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Influence of the average molecular weight and the concentration of plasticizer on the orientational dynamics of chromophores in guest-host polymers

J. C. Ribierre,^{a)} L. Mager, F. Gillot, and A. Fort

Groupe d'Optique Non Linéaire et d'Optoélectronique, Matériaux Organiques pour l'Optique Nonlinéaire, IPCMS, UMR CNRS-ULP 7504, 23 rue du Loess, BP43, 67037 Strasbourg Cedex 2, France

S. Méry

Groupe des Matériaux Organiques, IPCMS, UMR CNRS-ULP 7504, 23 rue du Loess, BP43, 67037 Strasbourg Cedex 2, France

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We report experimental results obtained from dielectric spectroscopy, electro-optic, and second harmonic generation dynamics measurements on different polymers doped with nonlinear optical chromophores. The polymers considered in this work are polyvinylcarbazole plasticized by ethylcarbazole and polystyrenes with different average molecular weights. Altogether the influence of temperature, average molecular weight of the polymer host, and concentration of plasticizer on the orientational processes of chromophores is investigated and described by polymer rheology laws. Finally, these results, which identify the major role played by the average molecular weight of polymers on the orientational dynamics of chromophores, suggest another possible way of optimization for low glass transition temperature photorefractive polymers, where fast orientational response times are required. © 2006 American Institute of Physics. [DOI: [10.1063/1.2234811](https://doi.org/10.1063/1.2234811)]

I. INTRODUCTION

Guest-host polymers for nonlinear optics have been in the past the subject of intensive researches in view of their great potential for electro-optical (EO) and photorefractive devices.^{1–6} In these systems, the push-pull EO chromophores doping the polymer host have to be oriented by an external electric field in order to observe second-order nonlinear optical (NLO) properties. Besides, upon removal of the electric field, the decay of EO responses arises then from the relaxation of the polar orientational alignment initially induced by the applied electric field. This reorientation of chromophores undergoes rotational Brownian motion and is affected by the mobility of polymer chains and the local free volume present in the vicinity of the chromophores. These processes have been the subject of significant inquiries. Previous studies^{7–9} have demonstrated that the orientational dynamics of chromophores are dominated by the viscoelastic properties of the polymer host. A coupling has been established between these orientational processes and the polymer α -relaxation dynamics which is associated to cooperative segmental motion of the polymer chains responsible of the glass transition temperature T_g .^{10–12} In parallel, the influence of T_g on the dynamics of both the electro-optic response and the photorefractive performances of guest-host polymers has been pointed out by Bittner *et al.*^{13,14}

In photorefractive guest-host polymers, the highest photorefractive performances are obtained in materials with T_g near room temperature, mainly due to the orientational enhancement effect.¹⁵ The most common technique to control T_g consists in incorporating low molecular weight plasticiz-

ing molecules into the polymer host. However, from previous studies in polymer rheology, an adjustment of the average molecular weight of the matrix can also be used to modify T_g and the viscoelastic properties of the materials. The strong interest carried out on the low molecular weight photorefractive glasses confirms such a purpose. In this work, the roles of both the plasticizer concentration and the average molecular weight of the polymer host on the orientational dynamics of chromophores are investigated in detail on a large range of temperature above and below T_g by dielectric spectroscopy,^{16,17} second harmonic generation (SHG),^{18,19} and EO dynamics measurements.^{20,21} By combining results from these experiments and interpreting them using polymer rheology laws based on local free volume, a complete description of chromophore relaxation in the glassy and rubbery states is proposed and the role of both the plasticizer concentration and the average molecular weight on these orientational processes of chromophores is clarified.

II. MATERIALS

Two kinds of polymer hosts are considered in this study: polyvinylcarbazole (PVK) and polystyrene compounds. To characterize the role of plasticizer on the orientational dynamics of chromophores, different amounts of ethylcarbazole (ECZ) are added to the PVK host. These systems are doped with 20 wt % of chalcone 9 (CHAL9). This chromophore is a push-pull molecule, which exhibits a permanent dipole moment of 6.5 D as well as large quadratic optical nonlinearities. Besides, it presents an absorption peak with a maximum at 440 nm and has a very small absorption above 550 nm. Five polystyrenes with different average molecular weights (M_w =3680, 18 700, 44 000, 212 400, and

^{a)}Electronic mail: jr43@st-andrews.ac.uk

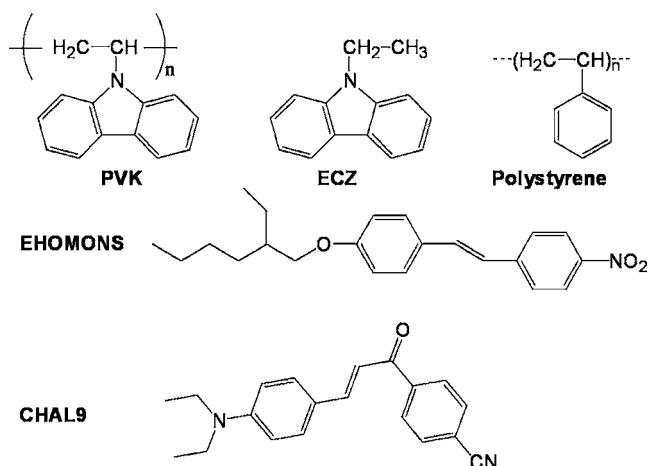


FIG. 1. Chemical structures of the different molecules considered in this study.

