION

Side chain liquid crystal polymers (SCLCP) are largely investigated because of their potential application as media for optical data storage [1]. In particular, SCLCP with azobenzene side groups were found to be appealing for nanorecording an optical information that can then be stored with a cooling procedure into the glass [2]. Naturally,

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diffusion processes and relaxation phenomena could play a crucial role in determining the long term performance of the memory. Therefore, the study of the physical aging of such systems is of great significance.

As a polymer is cooled from the melt, its molecular mobility dramatically slows down and a temperature range is found where the system falls off thermodynamic equilibrium and becomes a glass. In this non-equilibrium state the physical properties of the polymer spontaneously change with time as the glass attempts to achieve the equilibrium. Many different experimental techniques can be used to study this phenomenon, and among them Differential Scanning Calorimetry (DSC) measurements are widely performed to monitor the enthalpy relaxation.

To describe the quantitative aspects of the aging process, Drozdov [3] has developed an approach which is based on the trap theory of Bouchaud and coworkers [4,5] and can be used to describe volume or enthalpy relaxation experiments. In this work we analyze some DSC data for an azobenzene polymethacrylate in terms of this trap model. The results will allow us to obtain an estimate the cooperativity length of this polymer that could strongly affect the maximum resolution of a nanorecorded optical memory.

The Drozdov model aims to reproduce the enthalpy loss on aging the sample in the glass as a function of the annealing time. This quantity can be evaluated from DSC experiments, through the relation [6]:

$$\Delta H(T_a, t_a) = \int_{T_1}^{T_2} \Delta C_p(T)dT \tag{1}$$

where $\Delta C_p(T) = C_p^{\text{aged}}(T) - C_p^{\text{unaged}}(T)$ is the difference between the curves of heat capacity versus temperature for the aged (over a period of time t_a) and the unaged glass ($t_a = 0$), and T_a is the annealing temperature. The temperatures T_1 and T_2 are references below and above the glass transition temperature of the system, where $\Delta C_p = 0$.

In the Drozdov model [3], the polymeric glass is treated as an ensemble of flow units or cooperative rearranging regions (CRRs) which are thought of as globules of long chains, short chains and free volume clusters. The CRRs are treated as mutually independent. According to the energy landscape picture [7,8], the CRRs are trapped in potential wells of different depth in the complex energy landscape profile of the system. According to the transition state theory [9,10], it is assumed that some reference liquid-like state exists on the energy landscape, where flow units can change their configurations. The structural relaxation is then depicted as a stochastic process with the CRRs that occasionally can jump (due to the thermal fluctuation) from their traps to the reference state, where they forget their previous configurations finally landing in the same or in a different trap. If $w > 0$ is the depth of the generic trap (assuming 0 the energy of the reference state), at each temperature the equilibrium thermokinetic structure of a glass is entirely determined by an equilibrium probability density of traps $p_{eq}(T, w)$, so that the structural relaxation after a quench from T_0 to T_{a} is described by the time dependent changes of $p(t, w)$ from $p_{eq}(T_{0,}w)$ to $p_{eq}(T_{a,}w)$. The number of CRRs (per unit mass) located in a potential energy within the range $(w,\ w + dw)$ that hop to the reference state per unit time is written as $\Xi_0 L(t, w) p(t, w) dw$, where Ξ_0 is the number of traps per unit mass and $L(t, w)$ is the probability per unit time for a flow unit located in a trap of energy w to reach the reference state. This is found to be [4,5]:

$$L(t, w) = \Gamma(t) \cdot \exp[-A \cdot (w - \Omega(t))] \tag{2}$$

where $\Gamma(t)$ is the average rate of hops (assumed independent of w), A is a material constant and $\Omega(t)$ is the excess energy of a CRR over the bottom level of its trap. Now it is assumed that the flow units changing their energy trap per unit time are proportional (through a new constant χ) to the excess of the current number of CRRs with a given energy w over their equilibrium number at the current temperature $T(t)$ (i.e. $p(t, w) \geqslant p_{eq}(T(t), w)$). These flow units are then redistributed proportionally to the difference between the equilibrium number and the current number of traps with appropriate potential energies. Without entering into further details, this procedure provides a couple of integro-differential equations [3] for $p(t, w)$ that can be numerically solved. Now, setting for the configurational entropy of a CRR:

