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Critical Temperatures in the Photorefractive Polymer Composite Behavior

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ABSTRACT Two critical temperatures, T_1 and T_2, which limit the range of the photorefractive (PR) response of polymer composites, have been determined from temperature dependence studies of the ac conductivity. T_1 represents the calorimetric glass transition temperature and sets the level under which chromophore orientation is drastically reduced. T_2 sets the level above which conduction mechanisms become dominated by temperature. In this study, we stress the importance of the T_2 parameter, generally ignored in literature, and the advantages of using dielectric spectroscopy to obtain both critical temperatures from a single experiment. In addition, impurity diffusion processes, which play an important role in PR property optimization, have been identified from the frequency dependence of the ac conductivity.

SECTION Electron Transport, Optical and Electronic Devices, Hard Matter
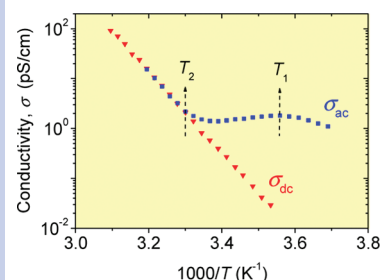
In the last years, there has been extensive research devoted to the investigation of photorefractive (PR) materials, mainly motivated by their potential applications in optical processing, phase conjugation, optical storage, and so forth.[1] One of the most widely investigated PR organic materials are polymer composites based on a photoconducting polymer, such as poly-*N*(vinylcarbazole) (PVK), doped with a nonlinear optical (NLO) chromophore and a sensitizer that provide the properties needed for photorefractivity.[1] In addition, after the discovery of the orientational enhancement effect in low glass transition temperature (T_g) systems, a plasticizer is often included to lower the T_g of the composite and, consequently, to facilitate chromophore reorientation at room temperature. Studies focusing on the temperature dependence of the various parameters involved in the PR performance of several types of composites have been published in the literature.[2–4] However, no general conclusions have been achieved yet in relation to determining the optimal T_g of the composite for a certain measurement temperature. This is mainly due to the following reasons: (i) In most cases, no complete information has been provided. For example, on some occasions, the conductivity has not been taken into account in the PR optimization.[2] In others, although all of the parameters have been considered, only data above T_g have been reported.[4] (ii) In these studies, the temperature at which changes in the behavior of the various PR parameters were observed was always coincident with the composite T_g; therefore, this has been the only relevant temperature considered in the optimization. In contrast, we have recently reported changes in the photoconductivity at a temperature called T_g(ph).[5] Although in some cases this parameter might coincide with the composite T_g, this is not generally the case. For example, for composites based on PVK doped with the NLO chromophore 4-piperidindicyanostirene (PDCST), the plasticizer butylbenzilephatlate (BBP), and the sensitizer C_{60}, T_g(ph) was around 26 °C higher than T_g.[5] Since the modulation of the internal space charge field in PR experiments depends on photoconductivity through the conductivity contrast,[6] it is obvious that this T_g(ph) parameter should be taken into account in order to optimize the PR response and not only the T_g, as is generally accepted in the literature. (iii) Finally, another important issue that has created some inconsistencies is the fact that T_g's of PR polymer composites are generally measured by differential scanning calorimetry (DSC), despite the difficulties that arise when used with composites.[5] For example, PVK/PDCST/BBP/C_{60} composites show two broad transitions in their DSC curves, and their definition depends on the amount of plasticizer. Apparently, in most cases, the T_g values reported correspond to the high-temperature transition, often close to room temperature.[7] However, there have been reports of the PR effect with very low T_g's (below 0 °C), surprisingly with good conductivity contrast.[3,8] That might be due to the assignment of T_g to the low-temperature transition observed in the DSC curve.

Within this context, the main objective of this work is to demonstrate the importance of the T_g(ph) parameter in the

optimization of the PR properties and the fact that its value does not generally coincide with the calorimetric T_g. In addition, we aim to provide a complete interpretation of the various transitions observed on the temperature dependence of the conductivity and to establish its relation with the transitions observed by DSC. For such purposes, we have employed dielectric spectroscopy (DS) to investigate the temperature and frequency dependence of dark conductivity. The main advantage of this technique with respect to DSC is that experiments are performed directly on the PR samples. The DS technique is also preferable to our recently reported method based on the temperature dependence of the photo-conductivity[5] because no light is needed. Note that in our previous analysis of the conduction mechanisms under a dc field, changes in the activation energy were observed only in the photoconductivity but not in the dark conductivity. Other advantages of using DS include its high sensitivity for low-energy transitions as well as its capability to provide information about chromophore orientation and conduction mechanisms simultaneously.[9] DS has been used recently to study the orientational dynamics of chromophores in guest—host polymers.[10] As far as we know, this technique has not been previously used with PR polymer composites. By carrying out temperature dependence studies of the conductivity at low frequency, we aim to identify the temperatures at which changes in the composite behavior take place and that consequently play an important role in the PR performance. Concerning frequency dependence, we intend to identify ionic impurity diffusion processes by performing the experiments at high temperature. This is particularly relevant, as recently suggested, in order to improve the PR properties of polymer composites by carrying out electric-field treatments prior to the PR characterization.[11]