891 000) and with a low polydispersity ($M_w/M_n \approx 1.1$) are also used as a host. Polystyrene-based composites do not exhibit any photorefractive effect due to their deficient photoconductive properties. However, polystyrene is chosen in this work, on account of the convenient location of its T_g and the comparative profusion of information concerning its various properties. These systems are doped with 20 wt % of CHAL9 or with 20 wt % of EHOMONS. This latter NLO molecule is also a push-pull chromophore and exhibits a maximum of absorption at 385 nm. The chemical structures of all these components are given in Fig. 1. To elaborate the samples, the different compounds are dissolved and mixed in chloroform. The solutions are then dried and placed in a vacuum oven at $T_g + 75^\circ\text{C}$ for approximately 12 h to eliminate the residual solvent. Their T_g is determined by differential scanning calorimetry (DSC) at a heating rate of $10^\circ\text{C min}^{-1}$. The doped polymers are then sandwiched between two parallel indium tin oxide (ITO) coated glass slides. Spacers of $105\ \mu\text{m}$ are used to achieve uniform sample thickness.

III. EXPERIMENT

A. Dielectric spectroscopy

The frequency dependence of the real and the imaginary parts of the dielectric constant is characterized by using an impedance analyzer (Quad Tech 7400) from 100 Hz to 500 kHz. The temperature of the samples was controlled in an oven with a precision of 0.1°C . These measurements are performed using the lumped circuit method in a parallel configuration. The samples are viewed as an ideal capacitor in parallel to a resistor describing the losses induced by the dipolar relaxation and the dc conductivity. In this case, the real part ϵ' and the imaginary part ϵ'' of the complex dielectric constant are given by

$$\epsilon' = \frac{C}{C_0},$$

$$\epsilon'' = \frac{1}{R\omega C_0}, \quad (1)$$

where R and C are the resistance and the capacitance of the samples measured at the oscillation frequency ω . The respective orders of magnitude are typically several picofarads and megaohms. C_0 corresponds to the capacitance of the equivalent condenser when the polymer is replaced by vacuum. In this work, the frequency dependence of the dielectric response is described by using the Havriliak-Negami (HN) equation:²²

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{[1 + (i\omega\tau)^{\alpha_{\text{HN}}}]^{\beta_{\text{HN}}}}, \quad (2)$$

where α_{HN} and β_{HN} are empirical parameters related to the shape and the width of the relaxation times distribution and ϵ_s and ϵ_∞ correspond to the values of ϵ' at, respectively, low and high frequencies and are called the relaxed and unrelaxed values of the dielectric constant. The strength of relaxation $\Delta\epsilon = \epsilon_s - \epsilon_\infty$ depends on the value of the chromophore dipole moment μ .²³ The evaluation of the dielectric response times τ is estimated here from the real part of the dielectric constant using the real part of HN equation.

B. Second harmonic generation measurements

This experimental setup^{19,24} is used here to study the influence of the average molecular weight of polymers on the orientational processes of chromophores below T_g . A p -polarized fundamental beam of a Nd:YAG (yttrium aluminum garnet) laser at a wavelength of 1064 nm with a 10 Hz repetition rate is incident on the sample at an angle of 45° . The samples are placed in an oven. Appropriate filters are positioned before and after the sample to detect properly the SHG response. A photomultiplier and a boxcar interfaced to a computer are used for the detection. A dc voltage with a magnitude of 1.5 kV is applied across the samples in order to break the centrosymmetry of the materials and to obtain a SHG signal. At steady state, the SHG intensity $I(2\omega)$ is given by

$$\sqrt{I(2\omega)} \propto NE_z \left(\frac{\mu\beta}{5kT} + \gamma \right), \quad (3)$$

where E_z is the dc electric field magnitude, N is the density of chromophores, γ characterizes a third order optical effect induced by the electric field, β is the quadratic hyperpolarizability of the chromophores, k is the Boltzmann constant, and T is the absolute temperature. The orientational response times are directly measured from the monitoring of the rise and the decay of the SHG responses. They are analyzed by using the Kohlrausch-Williams-Watts (KWW) equation commonly used to describe relaxations in polymeric systems in the temporal domain:²⁵

$$y = \exp \left[- \left(\frac{t}{\tau} \right)^{\beta_{\text{KWW}}} \right], \quad 0 < \beta_{\text{KWW}} \leq 1, \quad (4)$$

where y is the relaxation parameter of interest, τ is the response time, and β_{KWW} is the stretching parameter which is related to the response times distribution breadth. An average

orientational response time $\langle\tau\rangle$ is generally introduced as follows:

$$\langle\tau\rangle = \frac{\pi\Gamma(1/\beta_{\text{KWW}})}{\beta_{\text{KWW}}}, \quad (5)$$

where Γ is the gamma function. Previous studies have shown the relationship between the HN and the KWW equations.²⁶ Here, the use of these laws is sufficient to show the relationship between polymer chain dynamics and orientational processes of chromophores.