$$S_0 = -k_B \cdot \int_0^{\infty} p(t, w) \ln[p(t, w)] dw \tag{3}$$

one easily finds for the excess of configurational entropy per unit mass

$$\Delta S(t) = \Xi_0 k_B \cdot \int_0^{\infty} \{p_{eq}(T(t), w) \ln[p_{eq}(T(t), w)] - p(t, w) \ln[p(t, w)]\} dw \tag{4}$$

where k_B is the Boltzmann constant. The specific excess enthalpy per unit mass $\Delta H_*(t)$, which is related to the measured data of conventional DSC experiments, is expressed in terms of $\Delta S(t)$ by means of the conventional formula:

$$\frac{\partial \Delta H_*(t)}{\partial \Delta S(t)} = T(t) \tag{5}$$

Integrating this equation with the boundary conditions $\Delta H_*(\infty) = \Delta S(\infty) = 0$ and assuming a perfect quench ($T(t) = T_0$ for $t \leq 0$ and $T(t) = T_a$ for $t \geq 0$) one obtains:

$$\Delta H_*(t) = \Xi_0 k_B T_a \cdot \int_0^\infty \{p_{eq}(T(t), w) \ln[p_{eq}(T(t), w)] \\ - p(t, w) \ln[p(t, w)]\} dw \tag{6}$$

This is the central formula because for each fixed annealing temperature T_a the excess enthalpy is easily related to the experimental data (enthalpy loss due to the aging) evaluated through Eq. (1):

$$\Delta H(T_a, t_a) = \Delta H_*(0) - \Delta H_*(t_a) \tag{7}$$

where naturally $\Delta H_*(0) = \Delta H(T_\mathrm{a}, \infty)$. As far as the equilibrium probability density of traps is con0cerned, the author assumed a Gaussian function, although alternative expressions have been proposed in literature [11]

$$p_{eq}(T, w) = N \cdot \exp\left\{ -\frac{(w - \bar{w}(T))^2}{2\sigma_{eq}^2(T)} \right\} \tag{8}$$

where N is a normalization factor, $\bar{w}$ and $\bar{\sigma}_{eq}$ are the mean energy of a CRR and the width of the distribution. The same form with a given $\bar{w} = \bar{w}_0$ and $\bar{\sigma}_{eq} = \sigma_0$ is also assumed for the $p(0, w)$, namely the probability density of traps at the beginning of the annealing process. Finally some additional hypotheses are employed in order to decrease and rationalize the model parameters. If the system is not too far from thermodynamic equilibrium, it is reasonale to assume a linear relation between the energy level Ω of a CRR in its current trap and the excess enthalpy per CRR ($\Delta h = \Delta H_*/\Xi_0$):

$$\Omega(t) = \beta \cdot \Delta h(t) \tag{9}$$

Moreover, treating hops of flow units in their traps as thermally activated processes and referring to the Eyring formula, [12] one obtains:

$$\Gamma(t) = \Gamma_{eq}(T(t)) \cdot \exp[\gamma \cdot \Delta h(t)] \tag{10}$$

being $\Gamma_{eq}(T)$ the average rate of hops in thermodynamic equilibrium at temperature T, and γ a material parameter. Combining Eqs. (2), (9) and (10) one finally obtains:

$$L(t, w) = L_{eq}(T(t), w)/a(t); \qquad \ln(a) = -(A\beta + \gamma)\Delta h(t) \tag{11}$$

TABLE 1 Physicochemical Parameters of Polymethacrylate PMA4

M_w(g/mol)	M_w/M_n	T_g (K)	T_{NI} (K)	ΔH_{NI}(J/g)
59000	3.17	294	353	1.8

The model parameter $C = (A\beta + \gamma) \cdot k_B$ explicitly appears in the equation driving the evolution of *p(t)* which in turns determines the enthalpy relaxation in this model (see Eqs. (11) and (6)).

