Dynamics of the photo-induced orientation and relaxation of new polymethacrylates containing carbazolyl and azobenzene pendant groups

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Abstract: Polarized-light-induced birefringence has been investigated in copolymers of [ω-(N-carbazolyl)alkyl methacrylate] and [2,5-dimethylphenyl-[(4-nitrophenyl)azo]phenoxyalkyl methacrylate]. Optical properties of the side-chain copolymers have been compared with materials in which the azo-dye was merely dispersed in a poly[ω-(N-carbazolyl)alkyl methacrylate] matrix. Increasing the temperature of the film has a dramatic depressive effect on the maximum of photo-induced orientation near and above the glass transition temperature (T_g) region, while its effect was restricted under this temperature. Kinetics of the photo-orientation and the thermal relaxation as a function of temperature have been analysed by a biexponential model based on two rate constants. The universal Williams–Landel–Ferry (WLF) theory has been used to correlate the writing process and relaxation relative time constants with the relative temperature, i.e. $T - T_g$. The validity of this model for the studied materials leads to the assumption that photo-orientation and relaxation processes are mainly dependent on the free volume in the polymer matrix. This hypothesis has been assessed in the case of [11-(N-carbazolyl)undecyl methacrylate]-based materials.
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INTRODUCTION

Azo-containing amorphous polymers have been studied for more than twenty years as suitable materials for reversible optical data storage.[1–3] The ability of a —N=N— azo double bond to isomerize under illumination from the stable *trans* form to the *cis* form leads to interesting properties such as photochromism and optical dichroism.[1,4] The optically induced birefringence makes azo-polymers suitable materials for erasable optical memory disks and tapes, or erasable holographic information storage media. Since Wendorff and co-workers[3] demonstrated this property in some liquid crystalline azo-polymer films, there has been a lot of interest in this field. The mechanism of writing and erasing has been extensively investigated. It has been found that when the polymer is irradiated with a linearly polarized laser beam at a wavelength close to the absorption of the dye, the dye optical axis tends to orient perpendicular to the polarization direction of the irradiating laser light. This orientation involves successive *trans–cis–trans* isomerizations until the dipole moment is aligned in the electric component of the electromagnetic field of the light.[1,5,6] The orientational order can be erased by illuminating the recorded media with a non-polarized light.

Azo-chromophores have also been used recently in photorefractive polymers that are of considerable interest in the field of optical communication and computing techniques. The most promising materials investigated so far are polymers based on a charge-transporting host such as poly(N-vinyl carbazole) doped with a photo-sensitizer and an electro-optic chromophore.[7,8] The low T_g of this type of material is favourable to the diffraction efficiency as a result of the improved orientation of the chromophore in the space-charge electric field.[9] Two contributions to the photorefractive grating are operative: the electro-optic or Pockels effect and the field-induced orientational birefringence.[7,10] In some cases, it has been shown that the second contribution accounts for up to 90% of the photorefractive grating.

The efficiency of the photoinduced are strongly dependent on the orientational freedom of the chromophores in the polymer matrix, and thus on

temperature with respect to the glass transition temperature of the matrix.[11]

Our group recently reported the synthesis of low T_g copolymers of [11(*N*-carbazolyl)undecyl methacrylate] and [2,5-dimethylphenyl-[(4-nitrophenyl)azo]phenoxyalkyl methacrylate].[12] The polarized-light-induced birefringence of thick films (70 μm) was investigated at a constant reduced temperature with respect to T_g ($T - T_g = 10°C$). The influence of dye grafting, the length of the alkyl spacer, the azo-dye content and the type of polymer matrix was studied, and showed that the writing process (amplitude and kinetics) is strongly dependent on the way the azo-dye is incorporated into the polymer. An increased mobility of both the azo-dye and the polymer backbone is favourable to a fast writing process. However, the opposite effect is observed for the maximum induced birefringence, or transmission efficiency, because a low chromophore mobility results, eg in transmission efficiency not exceeding 10% in case of a statistical copolymer of [11-(*N*-carbazolyl)undecyl methacrylate] and 10 wt% [4-(6-methacryloylhexyloxy)-2,5-dimethylphenyl](4-nitrophenyl)diazene. The bi-exponential approximated model, developed by Rochon, Natansohn and co-workers,[13] and based on a fast and a slow writing rate constant (k_f and k_s), allows a good description of the behaviour of the azo-dye in these low T_g materials.

