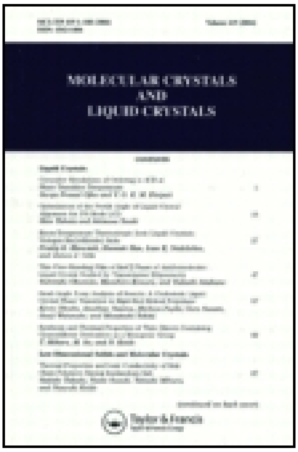

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Enthalpy Relaxation at the Glass Transition in a Side Chain Liquid Crystal Polymer for Optical Data Storage

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Abstract Physical aging of a side chain liquid crystal polymethacrylate is investigated by following the enthalpy recovery in DSC experiments after proper annealing procedures at temperatures below the glass transition. Data are analyzed according to a three-parameter model. The temperature dependence of the aging parameters is established and a comparison with data pertaining to PMMA is performed.

Keywords Side chain liquid crystal polymers, physical aging, enthalpy relaxation, differential scanning calorimetry.

INTRODUCTION

Liquid crystal polymers with azobenzene side chains have been largely investigated in the last years because of their potential application in the field of optical data storage[1]. In the thermodynamically stable trans configuration, azobenzene units are mesogenic, forming nematic phases, whereas in the isomeric cis configuration they are not mesogenic and the mesophase is lost. By irradiating with a proper wavelength, it is possible to induce trans-cis-trans isomerization cycles driving optical anisotropy at a molecular level[2] . Naturally, for viable commercial use these materials should fulfill several pre-requisites, including high resolution and long-term performance around ambient temperature. In order to select the best material, a great number of parameters have to be considered, which depend in a complex way on the molecular architecture of the polymeric matrix. Relaxation phenomena and diffusion processes may strongly affect the long-term properties of the optical memory, while the cooperative length of the system can influence the resolution capabilities.

As a polymer is cooled through its glass transition, the molecular mobility which maintains it in conformational equilibrium dramatically slows down and the material becomes a thermodynamically unstable glass. In this non-equilibrium state the physical properties of the polymer spontaneously change with time as the glass attempts to achieve the equilibrium by very slow changes in the molecular conformation. One important feature, common for the structural relaxation in different polymers, is the strongly non-exponential character that reflects in the so-called memory effect of polymers[3] . In many experimental studies, the function:

$$\phi(t) = exp[-(\frac{t}{\tau})^{\beta}] \tag{1}$$

was used to describe the response function[4]. In this expression, β ($0 < \beta < 1$) is the stretching parameter and τ is the relaxation time. From a mathematical point of view, a non-exponential decay function $\phi(t)$ (as expressed for example by Eq. 1) is equivalent to a distribution of different exponential relaxation functions:

$$\phi(t) = \int_{-\infty}^{+\infty} g(\ln\tau) \exp\left(-\frac{t}{\tau}\right) d\ln\tau \tag{2}$$

$$\text{with} \quad \int_{-\infty}^{+\infty} g(\ln\tau)\, d\ln\tau = 1 \tag{3}$$

In this way, the non-exponential β parameter in Eq. 1 may be related to the width of the corresponding distribution of relaxation times g (ln τ). Isothermal physical aging may be studied by following the time-dependent change of different physical properties such as the specific volume, the mechanical and dielectric responses, or the enthalpy. In particular, the enthalpy recovery can be calorimetrically evaluated using the integral expression[3]:

$$\Delta H(T_a, t_a) = \int_{T_1}^{T_2} \Delta C_p(T)\, dT \tag{4}$$

where $\Delta Cp(T)$ is the difference between the curves of heat capacity versus temperature for the aged (after a period of time t_a) and the one of the unaged glass ($t_a = 0$) and T_a is the annealing temperature. $\Delta H(T_a, t_a)$ represents the enthalpy excess loss during the annealing. The temperatures T_1 and T_2 are references below and above the glass transition temperature of the system, where $\Delta C_p = 0$. Differently from structural relaxation experiments in the melt region, when the physical aging is considered one has to bear in mind the strongly non-equilibrium character of the glassy state. It manifests in non-linear self-retarding structural relaxation below the glass transition temperature. Some phenomenological expressions have been proposed to take into account the time dependence of relaxation rates in the glassy state[3,5] . These models, however, appear quite criticizable for the absence of real physical bases[6] . As observed by Cowie and Ferguson[7] a good description of the experimental values of $\Delta H(T_a, t_a)$ is obtained by directly using the relation:

$$\Delta H(T_a,t_a) = \Delta H_\infty(T_a)[1 - exp(-(\frac{t_a}{\tau})^\beta)] \tag{5}$$

In Eq. 5, $\Delta H_\infty(T_a)$ represents the maximum amount of relaxable enthalpy. It is worth noting that the parameters τ and β in Eq. 5 have to be considered with care because of the presence of non-linear effects.