EXPERIMENTAL

The polymer under investigation, acronym PMA4, was synthesized by following a literature procedure [13]. The principal physicochemical parameters are reported in Table 1, where the average molar masses M_n and M_w are the first and second moments of the distribution function, respectively, T_g is the glass transition temperature (midpoint), T_{NI} the isotropization temperature, and ΔH_{NI} is the isotropization enthalpy of the nematic phase. The chemical structure is shown in Figure 1.

Differential scanning calorimetry measurements were carried out with a Perkin-Elmer DSC 7 that was frequently calibrated with indium and zinc standards. One sample (ca. 15 mg) was used for all the measurements. According to our protocol the sample was:

a) firstly heated to 115°C for 15 min, well above the nematic-isotropic transition, in order to erase any previous thermal history, and
b) then quenched (nominal rate 200°C/min) to the selected temperature T_a where it was annealed for an aging period t_a, and

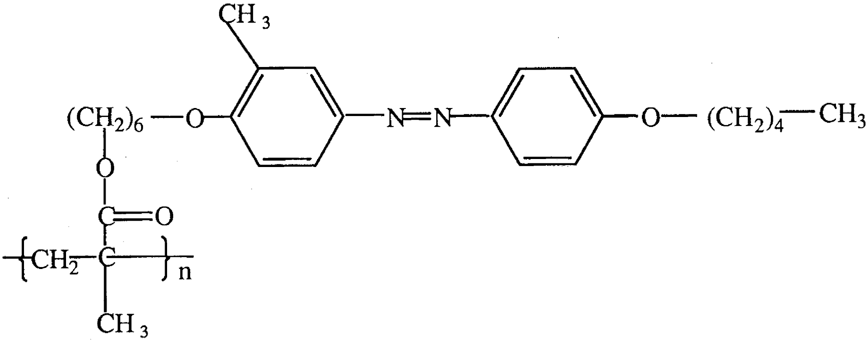

FIGURE 1 Chemical structure of the polymethacrylate PMA4.

c) finally quenched to a temperature well below the glass transition ($T_g - 70°C$) and a scan was recorded on heating with a rate of 20°C/min. After each measurement, a reference trace was recorded with the same thermal procedure but without any annealing at T_a in order to evaluate the enthalpy loss in the aging, through Eq. (1). We found that the heating rate does not affect the values of the enthalpy loss $\Delta H(T_a,t_a)$.

RESULTS AND DISCUSSION

A typical DSC trace recorded after an annealing procedure in the glass is shown together with the reference scan in Figure 2. As can be noted an endothermic peak appears as an effect of the aging of the sample. According to Eq. (1) the area enclosed between the two traces of figure 2 is a measure of the enthalpy loss due to aging. The experimental errors in its evaluation are mainly related to the possible shift of the DSC baseline (to be subtracted from the signal) which results in small differences of the two traces of figure 2 at temperatures well below and above the glass transition. By comparing the results obtained performing the same experiment more times we evaluated the errors in the order of 5–10%. We performed several DSC experiments providing the enthalpy relaxation isotherms at five different aging temperatures. In the theoretical framework of the Drozdov model, the enthalpy relaxation isotherms are described by eight parameters: $A,\ C, \Gamma_0(T_a) = \chi\Gamma_{eq}(T_a),\ \Xi_0, \bar{w}_0, \sigma_0, \bar{w}(T_a)$ and $\sigma_{eq}(T_a)$.