This paper aims to report the influence of temperature of the polarized-light-induced orientation and relaxation processes in copolymers of [ω-(*N*-carbazolyl) alkyl methacrylate] and [4-(11-methacryloylundecyloxy)-2,5-dimethylphenyl]-(4-nitrophenyl)diazene. Two spacer lengths between the carbazole entity and the polymer backbone will be considered, i.e. hexyl and undecyl spacers, resulting in matrices with a T_g of about $-5°C$ and 58°C, respectively. The influence of both the actual temperature and the glass transition temperature on the amplitude of orientation and on the writing and relaxation kinetics will be discussed in line with the Williams–Landel–Ferry (WLF) universal model.[14] The correlation between the photo-orientation dynamics and the free volume in the polymer matrix will also be discussed.

EXPERIMENTAL

The synthesis of 11-(*N*-carbazolyl)undecyl methacrylate, [4-methoxy-2,5-dimethylphenyl](4-nitrophenyl)diazene and [4-(11-methacryloylundecloxy)-2,5-dimethylphenyl] (4-nitrophenyl)diazene and their copolymers was reported in a previous paper.[12] 6-(*N*-Carbazolyl)hexyl methacrylate was prepared as reported in the literature, i.e. by alkylation of carbazole with 1-bromo-5-hexene followed by hydroboration of the terminal C=C double bond by 9-borabicyclononane (BBN).[15] The 6-hydroxy function was finally functionalized by reaction with methacryloyl chloride. Methacrylic monomers were polymerized in dry DMF in the presence of azo-bis-iso-butyronitrile (AIBN, 2 wt%) as an initiator. The polymerization medium was degassed twice before heating and stirring overnight at 65°C. The reaction was stopped by pouring the polymerization mixture into methanol previously cooled to $-78°C$. The isolated polymer was redissolved in THF and precipitated again in cold methanol, filtered and finally dried under vacuum overnight. Glass transition temperatures were measured by differential scanning calorimetry (TA Instruments) at a heating rate of $20°C\ min^{-1}$.

Copolymers (or polymer blends) were dissolved in THF, and the solutions were filtered through a 0.45 μm filter. The solvent was removed under reduced pressure, and the isolated material was dried overnight at room temperature under vacuum (0.1 mmHg). The polymer was then crushed and the fine powder was spread on a clean glass side before being heated to 100°C and covered by a second slide. The film thickness was controlled by using a 70 μm glass spacer between the glass slides. Homogeneous films of good optical quality were accordingly prepared.

The experimental equipment for the measurement of the polarized-light-induced birefringence was described in a previous paper.[12] A linearly polarized Ar laser beam ($λ = 514\ nm$) of a $5.0\ mW\ cm^{-2}$ incident intensity, whose polarization axis could be fitted with a half-wave plate, was filtered and expanded before being strongly absorbed by the sample. A second and nearly parallel HeNe beam ($λ = 633\ nm$, 36.5 μW), extended to a diameter of analysis of 8 mm, crossed the sample and then an analyzer rotated at 90° with respect to the incident polarization. A filter, with its absorption spectrum centred at 514 nm, was placed before the detector in order to stop any diffuse or direct light coming from the Ar laser. The transmission efficiency was defined as the ratio between the transmitted HeNe intensity and the incident intensity.