C. Ellipsometric measurements

A classical transmission ellipsometry setup is also used in this work. This technique is an efficient tool to characterize the changes of refractive index induced by the application of an external electric field.^{27,28} The light source is a laser diode emitting at a wavelength of 670 nm with a 1 mW power. The applied dc voltage has a magnitude of 2 kV. The variation of transmitted light ΔI , which is measured with a photodiode and monitored by a (Tektronix TDS 410A) numerical oscilloscope, is directly proportional to the induced birefringence as follows:²⁸

$$\frac{\Delta I}{I_0} = \frac{\pi d}{\lambda G} \Delta n, \quad (6)$$

where I_0 is the incident intensity, λ is the wavelength, G is a geometrical factor here equal to 4.6, and d is the sample thickness. The induced birefringence Δn corresponds to the difference between the induced variations of the extraordinary and ordinary refractive indices and is due to the orientation of the chromophores by the electric field. These refractive index changes are related to the products $\mu^2\Delta\alpha$ and $\mu\beta$ of the chromophores, where $\Delta\alpha$ is the anisotropy of linear polarizability. The ellipsometry technique not only enables the determination of the parameters $\mu^2\Delta\alpha$ and $\mu\beta$ but also provides information on the orientational dynamics of chromophores. From the electric field induced birefringence curves, the estimation of the orientational response time is achieved by using the KWW equation.

IV. RESULTS AND DISCUSSION

A. Determination of the glass transition temperature T_g

DSC measurements were performed in PVK doped with 20 wt % of CHAL9 and plasticized with different concentrations of plasticizer ECZ ranging from 0 to 40 wt %. Pure PVK is known to exhibit a T_g of 200 °C. Doped with 20% of CHAL9, T_g decreases to 112 °C, illustrating the plasticizing effect of doping chromophores. Figure 2 shows the decrease of T_g with increasing ECZ concentrations. This evolution is associated to the additional fractional free volume introduced by the plasticizer. It has been previously demonstrated that the incorporation of low molecular weight depresses T_g linearly for small concentrations of plasticizer (typically <15%).²⁹ However, this linearity disappears when the concentration of plasticizer becomes too high. As depicted in

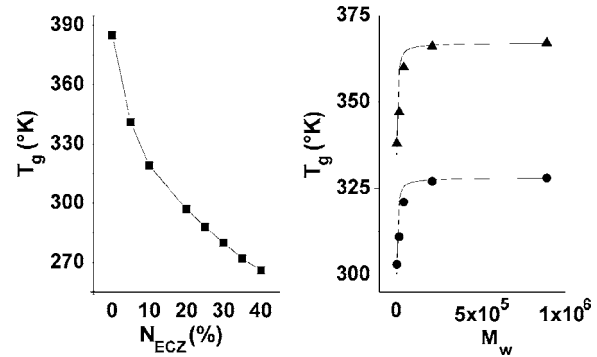


FIG. 2. On the left side, evolution of T_g in PVK doped with CHAL9 plotted vs the ECZ concentration N_{ECZ} . On the right side, T_g values of polystyrene doped with CHAL9 (triangle) and with EHOMONS (circle) are plotted vs the molecular weight M_w . These data are fitted by the Kanig-Ueberreiter equation.

Fig. 2, the behavior of T_g , which here is clearly nonlinear, was expected in view of the very high concentration of chromophores and plasticizer.

The average molecular weight dependence of T_g for polystyrene doped with chromophores CHAL9 and EHOMONS was also determined by DSC and is shown in Fig. 2. Above a critical average molecular weight M_c , T_g becomes roughly independent of the molecular weight. However, a strong decrease of T_g is observed below M_c with decreasing molecular weights. For linear polymers, the molecular weight dependence of T_g can be expressed by the empirical Kanig-Ueberreiter equation:³⁰

$$T_g^M = \left(\frac{1}{T_g^\infty} + \frac{K}{M_w} \right)^{-1}, \quad (7)$$

where T_g^M is the glass transition temperature of the polymer at a molecular weight M_w . The limiting value at high M , T_g^∞ , corresponds to a polymer chain length sufficiently long so that the chain end contribution to the configurational rearrangements becomes negligible. The respective values of T_g^∞ and the fitting parameter K are 374 K and 7.8×10^{-4} mol/kg for pure polystyrene, 367 K and 9.7×10^{-4} mol/kg for polystyrene doped with 20% of CHAL9, and 328 K and 1.05×10^{-3} mol/kg for polystyrene doped with 20% of EHOMONS. The large differences of T_g between the two doped polymers are unexpected and show that EHOMONS is a better plasticizing molecule than CHAL9 in a polystyrene host.

The most standard technique to lower T_g in NLO guest-host polymers is to add a plasticizer such as ECZ for PVK based composites. The DSC measurements performed on doped polystyrene illustrate well the influence of the molecular weight on T_g . These data suggest that a lowering of M instead of the incorporation of plasticizer could be used to optimize T_g and consequently the photorefractive performances of low T_g guest-host polymers. However, in order to establish definitive conclusions, a detailed comparison and a characterization of the role played by these two parameters on the orientational dynamics of chromophores should be carried out.

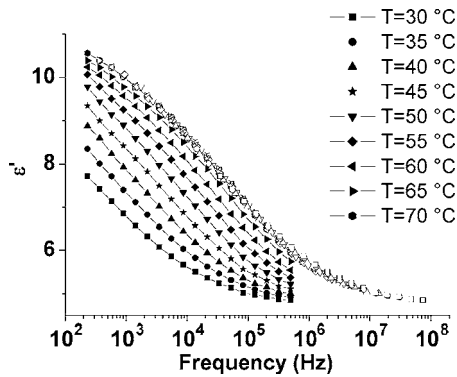


FIG. 3. Real part of the dielectric constant ϵ' as a function of the oscillation frequency in PVK:ECZ:CHAL9 (40:40:20 wt %) at several temperatures above T_g . Data are fitted by the Havriliak-Negami equation. Master curve (open symbols) is constructed at 70 °C.