In this work we investigated the aging, i.e. the structural relaxation in the glassy state, of a liquid crystal polymethacrylate (see figure 1) containing azobenzene mesogenic side chains. The study was carried out by detecting the enthalpy recovery in Differential Scanning Calorimetry (DSC) traces recorded on heating, after long-time annealing procedures below the glass transition temperature. We followed the approach based on Eq. 5 to describe the enthalpy relaxation results.

EXPERIMENTAL

The polymer, for which the acronym PMA4 will be used, was synthesized by following a general literature procedure[8] . Its chemical structure is shown in Figure 1, while the principal physicochemical parameters are reported in Table 1. Mn and Mw are the first and second moment of the wheight distribution function respectively, T_g is the glass transition temperature and T_{NI} the isotropization temperature. ΔH_{NI} Is the isotropization enthalpy of the nematic phase.

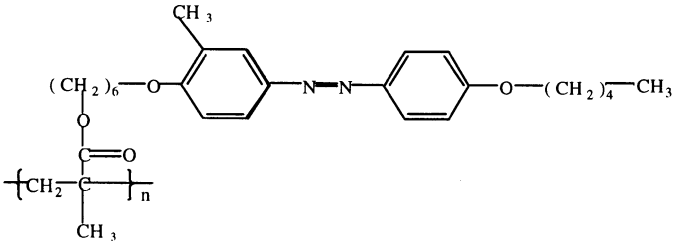

FIGURE 1: Chemical structure of PMA4 monomer.

M_w	M_w / M_n	T_g (K)	T_{NI} (K)	ΔH_{NI} (J/g)
59000	3.17	293	353	1.8

TABLE 1: Physicochemical parameters of PMA4

Differential scanning calorimetry measurements were carried out with a Perkin-Elmer DSC 7 calibrated with indium and zinc standards. For the annealing experiments, the sample (ca. 15 mg) was firstly heated to 115 °C, well above the nematic-isotropic transition.
It was mantained at 115 °C for 15 min in order to erase any previous thermal history, then it was rapidly quenched (200 °C/min) to the temperature of interest T_a where it was annealed for an aging period t_a. Finally, it was rapidly 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. For $T_a < T_g$ the excess enthalpy loss due to the physical aging was evaluated from the area between the scan of the annealed sample and the reference scan, according to Eq. 4. It has been found that the heating rate does not affect the values of the enthalpy loss ΔH (T_a, t_a).

RESULTS AND DISCUSSION

The polymer studied formed a nematic mesophase above its glass transition temperature (T_g) which cleared at T_{NI} = 80°C (Table 1). Several definitions for the location of the glass transition temperature on a C_p versus T plot are in use. The most widely used are the extrapolated onset T_g, the midpoint T_g, and the enthalpic T_g. Having in mind to follow physical aging in the glassy state with enthalpy relaxation measurements, we used this last definition for T_g as the intersection of the extrapolated liquid and glassy enthalpy curves[9] .

Systematic annealing experiments were carried out at temperatures below T_g. In the DSC heating scans, after annealing at T_a

$< T_g$ an endothermic peak appeared as an overshoot to the glass transition (see Figure 2).

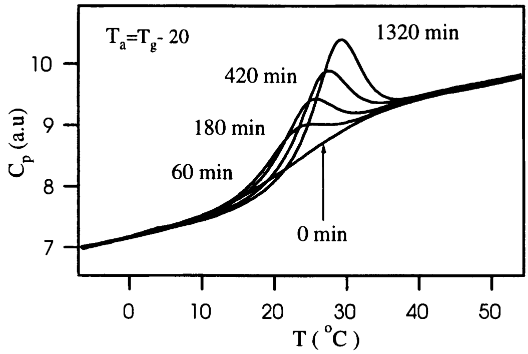

FIGURE 2: DSC heating scans after annealing at T_g-20 °C for different times. The dotted line is the reference scan. The heating rate is 20 °C/min

The effect of the annealing time t_a on enthalpy relaxation is exemplified in Figure 2 where some representative experimental scans pertaining to the aging at $T_a = T_g - 20$ °C are reported. Typical features of the aging process are the increasing area below the DSC peak and the upward shift of the peak as t_a is increased. An analogous behavior wasobserved at all the investigated temperatures.