RESULTS AND DISCUSSION
Polymer characterization
Polarized light induced photo-orientation and thermal relaxation of azo-dyes in poly [ω(*N*-carbazolyl)alkyl methacrylate] was studied for the materials shown in Fig 1 and designated by the same nomenclature as used in our previous paper.[12] The matrices **P2** and **P3** have been synthesized in which the carbazole entity is grafted onto the methacrylic backbone through an undecyl and an hexyl spacer, respectively. The azo-dye **8c** has been either merely dispersed in the matrix (**P2-disp-8c** and **P3-disp-8c**) or covalently linked to it by means of an undecyl spacer (**P2-co-8b** and **P3-co-8b**). The weight composition of the azo-dye in the matrix is 15 wt% in all the materials. The main characteristic features of the
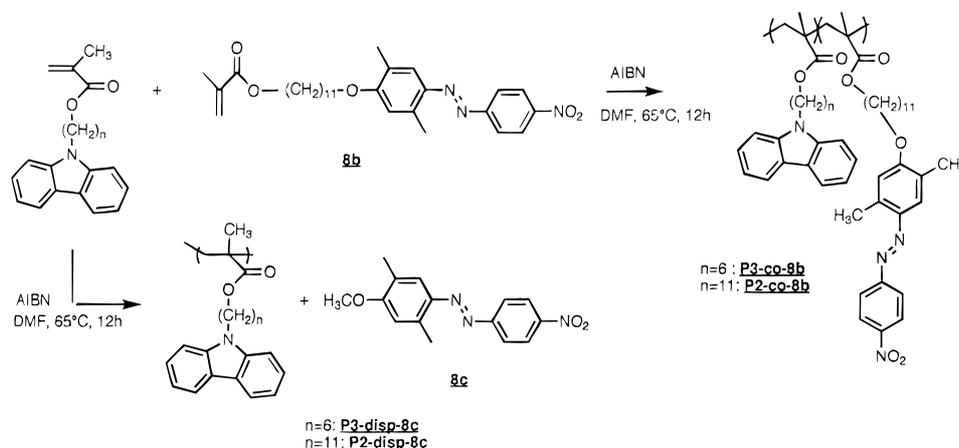
Figure 1. Structure of carbazolyl azo-dye side chain copolymers and blends.

homo- and copolymers are listed in Table 1. The composition of the copolymers has been analysed by ¹H NMR, by comparison with the ¹H NMR spectrum of the parent homopolymers **P2** and **P3**. Polymers with number average molecular weight up to 12 000 have been synthesized by free radical polymerization initiated by AIBN in DMF at 65°C. In contrast to Strohriegl,[15] DMF was used instead of toluene as the polymerization solvent in order to increase the monomer and polymer solubility and to decrease the polymer polydispersity.

As previously reported for **P2** homo- and copolymers, the glass transition temperature measured for **P3** in this work (59°C) is significantly different from the literature data (73°C).[15] Residual monomer has not been detected by NMR after careful purification of (co)polymers **P2** and **P3**, which could explain this discrepancy. This difference might be due to some unreacted methacrylic acid and/or methacryloyl chloride along the polymeric backbone in the latter case, as a result of a non-quantitative reaction of poly(methacryloyl chloride) with ω-hydroxyalkyl carbazole. Modification of the **P2** and **P3** matrices by grafting or dispersion of the azo-dye has a small depressive effect on the glass transition temperature. The T_g of **P2** (−5°C) is decreased to −11°C by copolymerization of **P2** with 15 wt% **8b** and to −10°C for the dispersion of 15 wt% **8c**. The depressive effect of the added chromophore on T_g is also

observed in **P3**, because T_g is decreased from 59°C to 56°C for **P3-co-8b** and 51°C for **P3-disp-8c**. No phase separation of the dispersed dye from the host polymers has been observed by DSC[12] or polarized optical microscopy.

Temperature dependence of the amplitude and kinetics of photo-orientation

The time dependence of the photo-induced birefringence, expressed as the transmission efficiency, has been investigated at various temperatures. The experimental set-up for temperature control has been described in a previous paper[16] and is limited to the 250–300 K range, so that it is impossible to directly compare **P2** and **P3** at the same reduced temperatures $T − T_g$. Figure 2 shows how the maximum of transmission efficiency (thus measured in the plateau region) depends on the reduced temperature $(T − T_g)$. Clearly, temperature has a strong influence on the **P2**-based systems. In these materials, a transmission efficiency of approximately 0.5 is observed when the writing process is performed at a temperature close to T_g. A dramatic decrease of the transmission efficiency down to 10^{-5} then occurs when the photo-induced orientation is carried out at room temperature, i.e. 30 K above glass transition