B. Effects of the plasticizer concentration

Dielectric spectroscopy measurements were performed above T_g on PVK doped with 20 wt % of CHAL9 and plasticized with different concentrations of ECZ ranging from 0% to 40%. Figure 3 shows the frequency dependence of the real part of the dielectric constant ϵ' measured at several temperatures in PVK:ECZ:CHAL9 (60:20:20 wt %). The curves exhibit a sigmoidal shape and are displaced towards the high frequencies when temperature increases. The temperature dependence of the dielectric constants ϵ' and ϵ'' of doped polymers follows the time-temperature superposition principle.²⁹ A superposition of the isothermal curves can be achieved at a reference temperature T_0 by a simple translation along the frequency axis leading to the construction of a master curve. Such a behavior suggests that the orientational response time distributions are not significantly affected by temperature changes above T_g . The temperature dependence of translation or shift factor a_T , which can be deduced from this superposition, follows the Williams-Landel-Ferry (WLF) equation:³¹

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + T - T_0}. \quad (8)$$

C_1 and C_2 are the WLF coefficients characterizing the polymer. They are related, respectively, to the fractional free volume f_{T_0} and to the thermal expansion coefficient α_f by

$$C_1 = \frac{1}{2.303f_{T_0}}, \quad (9)$$

$$C_2 = \frac{f_{T_0}}{\alpha_f}.$$

This behavior is related to the α relaxation responsible of the glass transition temperature, which is associated to cooperative segmental motion of polymer chains. It has been demonstrated that the WLF equation, which was first used to describe the temperature dependence of the polymer zero shear viscosity, can also be employed to characterize the influence of the temperature on the orientational dynamics of chromophores above T_g . Doing so, Dhinojwala *et al.* have shown the coupling between the polymer chains dynamics

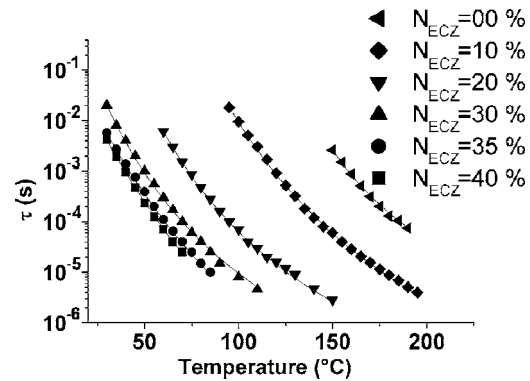


FIG. 4. Temperature dependence of the dielectric response times for doped PVK plasticized with different concentrations of ECZ. The curves are fitted by using a Williams-Landel-Ferry equation leading to the evaluation of the coefficients C_1 and C_2 listed in Table I.

and the orientational processes of chromophores.^{10,11} From these dielectric measurements, the temperature dependence of the relaxation times is deduced by using the HN equation and is plotted in Fig. 4. A fit of these data is obtained by using the WLF equation leading to the determination of the coefficients C_1 and C_2 and consequently the fractional free volume f_{T_0} as well as the thermal expansion coefficient α_f . However, to compare these parameters, a common reference temperature, arbitrarily chosen, is required. Because of the strong influence of the plasticizer on the viscoelastic and dielectric properties of polymers, no common reference temperature could be directly taken for the analysis of these data. It was necessary to use for this purpose the following equations:

$$C'_1 = \frac{C_1 C_2}{(C_2 + T'_0 - T_0)},$$

$$C'_2 = C_2 + T'_0 - T_0, \quad (10)$$

where T'_0 is the new reference temperature and C'_1 and C'_2 are now the WLF coefficients at T'_0 . Here, a reference temperature of 120 °C is taken in order to evaluate these two coefficients for all the samples, listed in Table I. At a constant temperature, C_2 increases whereas C_1 decreases when increasing the amount of plasticizer. This is consistent with results obtained in polymer rheology.²⁹ When increasing the concentration of diluents, the temperature dependence, as referred at T_0 , of the mechanical response times, and as demonstrated here for the dielectric response times, becomes less pronounced as T_g lowers more and more below T_0 . The calculations of fractional free volumes and thermal expansion coefficients at 120 °C were carried out for all the samples. As expected, the fractional free volume f increases with the adding of plasticizer. The WLF coefficients of these doped polymers were also calculated with a reference temperature chosen equal to T_g . In this case, they are found not to change with the plasticizer concentration, which proves that the plasticizer modifies the temperature dependence of the orientational dynamics of the chromophores, mainly through its effects on T_g .

We characterized the temperature dependence of the dielectric response times for different amounts of plasticizer by

TABLE I. T_g values for polyvinylcarbazole doped with 20 wt % of CHAL9 and plasticized with N_{ECZ} (wt %) of ECZ. The WLF coefficients are determined at the reference temperatures $T_0=120^\circ\text{C}$ and $T_0=T_g$. The fractional free volumes and the thermal expansion coefficients are calculated at 120°C .