The enthalpy relaxation data $\Delta H(T_a, t_a)$ at four temperatures are presented in Figure 3. The dotted lines represent the best fits obtained by using eq. 5.

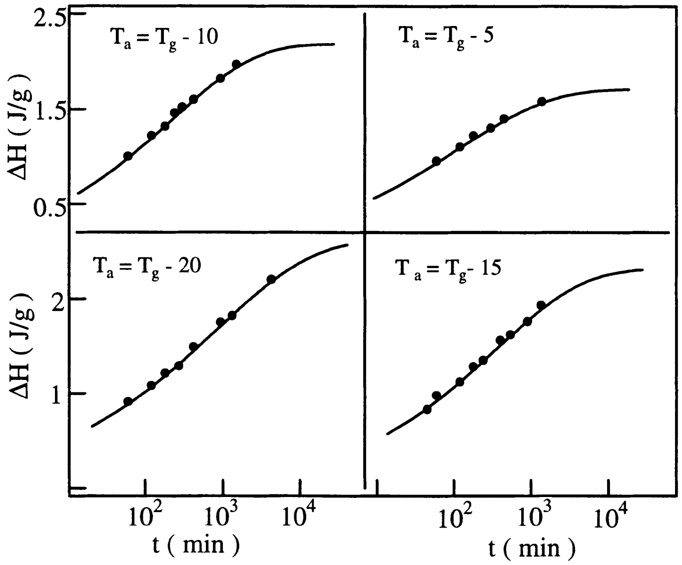

FIGURE 3 Enthalpy relaxation data at the different temperatures. The dotted lines are the best fit obtained by using Eq. 5

The good agreement between the theoretical curves and experimental results is evident. The parameters of the fit at the different temperatures are reported in Table 2. Previous studies on enthalpy relaxation of some polymeric systems observed that the β parameter approached the unity as the temperature increased approaching T_g[10,11]. However, this was not the case for PMMA[12] . From Table 2 it is evident that β is almost constant for PMA4 with an average value of 0.37.

T_g-T_a (K)	τ (min)	β	ΔH_∞ (J/g)
20	774 ± 41	0.34 ± 0.06	2.64 ± 0.13
15	336 ± 22	0.38 ± 0.09	2.33 ± 0.16
10	172 ± 16	0.42 ± 0.07	2.10 ± 0.12
5	110 ± 9	0.35 ± 0.08	1.74 ± 0.11

TABLE 2: Parameters obtained by fitting experimental data with eq. 5.

Therefore, the spectrum of relaxation times seems to be temperature independent in the range studied, and the system behaves in a thermorheologically simple way.

In fact, a good master curve can be generated by plotting the quantity

$$\phi = 1-\frac{\Delta H(t_a,T_a)}{\Delta H_\infty(T_a)} \qquad (6)$$

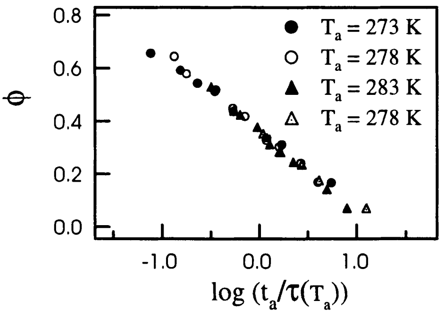

FIGURE 4: Reduced plot for the ageing of PMA4 obtained with the procedure described in the text.

with respect to $\log(t_a/\tau(T_a))$. The reduced plot is shown in Figure 4.