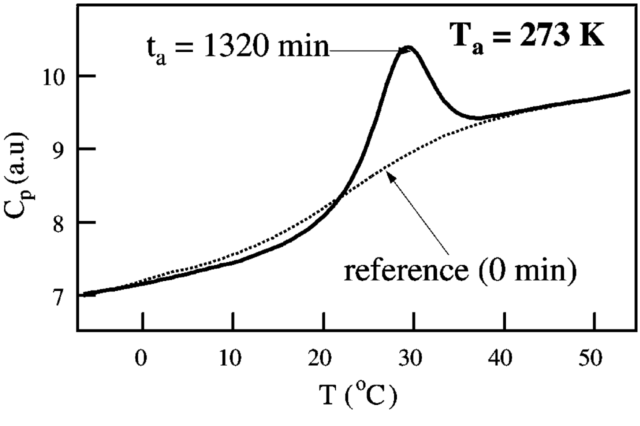

FIGURE 2 DSC trace recorded after annealing the sample for 1320 min at $T_a = 273$ K along with the reference scan at 0 min.

However, it is convenient to introduce dimensionless energies of traps $w^* = w/W$ where W is some characteristic energy and replace A, $\bar{w}_0$, σ_0, $\bar{w}(T_a)$, and $\sigma_{\mathrm{eq}}(T_{\mathrm{a}})$ by their dimensionless counterparts. Now $A^* = A \cdot W$ can be chosen arbitrarily because it only defines a scale for the potential energies of CRRs. We set $A^* = 1$ for numerical convenience (the superscript asterix will be omitted in the following). Furthermore, as noted by the author and confirmed by us with proper numerical analysis, the value of $\Delta H^*(t)$ (see Eq. (6)) results to be almost independent of the average energies $\bar{w}_0$ and $\bar{w}(T_{\mathrm{a}})$ that can be both then arbitrarily fixed. We here set $\bar{w}_0$ and $\bar{w}(T_{\mathrm{a}}) = 1$. In this way we are left with five adjustable parameters to describe our experiments. It is worth noting that only two of the parameters ($\Gamma_0(T_{\mathrm{a}})$ and $\sigma_{eq}(T_{\mathrm{a}})$) depend on the selected annealing temperature T_{a}. For this reason, in order to find the five model parameters, we performed simultaneous fitting procedure involving the different experimental isotherms. In Figure 3 we show the results of the fitting for the relaxational isotherm at $T_{\mathrm{a}} = 288\,\mathrm{K}$, while in Figure 4 we show the fits pertaining to the other annealing temperatures. All the model parameters are reported in the figures (the common parameters, Ξ_0, C, σ_0 are reported only in figure 3).

The good agreement between theory and experiment for all the annealing temperatures selected in this work can be appreciated. As an example, for the fit reported in figure 3 we found a standard

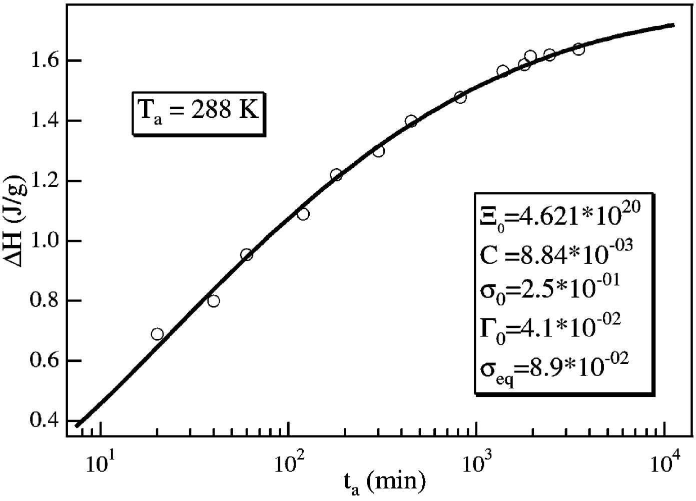

FIGURE 3 Fit of the experimental isotherm recorded at 288 K with the Drozdov trap model.