N_{ECZ} (wt %)	T_g ($^\circ\text{C}$)	C_1^{120} ($^\circ\text{C}$)	C_2^{120} ($^\circ\text{C}$)	f	α_r ($^\circ\text{C}^{-1}$)	C_1^g ($^\circ\text{C}$)	C_2^g ($^\circ\text{C}$)
0	112	10.4	74	0.042	5.7×10^{-4}	11.7	66
10	46	5.3	137	0.082	6×10^{-4}	11.5	63
20	27	4.8	160	0.09	5.6×10^{-4}	11.5	67
30	7	4.2	181	0.103	5.7×10^{-4}	11.2	68
35	-1	4	187	0.109	5.8×10^{-4}	11.3	66
40	-7	3.8	189	0.114	6×10^{-4}	11.6	62

using the WLF equation. Such procedure enables the analysis of the plasticizer concentration effects, at a reference temperature T_0 , on the fractional free volume and on the thermal expansion coefficient without having to directly compare the values of response times at different concentrations. These response times can be also directly compared by introducing a shift factor a_c . The incorporation of plasticizer displaces the time scale by several orders of magnitude due to the decrease of T_g . Similarly to the WLF equation, a translation factor can be defined as

$$\frac{[\tau_{\text{diel}}]_c}{[\tau_{\text{diel}}]_p} = a_c, \quad (11)$$

where $[\tau_{\text{diel}}]_p$ and $[\tau_{\text{diel}}]_c$ are the dielectric response times at a given temperature, respectively, for pure polymer and for polymer doped with chromophores at a concentration c . We consider here that the PVK doped with 20 wt % of CHAL9 corresponds to the reference. Figure 5 shows $\varepsilon'(\omega)$ at 70°C for doped PVK plasticized with different amounts of ECZ. A superposition of these curves can be approximately obtained after normalization by a translation along the frequency axis leading to the determination of the shift factor. A master curve is constructed at a plasticizer concentration arbitrarily equal to 40 wt %. However, because of the spectacular changes of time scale induced by the plasticizer, the dielectric response times can not be directly determined at a given temperature for all the considered concentrations of ECZ. An extrapolation of response times, using the WLF equation, is required. Figure 6 shows the evolution of the shift factor a_c

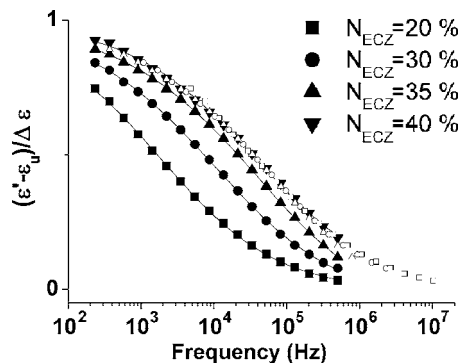


FIG. 5. Normalized $\varepsilon''(\omega)$ at 70°C in PVK doped with 20 wt % of CHAL9 and plasticized with different concentrations N_{ECZ} (wt %) of ECZ. Curves are fitted by the HN equation. A superposition of the curves is obtained by a simple translation along the frequency axis. A master curve (open symbols) is constructed at a reference concentration $N_{\text{ECZ}}=40$ wt % of ECZ.

at several temperatures. By considering that the fractional free volume is a linear function of the weight fraction of plasticizer v_1 , Fujita and Kishimoto have established an empirical law describing the evolution of a_c at a given temperature as follows:^{32,33}

$$\ln a_c = -\frac{1}{f_2 + f_2^2/v_1 f_1}, \quad (12)$$

where f_2 and f_1 are, respectively, the fractional free volume of the pure polymer and of the plasticizer. As seen in Fig. 6, a very good fit of the concentration dependence of the dielectric response times is obtained by using Eq. (12). At $T=120^\circ\text{C}$, the values of the polymer fractional free volume, deduced by using the two methods, are in very good agreement. The temperature dependence of the doped polymer fractional free volume f_2 is linear, as predicted by the theory (Fig. 7). The fractional free volume f_1 of ECZ is equal to 0.14, which is a reasonable value for low molecular weight molecules. To establish a comparison, a value of 0.13 was found in polyisobutylene-*n*-hexadecane system.²⁹ As shown in Fig. 6, the more temperature of the doped polymer without plasticizer is near T_g , the more the incorporation of low molecular weight molecules induces large variations in orientational response times. Furthermore, it can be seen that the plasticizing effectiveness quickly increases as the temperature is lowered and as T_g is approached. These results show that the most important parameter of the plasticizer on this effect is its own free volume.

Ellipsometric measurements were performed in PVK doped with 20 wt % of CHAL9 and plasticized with 20, 30, and 40 wt % of ECZ at different temperatures above T_g . Fig-

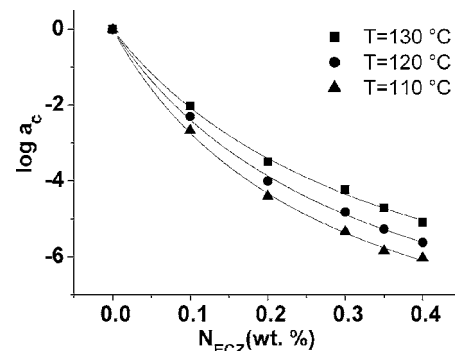


FIG. 6. Influence of the plasticizer concentration on the shift factor a_c and the dielectric response times at different temperatures. Curves are fitted by Eq. (12).