Table 1. Molecular characteristics of homo- and copolymers

Polymer	wt.-% 8[a]	Mn (*10⁻⁴)[b]	Mw/Mn	T_g (K)[c]
P2	0	0.73	1.5	268
P2-co-8b	15	1.2	1.7	262
P2-disp-8c	15	—	—	263
P3	0	0.65	1.6	332
P3-co-8b	15	0.97	1.7	329
P3-disp-8c	15	—	—	324

[a] ¹H NMR analysis.
[b] SEC analysis in CHCl₃ (calibration with polystyrene standards).
[c] DSC (heating rate = 20°C/min, second scan).
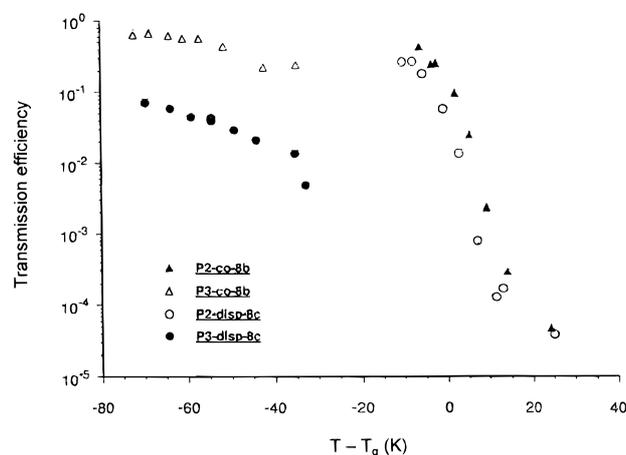
Figure 2. Dependence of the maximum of transmission efficiency on reduced temperature $(T − T_g)$.

temperature. In comparison, the transmission efficiency decreases from 0.5 to 0.1 when **P3-co-8b** is heated from 70 K below T_g to room temperature. Under the same temperature conditions, a decrease in the transmission efficiency from 10^{-1} to 10^{-2} is observed for the parent dispersed material **P3-disp-8c**.

The transmission efficiency is systematically higher in the grafted materials than in the parent dispersed ones, whatever the reduced temperature. This observation indicates that the chemical bonding of the chromophore to the matrix actually limits the rotational motion of the chromophore, although photo-induced orientation remains possible. These results are in very good agreement with the observations by Mohajerani *et al*[17] who studied the effect of dye grafting on the polarization sensitive optical phase conjugation (an orientation-dependent phenomenon associated with photo-induced birefringence) in Disperse Red 1-poly(methyl methacrylate) copolymers and blends. They reported that the chemical grafting of the chromophore onto the polymer resulted in a more intense polarization-sensitive phase conjugate signal, compared with the chromophore/polymer mixture. This improvement was explained by the inhibited rotation and large-scale diffusion of the chromophore through the polymer system.

As reported elsewhere,[12,13] the photo-induction of birefringence in polymers below or close to the glass transition temperature can be split into two different modes: an initial fast one and a second slow response mode. The writing curves or the time dependence of the birefringence can indeed be fitted by a bi-exponential equation:

$$y = A(1 - e^{-k_f t}) + B(1 - e^{-k_s t}) \quad (1)$$

where k_f and k_s are the rate constants for the fast process and the slow process, respectively.

Actually, k_f has been shown to depend on the quantum yield of the isomerization reaction, the isomerization rate and the local mobility of the azo-dye, which are affected by the size of the azo moiety, the free volume around it, and the strength of the coupling interactions between azo-dye and the polymer backbone. The magnitude of k_s depends mainly on the polymer mobility.

The relaxation of the birefringence on removal of

the laser beam can also be split into an initial fast decay and a slow decay. For the decay of the written birefringence, Ho *et al*[13] proposed a bi-exponential function similar to eqn (1), that fits the relaxation curves:

$$y' = A'e^{-k'_f t} + B' e^{-k'_s t} \quad (2)$$

The 'fast' decay would be due to the fast component of the thermal *cis–trans* isomerization and dipole reorientation, whereas the 'slow' decay would be associated with the mobility and relaxation of the polymer backbone.