One should note that a β value of 0.37 corresponds to a broad distribution of relaxation times extending for almost 3 decades

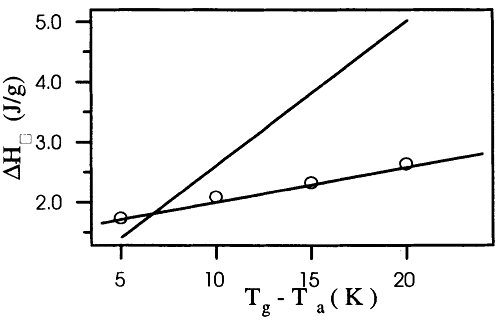

FIGURE 5: Temperature dependence of $\Delta H_\infty(T_a)$. The solid line is the linear best fit, whereas the dotted oneis obtained by using Eq 8.

A value lying in the range $0.3 < \beta < 0.4$ has also been reported for enthalpy relaxation in PMMA[12] . In Figure 5 the values of $\Delta H_\infty(T_a)$ at the different temperatures are reported.

The data (J/g) are well described by a linear fit:

$$\Delta H_\infty(T_a) = 1.46 + 0.0059 \bullet (T_g - T_a) \qquad (7)$$

For comparison, in Figure 5 the behavior of the function:

$$\Delta H(T_a) = \Delta C_p(T_g) \bullet (T_g - T_a) \qquad (8)$$

is also reported (dotted line). Eq. 8 is an approximate relation widely used to evaluate the maximum amount of relaxable enthalpy[3,13]. It is apparent that this relation dramatically overestimates the experimental value of this parameter. Therefore, the validity of extrapolating liquid enthalpy curves to temperatures below the glass transition to obtain $\Delta H_\infty(Ta)$ is questioned. In order to better elucidate this point, experiments with very long annealing times are currently in progress.

In Figure 6, the 1000/T dependence of τ is shown in the overall studied range of temperature. The relaxation times seem well described by an Arrhenius law with an activation energy of 90 ± 4 kJ/mol.

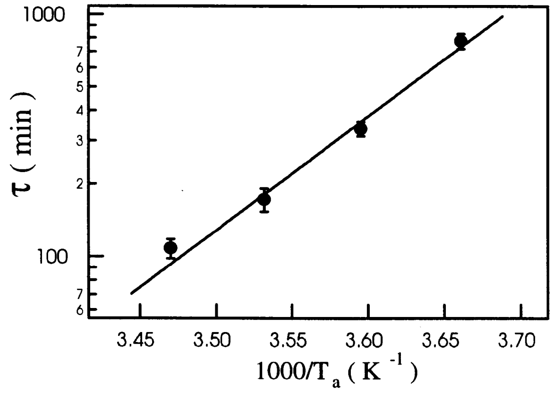

FIGURE 6: Arrhenius plot of the relaxation times. The best fit with ΔE = 90 ± 4 kJ/mol is superimposed

For PMMA, an activation energy of about 180 kJ/mol. has been found[12] According to the discussion in ref[12], the comparison suggests the presence during physical aging, of dynamical processes less cooperative in character in PMA4 than in PMMA. However τ is a kinetic parameter which describes relaxation toward non-equilibrium states. So, a more correct comparison between two systems is obtained by plotting τ versus a reduced temperature which takes into account the relative departure from equilibrium. This may be done by setting

$$T^* = \frac{(T_g - T_a)}{T_g} \tag{9}$$

The resulting reduced plot is shown In Figure 7. It is evident that the reduced temperature collapses the aging data approximatively on a single curve. This feature seems to confirm the general idea that physical aging probes limited segmental motions of the polymer backbone[3,12-14] .

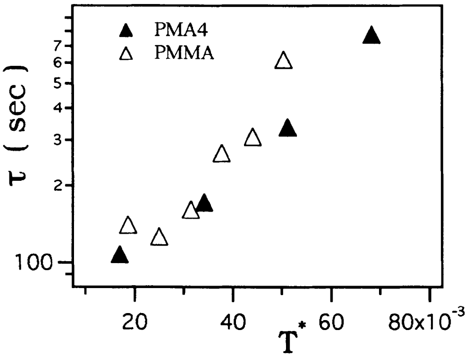

FIGURE 7: Relaxation times for PMA4 and PMMA[12] as a function of the reduced scale defined in Eq. 9

In conclusion, the study of enthalpy relaxation in a side chain liquid crystal polymethacrylate evidenced thermorheological simplicity in the investigated range of temperature. The comparison with PMMA suggests the presence of symilar relaxation processes.

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