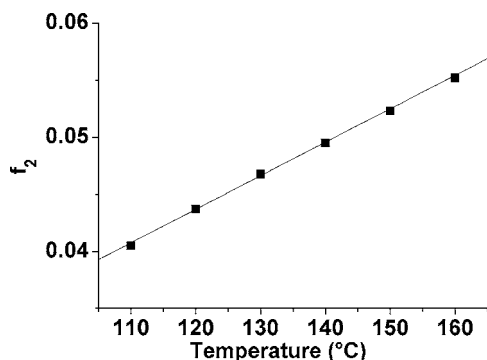


FIG. 7. Fractional free volume f_2 deduced from the plasticizer concentration dependence of dielectric response times as a function of the temperature. This dependence is linear.

ure 8 shows that the temporal EO rises in PVK:ECZ:CHAL9 (40:40:20 wt %). They are normalized by taking into account the values of the induced variation of intensity reached at the steady state. For reasons of clearness, these responses are plotted only during a period of 1 s. For the lowest temperatures, they reach their steady state at a longer time. The orientational response times are evaluated from the EO rise curves by using the KWW equation. The stretching parameter β_{KWW} yields a value between 0.7 and 0.75. The response times for the EO decays and rises follow the WLF equation. The coefficients C_1 and C_2 deduced from these measurements are found to be similar to those measured by dielectric spectroscopy. This result confirms that the EO and dielectric responses exhibit the same behavior and are ruled by the viscoelastic properties of polymers. Besides, although the empirical approach proposed here does not provide information on the molecular mechanisms, the experimental results modeled by rheological laws precisely establish the effects of the plasticizer incorporation on the orientational dynamics of chromophores. A similar analysis devoted to the effects of the average molecular weight on these orientational processes must now be carried out.

C. Effects of the average molecular weight

The minimum molecular weight M_c of pure polystyrene for coupling entanglement formation is known to be 38 000. The mechanical properties of polymers strongly differ above

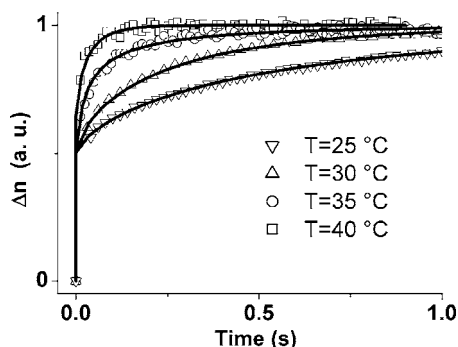


FIG. 8. Normalized EO onset curves obtained in PVK:ECZ:CHAL9 (40:40:20 wt %) at several temperatures. A dc voltage, with a magnitude of 2 kV, was applied across the samples at $t=0$. The data are fitted by the Kohlrausch-Williams-Watts equation.

and below this molecular weight. Both the elastic and viscous properties are modified by entanglements, which appear for high molecular weight polymers ($M > M_c$). They can be inferred from the existence of a rubbery plateau in the compliance $J'(\omega)$ curves. In this region, the molecules return to their average configuration due to the presence of entanglements. Below M_c , the viscoelastic properties of linear polymers are described at a microscopic scale by the Rouse model.³⁴ In this molecular weight range, the zero shear viscosity η_0 is proportional to $\xi_0 M$, where ξ_0 corresponds to the monomeric friction coefficient. Above M_c , modifications of the Rouse approach are required and other approaches, such as the reptation model,³⁵ have been developed, taking into account the role of the entanglement networks. It has been shown that for polymers with $M > M_c$, η_0 increases approximately with a 3.5 power law of the molecular weight. In this region, the friction coefficient ξ_0 has reached a constant limiting value ξ_{00} due to the presence of these entanglements. Fox and Flory have determined empirically the evolution of ξ_0 as a function of the molecular weight at a given temperature:³⁶

$$\log \xi_0 = \log \xi_{00} + (B/2.303)(1/f_M - 1/f_0),$$

$$f_M = f_0 + A/M, \quad (13)$$

where f_M is the fractional free volume at a molecular weight M , f_0 is the fractional free volume at high molecular weight, B is a constant generally taken as equal to unity, and A is a constant associated to the additional molecular free volume accompanying molecular ends. This dependence is assigned to the number of molecular ends per unit volume, which depends on $1/M$ and becomes consequently negligible for high molecular weight. Since the diffusion coefficient of small molecules in polymers is inversely proportional to the friction coefficient as shown by the Bueche theory,³⁷ the orientational response times of chromophores should fundamentally follow the law proposed by Fox and Flory [Eq. (13)].

To establish the effects of M on the orientational dynamics of chromophores, dielectric spectroscopy measurements were performed on different polystyrenes doped with 20 wt % of CHAL9. Figure 9 shows the master curve constructed from the superposition of $\varepsilon''(\omega)$ measured at several temperatures in a polystyrene with an average molecular weight $M_w=44$ 000. Similarly to the dielectric response obtained with the PVK:ECZ:CHAL9 systems, the curves follow the time-temperature superposition principle. The evolution of the dielectric response times as a function of the temperature determined by using the HN equation follows the WLF equation, as shown in Fig. 10. The WLF coefficients determined at a reference temperature arbitrarily taken equal to 150 °C are listed in Table II. The fractional free volume and the thermal expansion coefficient are then calculated as a function of the average molecular weight. An increase of free volume is obtained at a given temperature when M decreases. This shows that the chromophore mobility is higher for the lowest molecular weight of polymers. Using Eq. (10), C_1 and C_2 were also calculated for a reference temperature equal to T_g . Their values are very close to