In a previous paper,[12] the fast and slow rate constants for the writing process were determined at a constant reduced temperature with respect to T_g, ie $T - T_g = 10°C$. It was found that the fast rate constant k_f at this reduced temperature was strongly dependent on the way the chromophore was dispersed in the polymer matrix. The restricted mobility of the chemically grafted dye resulted in a much smaller rate constant for the so-called 'fast' process. The same tendency was observed for the rate constant k_s for the slow process.
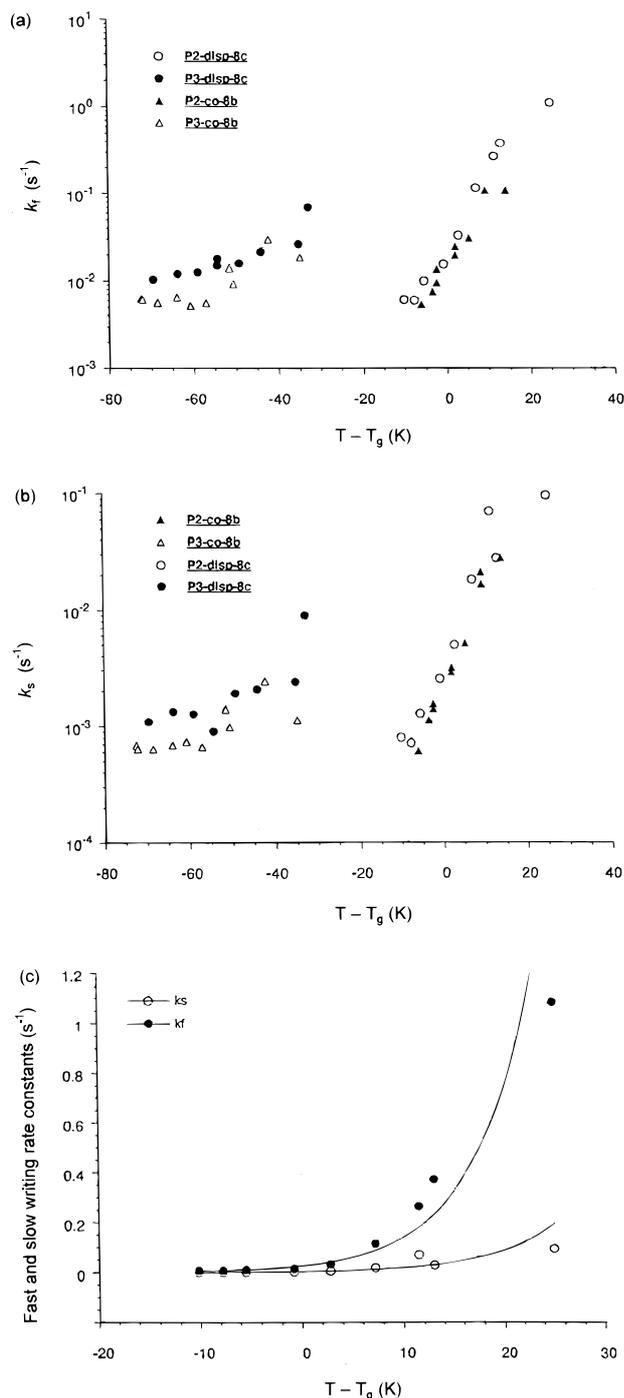
The fast and slow rate constants for both the writing and the relaxation process have been determined in this work by fitting the time dependence of the transmission efficiency by the bi-exponential eqns (1) and (2). The rate constants for the two processes at the glass transition temperature are listed in Table 2 for **P2** and **P3** materials. The ratio of the fast rate constant to the slow one is of the same order of magnitude for both the writing and the relaxation phenomena. As already observed at 10 K above T_g, the local mobility of the azo-group at the glass transition temperature is restricted by the grafting on the polymer backbone, because k_f for the orientation process increases from 14.1×10^{-3} s^{-1} in the case of the grafted material **P2-co-8b** to 26.2×10^{-3} s^{-1} for the dispersed material **P2-disp-8c**. The restricted mobility of the azo-dye in the copolymer, compared to the dispersed material, is also confirmed by the relaxation rate constants k'_f. Similarly, the magnitude of k_s and k'_s, which depends on the mobility of the polymer segments, is smaller for the copolymers than for the dispersed analogues. This indicates that the grafting of a highly dipolar co-monomer onto the backbone also decreases the mobility of the polymer segments, in qualitative agreement