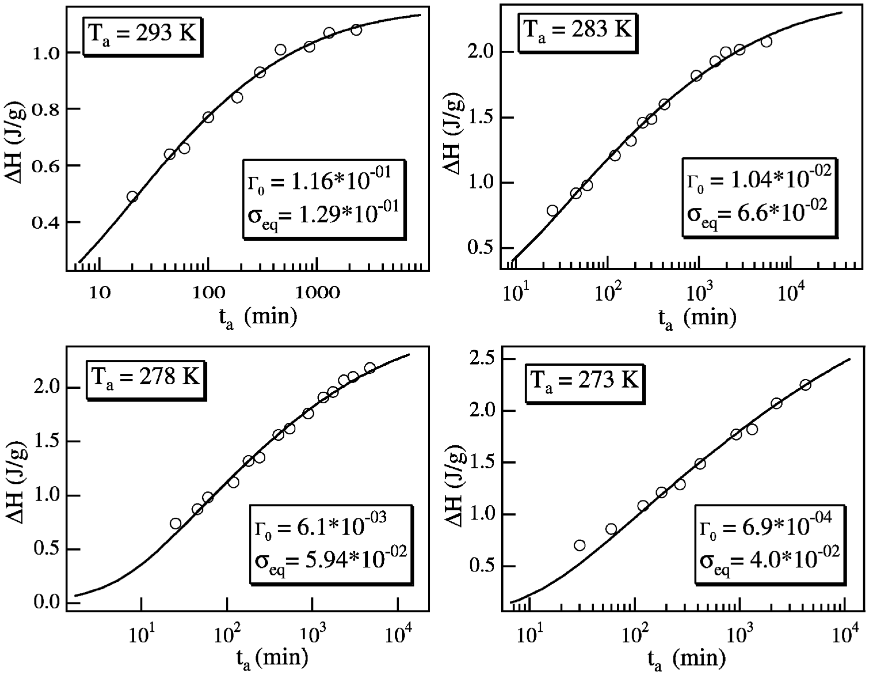

FIGURE 4 Fits of the experimental data at the different annealing temperatures by the trap model. The parameters Ξ_0, C, and σ_0 are reported in figure 3.

deviation of 0.28. Because we assumed that random hops of CRRs were thermally activated, it is expected that the Eyring formula should describe the effect of temperature on the equilibrium rate of hops:

$$\Gamma_0(T) = \Gamma_* \cdot \exp\left(\frac{-\Delta\mu}{RT}\right) \tag{12}$$

where $\Delta\mu$ represents the activation energy which is necessary for flow units to change their trap. Because $|T_a - T_g| << T_g$, from Eq. (12) it is immediately found:

$$\ln\{\Gamma_0(T)\} = a + b \cdot (T - T_g) \tag{13}$$

where $a = \ln(\Gamma_0(T_g))$ and $b = \Delta\mu/RT_g^2$. The values of $\ln(\Gamma_0(T_a))$ found from the fitting procedures are shown in Figure 5 as a function of $T_g - T_a$ together with a linear fit.

It can be noted that Eq. (13) works quite well. From the fit we found $\Delta\mu \approx 180\,\mathrm{kJ/mol}$. This value, however, is less than half of the

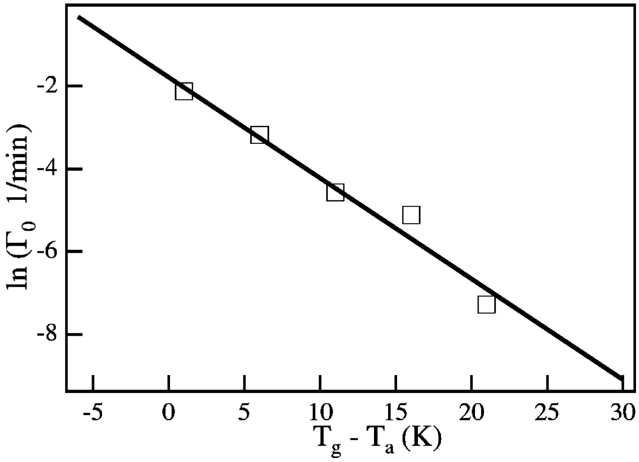

FIGURE 5 Temperature dependence of the equilibrium rate of hops of flow units (landing in new traps). The line is the best fit according to Eq. (13).