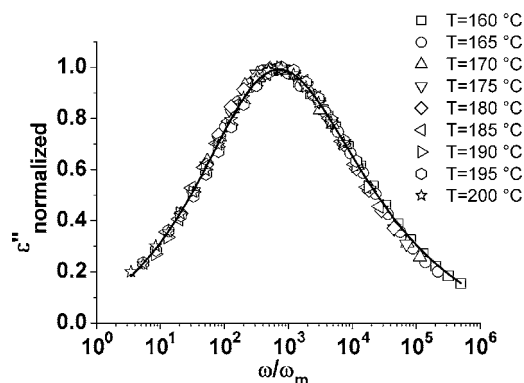


FIG. 9. Master curve (solid symbols) created at a reference temperature of 160 °C in polystyrene ($M_w=44\,000$) matrix doped with 20 wt % of CHAL9 from the superposition of the normalized $\varepsilon''(\omega)$ measured at several temperatures. Line corresponds to the fit obtained by using the Havriliak-Negami equation. The frequency ω_m is associated to the maximum value of each isothermal dielectric loss peaks.

those reported by Ferry for pure polystyrene ($C_1^g=14$ and $C_2^g=50$).¹³ The little variations of these coefficients at $T_0=T_g$ show that the average molecular weight, similarly to the plasticizer concentration, modifies the temperature dependence of the orientational dynamics of the chromophores, mainly through its effects on T_g . Figure 10 illustrates how the role of the temperature and of the molecular weight are important on these orientational processes. A difference of one order of magnitude in response times is almost obtained for a temperature change of 20 °C above T_g and, at a given temperature, a variation of three orders of magnitude is observed between the polystyrenes with $M=891\,000$ and $M=3680$. The fit of the temperature dependence of the orientational response times above T_g by a WLF law confirms once again the coupling between the rotational dynamics of chromophores and the polymer chain dynamics.

SHG onset dynamics measurements were carried out on the different M polystyrenes doped with 5 wt % of EHOMONS for temperatures below T_g . To erase the thermal history and to prevent the anelastic memory effects of the polymer host, the samples were heated above T_g between each measurement. The temperature dependence of the SHG onset response times obtained from these doped polymers by using KWW equation is shown in Fig. 11. The stretching parameter β_{KWW} does not change significantly with the tem-

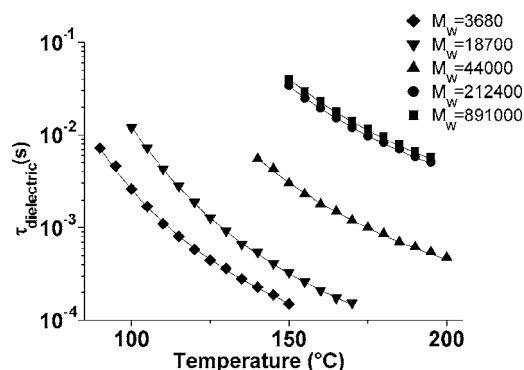


FIG. 10. Temperature dependence of the dielectric response times in polystyrenes with different average molecular weights. The data are fitted by a Williams-Landel-Ferry equation.

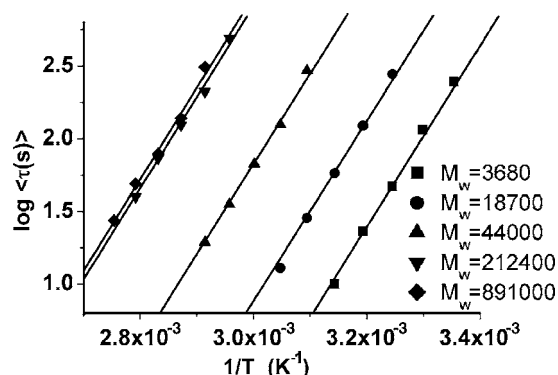


FIG. 11. Temperature dependence of the SHG onset response times in polystyrene:EHOMONS (80:20 wt %). The data are fitted by an Arrhenius equation leading to the determination of the activation energy as a function of M .

perature and with the samples and typically yields a value between 0.6 and 0.65. The temperature dependence of the response times $\langle\tau\rangle$ below T_g is described by an Arrhenius law:

$$\langle\tau(T)\rangle = \langle\tau(T_0)\rangle e^{(\Delta H/R)(1/T - 1/T_0)}, \quad (14)$$

where ΔH is interpreted as an activation energy specific to the polymer and characterizes the energy necessary for a chain segment to move. This behavior is associated to local segmental motions of the polymer chains in the glassy state, without any cooperation between segments. This activation energy is found to be independent of the average macromolecular weight and is equal to 30.5 kcal/mol. This result demonstrates that, below T_g , the average molecular weight of the polymer host affects also these orientational processes of chromophores through its effect on T_g .