Table 2. 'Fast' and 'slow' writing (k_f and k_s) and relaxation (k'_f and k'_s) rate constants calculated by the biexponential model at the glass transition temperature

Polymer	T_g (°K)	k_f (*10^3 s^{-1})	k_s (*10^3 s^{-1})	k'_f (*10^3 s^{-1})	k'_s (*10^3 s^{-1})
P2-co-8b	262	14.1	2.2	26.8	2.6
P2-disp-8c	263	26.2	3.6	53.7	5.2
P3-co-8b	329	87.3	4.1	15.8	1.0
P3-disp-8c	324	68.2	5.6	53.4	6.3

with T_g for the **P3-disp-8c** guest–host system ($T_g = 324\,K$) compared to the **P3-co-8b** grafted material ($T_g = 329\,K$).

Figure 3(a,b) shows the dependence of the fast and slow writing rate constants (logarithmic scale) on the relative temperature $T - T_g$ for **P2** and **P3** polymers. It is clear that the writing rate constant dramatically increases with temperature for **P2** materials in a temperature range above T_g, in contrast to **P3** materials below T_g. Figure 3(c) illustrates the depen-
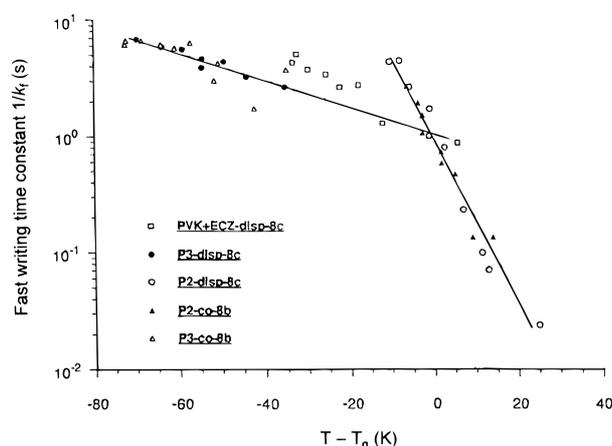
dence of k_f and k_s (linear scale) on reduced temperature for the dispersed **P2-disp-8c** sample.

An exponential dependence is clearly observed with a sharp increase from 10 K above the glass transition temperature. This observation is consistent with the increase in mobility of the chromophores and the polymer segments[18] above T_g, which drastically affects the kinetics of photo-orientation.
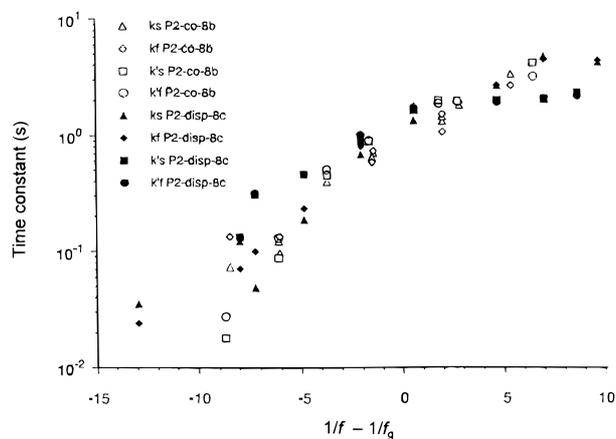
The WLF model and photo-orientation or relaxation kinetics

The mechanical and dielectric relaxation times in polymers and their temperature dependence are usually discussed on the basis of the empirical Williams–Landel–Ferry (WLF) equation.[14] The ratio a_T of the relaxation time at a temperature T to the value at a reference temperature (often chosen as T_g) can be expressed on a semi-logarithmic plot of log a_T versus reduced temperature, ie $T - T_g$. This relationship has been found to describe suitably the viscoelastic behaviour of a wide variety of polymers, polymer solutions and glass-forming organic liquids. A WLF model allowed Eisenbach[19] to account for the photoisomerization kinetics of azo-dyes in (meth)acrylic polymers. The analysis of the thermal relaxation of the excited *cis* form back to the *trans* form by this model led to the assumption of a free-volume dependency for the isomerization process. It appears therefore that not only the relaxation process, but also the photo-orientation kinetics, could be described by the WLF model.