apparent activation energy at the glass transition characterizing the effect of temperature on shift of mechanical or dielectric relaxation spectra as obtained from the universal Williams-Landel-Ferry equation [14]. This finding could suggest that the hypothesis of uncorrelated dynamics between CRRs does not properly apply due to the liquid crystalline nature of our sample. The other relevant parameter which depends on the temperature is the width of the equilibrium probability density of traps $\sigma_{eq}(T_a)$. In Figure 6 we report the values of such parameter as found from the fitting procedure for the annealing temperatures selected in this study. We can see that this parameter shows a linear behaviour as a function of $T_\mathrm{g} - T_\mathrm{a}$, at least in the small range of temperatures investigated. One intriguing explanation for the decrease in $\sigma_{eq}(T_\mathrm{a})$ with decreasing temperature is that the system explores the potential energy hypersurface more in detail as the temperature is lowered. In other words, due to the limited thermal energy, the CRRs are confined in very deep traps with the accessible phase space becoming more and more limited. At the same time, the complex profile of the bottom of the potential wells with its microrugosity is resolved and decomposed in different traps with smaller barriers. In this viewpoint it is expected that the dispersion in the values of the explored trap energy decreases.

To conclude the discussion of our results, we consider the parameter Ξ_0. It represents the number of traps per unit mass, so that through the value of the density δ of the polymer it is possible to evaluate

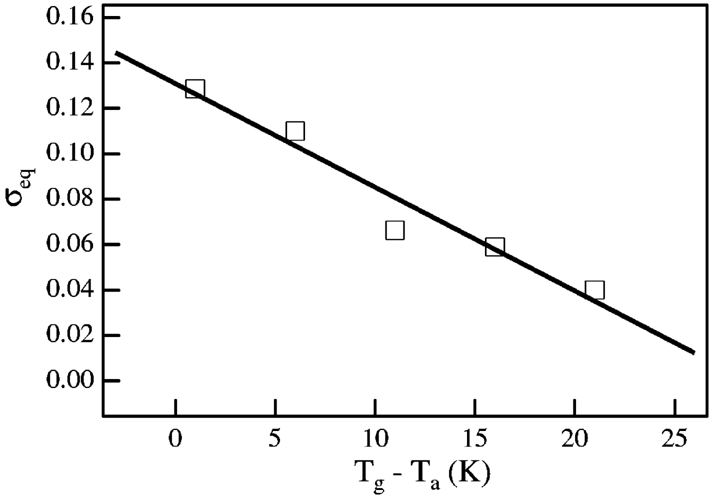

FIGURE 6 Temperature dependence of the width of the equilibrium probability density of traps.

the average volume of each CRR: $V_c = 1/(\Xi_0 \cdot \delta)$. This is a way to estimate the cooperative length of the system, a fundamental parameter as far as the possible use of this polymer as a substrate for optical data storage is concerned. In fact, it represents a limit value for the bit resolution. As we do not know the density value of PMA4, we used the density of poly(methyl methacrylate) ($\delta = 1.15\,\mathrm{g/cm^3}$) that has the same main architecture as PMA4 to obtain at least an approximate value of V_c. We found a value of $V_c \approx 1.9 \cdot 10^{-21}\,\mathrm{cm^3}$ corresponding to a sphere of diameter $d \approx 1.54\,\mathrm{nm}$. This value is of the same order of other estimates obtained by means of different experimental techniques in several polymers and low molecular weight glass-formers [15–17], which supports the analysis of DSC data of this work.

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