For the evidence of the influence of the average molecular weight on the orientational processes of chromophores, response times obtained from dielectric spectroscopy [in polystyrene:CHAL9 (80:20 wt %)], ellipsometry [in polystyrene:EHOMONS (80:20 wt %)], and SHG [in polystyrene:EHOMONS (95:5 wt %)] measurements are plotted against M_w (Fig. 12). The results illustrate the importance of this parameter, since they reveal differences of several orders of magnitude between the dynamics of these different doped

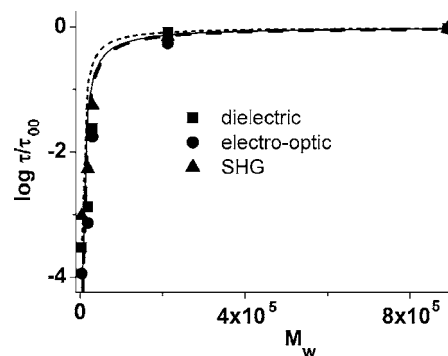


FIG. 12. Molecular weight dependence of the orientational response times. The data are fitted by using Eq. (13): (line) dielectric spectroscopy in polystyrene:CHAL9 (80:20 wt %) at 150 °C, (dash line) ellipsometric measurements in polystyrene:EHOMONS (80:20 wt %) at 30 °C and (short dash line) SHG measurements in polystyrene:EHOMONS (95:5 wt %) at 35 °C.

TABLE II. Physical parameters deduced from dielectric spectroscopy measurements on polystyrenes doped with 20 wt % of CHAL9 at a reference temperature T_0 of 150 °C. The values of the Williams-Landel-Ferry coefficients C_1^g and C_2^g , with the reference temperature equal to T_g , are calculated using Eq. (10).

M_w	T_g (°C)	C_1^{150} (°C)	C_2^{150} (°C)	f_0	α_f (°C ⁻¹)	C_1^g (°C)	C_2^g (°C)
3 680	65	4.75	134	0.09	6.8×10^{-4}	13	49
18 700	74	5.7	128	0.076	6×10^{-4}	14	52
44 000	87	6.3	115	0.069	6×10^{-4}	14	52
212 400	93	6.5	107	0.066	6.2×10^{-4}	14	50
891 000	94	6.5	107	0.066	6.2×10^{-4}	14	51

polystyrenes. The orientational response times tend at high M to an asymptotic limiting value τ_{00} , and they strongly decrease with M below a critical molecular weight, corresponding to the minimum value for entanglement coupling. This is in good agreement with the theoretical behavior of the local friction coefficient and shows the role of the entanglement network on the orientational processes of chromophores. The curves fitted using Eq. (13) lead to the determination of the constant A and to the fractional free volume f_0 . Their values are listed in Table III and exhibit a consistent order of magnitude as compared to results previously reported. Below and near T_g , the fractional free volume typically yields a value close to 0.03 in polystyrene systems, whereas it linearly increases with temperature above T_g . The fractional free volume, estimated from the temperature dependence of the dielectric response times, is in very good agreement with that obtained from the molecular weight dependence. Concerning the constant A , Pierson and Kovacs have analyzed the temperature dependence of viscosity for pure polystyrenes of sharp molecular weight distribution and for a wide range of molecular weights. They have found that this constant was equal to 54 g/mol,²⁹ which is lower than the data listed in Table III. When the average molecular weight of polymer is sufficiently high to observe entanglements, the average effective spacing between two coupling points is increased by the introduction of low molecular weight molecules. Consequently, the incorporation of chromophores in the polymer matrix induces a slight increase of its critical entanglement weight and of the constant A .

These results have pointed out the influence of the average molecular weight of the polymer host on the orientational dynamics of chromophores in a large range of temperature. They show that the incorporation of plasticizer or a decrease of the molecular weight of the host is roughly equivalent to control the T_g of NLO guest-host polymers and can be both used to optimize this orientational kinetics. It has

been previously demonstrated that the photoconductive and the photorefractive performances of PVK based materials are greatly improved by plastification.^{38,39} Because the photoconductivity in PVK is enhanced as well with a decrease of the molecular weight,⁴⁰ these results suggest that varying the molecular weight of the polymer host could be an interesting alternative for the optimization of efficient photorefractive polymers. This approach would present the advantage to suppress one of the components in the plasticized guest-host materials, reducing the problems associated with phase segregation and improving the stability of the photorefractive sample toward the electric field.

V. CONCLUSION

The orientational dynamics of push-pull chromophores in PVK plasticized with different amounts of ECZ and in polystyrene with various molecular weights have been investigated in details by dielectric spectroscopy, ellipsometric, and SHG dynamics measurements. The temperature dependencies of the electro-optic and dielectric responses in these guest-host materials follow the time-temperature superposition principle and are well described by the William-Landel-Ferry equation. Our results confirm that the orientational processes of doping chromophores in NLO guest-host polymers are dominated by the viscoelastic properties of the polymer host and are strongly coupled to the polymer chain relaxations. In addition, the effects of the average molecular weight and the concentration of plasticizer on the orientational processes of chromophores are pointed out and are fully interpreted by empirical laws generally employed in polymer rheology and based on the free volume theory. This study provides evidence that both these parameters affect the orientational kinetics mainly through their effects on T_g . Finally, our results suggest an approach for the optimization of photorefractive guest-host polymers based on the control of the average molecular weight of the polymer host. Such an alternative approach might offer the possibility to reduce phase segregation and to improve the stability of the devices based on these materials.

TABLE III. Values of the limiting high M orientational response times τ_{00} , the fractional free volume f_0 at high M , and the constant A deduced from dielectric spectroscopy [in polystyrene: CHAL9 (80:20 wt %)], ellipsometry [in polystyrene:EHOMONS (80:20 wt %)], and SHG [in polystyrene:EHOMONS (95:5 wt %)] measurements at the reference temperature T_{ref} .

	T_{ref} (°C)	τ_{00} (s)	f_0	A (g/mol)
SHG	35	49 170	0.027	62
EO	40	840	0.031	72
Dielectric	150	0.325	0.065	73

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