We have accordingly investigated the dependence of the reduced time constants (ie ratio of the reciprocal of the first order rate constant at a temperature T to the value at T_g) on the reduced temperature $T - T_g$. The time constants at the glass transition temperature are the reciprocal of the rate constants listed in Table 2. The WLF plot for the fast writing time constants for the four polymers is shown in Fig 4. A linear relationship between the reduced time constant (logarithmic scale) and the reduced temperature is observed for the two series of polymers

Figure 3. Semi-logarithmic plots of the writing 'fast' (a) and 'slow' (b) rate constants versus reduced temperature ($T - T_g$). (c) Linear plot of the writing 'fast' and 'slow' rate constants for the **P2-disp-8c** samples.

Figure 4. WLF plot for the 'fast' writing time constants.

Figure 5. Dependence of the relative 'fast' and 'slow' writing and relaxation time constants on the corresponding fraction *f* of the free volume at that temperature.

P2 and **P3**. The same dependence is observed for the slow writing time constants and the relaxation time constants. However, there is a discontinuity in the slopes at the glass transition temperature, in agreement with a previous report by Eisenbach.[19]

In order to check the validity of the WLF relationship for other polymers, we have similarly analysed the fast and slow time constants for the writing process in poly(*N*-vinyl carbazole) (PVK) doped with 10 wt% DMNPAA **8c** and plasticized by 33 wt% *N*-ethylcarbazole (ECZ). As shown in Fig 4, the kinetics of the photo-induced orientation in this material are well fitted by the WLF model, because the data fall on the straight line observed for **P3** samples (Fig 4).

According to the WLF model, the thermal dependence of viscosity is closely associated with the thermal dependence of free volume, which is expressed by a universal relationship[20]

$$f = f_g + \alpha_2(T - T_g) \qquad (3)$$

where α_2 is the difference between the thermal expansion coefficients above and below the glass transition temperature ($\alpha_2 = 4.8 \times 10^{-4} \, \mathrm{K}^{-1}$), f is the fraction of free volume at temperature T, and f_g is the free volume fraction at T_g (generally 0.025).

The free volume theory and the WLF relationship were originally found to be valid in the $T_g < T < T_g + 100$ temperature range.[14] Later on, the validity of this theory was reported to be maintained at temperatures down to 80°C below T_g. In this study, no deviation with respect to the WLF model is found until temperatures as low as $T_g - 70$ are reached. In order to confirm that photo-induced writing and relaxation phenomenon actually depend on the free volume of the polymer under study, we have plotted the reduced writing and relaxation time constants (ie the ratio of the reciprocal of the first order rate constant at temperature T with respect to T_g) at different temperatures T against the free volume fraction f calculated from eqn (3) at the same temperatures. Figure 5 shows the semilogarithmic plot of the rela-

tive time constant versus the reduced free volume fraction $1/f - 1/f_g$ for the **P2** series. This plot is quite comparable to the one previously reported by Eisenbach.[19] Both the writing and relaxation constants fall on the same curve and confirm a well defined dependence of the orientational and the relaxation processes on the free volume content: the higher the free volume in the polymer matrix, the faster the chromophores are aligned in the polarized laser beam and relaxed when it is switched off.

CONCLUSIONS

The polarized-light-induced birefringence and thermal relaxation in copolymers of [ω-(*N*-carbazolyl)alkyl methacrylate] and [2,5-dimethylphenyl-[(4-nitrophenyl) azo]phenoxyalkyl methacrylate] are strongly dependent on temperature close to and above the glass transition temperature region. Below T_g this effect is severely restricted. The restricted mobility of the azo-dye in the grafted material, compared to the situation where the dye is physically dispersed in the polymer matrix, accounts for a less extended photo-orientation in the former case. The thermal dependence of the kinetics of photo-orientation and thermal relaxation agrees with a two step process, which has been analysed by a biexponential equation based on a fast and a slow process. The universal Williams–Landel–Ferry (WLF) model accounts for the thermal dependence of the writing and relaxation behaviours. The validity of this model indicates that the photo-orientation and relaxation processes are mainly controlled by the free volume fraction in the low T_g matrix, under consideration in this work.

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