PR samples consisted of 10 μm thick films of polymer composite of the type PVK (49.5 wt %)/PDCST (35 wt %)/BBP (15 wt %)/C_{60} (0.5 wt %), sandwiched between two indium tin oxide electrodes. For this composite, the T_g measured by DSC was 12 °C, and the T_g(ph), measured from photoconductivity data, was 38 °C.[5] The real part of the conductivity, usually called ac conductivity (σ_{ac}), was determined by measuring the complex impedance of the samples under a sinusoidal voltage of amplitude 10 V, as a function of frequency and at different temperatures. We did not observed dielectric breakdown up to 80 °C, and samples could be reused. However, to erase the thermal history and to prevent memory effects, these samples were maintained at 120 °C for a few seconds between each experiment. Measurements were also performed under a 50 Hz signal of amplitude 200 V, that is, an electric field of 20 V/μm (typical conditions for conductivity measurements in PR composites). Since results were similar to those obtained at 10 V, all data displayed below correspond to this lower voltage.

Figure 1 shows the frequency dependence of σ_{ac} plotted on a double-logarithmic scale at various temperatures. At room temperature (25 °C), three different regimes can be distinguished. For frequencies below 0.5 Hz (regime I), σ_{ac} tends to a constant value (1.0 pS/cm) which coincides with that measured under a dc voltage. Then, for over 6 decades of frequencies (regime II), σ_{ac} varies strongly and almost linearly.
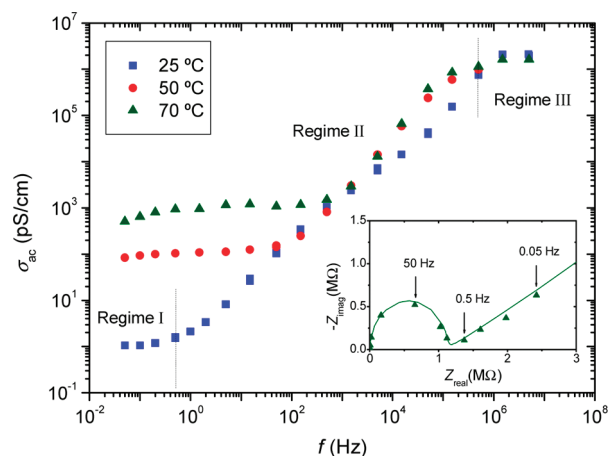
Figure 1. Frequency dependence of ac conductivity (σ_{ac}) for a PVK/PDCST/BBP/C_{60} (49.5:35:15:0.5 wt %) composite at various temperatures. I, II, and III are regimes corresponding to the 25 °C temperature curve (see text). Inset: Nyquist plot of complex impedance for the data obtained at 70 °C, where the continuous line is the fit to data using an electrical circuit made of a capacitance in parallel with a resistance and a constant phase element.

This combined behavior follows the so-called Jonscher power law, $\sigma_{ac} = \sigma_{dc} + A\omega^s$, with $s = 0.87$. This law is generally accepted to be universal for disorder solids, such as conducting polymers, where the hopping transport mechanism dominates.[12,13] At very high frequencies (regime III), σ_{ac} becomes constant again. Although this saturation region in which $s \ll 1$ is not commonly mentioned, it has been observed in some conducting polymers[14] and recently explained by theoretical models.[15]

Experiments at high temperatures show an additional fourth regime at very low frequencies, consisting of a decrease of σ_{ac} with respect to the dc value, when the frequency diminishes. The three regimes described at room temperature are also observed, although the frequency at which σ_{ac} reaches the dc value extends to higher frequencies. This decrease of σ_{ac} in the dc region has been observed at room temperature in aqueous polymeric solutions[16] and at higher temperatures in other materials such as single crystals[17] and metal—insulator—metal capacitors.[18] In the literature, this effect is generally attributed to accumulation of ionic charges at electrode boundaries. Thus, our results support the hypothesis of ionic conduction reported in our previous work with PVK-based composites. These ionic conduction processes are of great relevance to understand and control the enhancement of the PR properties by performing electric field treatments prior to the PR characterization.[11] This regime has not been observed in the experiments at room temperature probably because its detection requires frequencies below 0.01 Hz. We also found that the exponent s at high temperatures is near 2. Although it is generally believed that s is a parameter less than 1, power exponents larger than 1 have been observed,[17] and recently, they are considered to be physically acceptable.[15] The frequency below which the fourth regime appears (0.2 and 1 Hz at 50 and 70 °C, respectively) can be more precisely assigned from the corresponding Nyquist plots, that is, the representation of imaginary
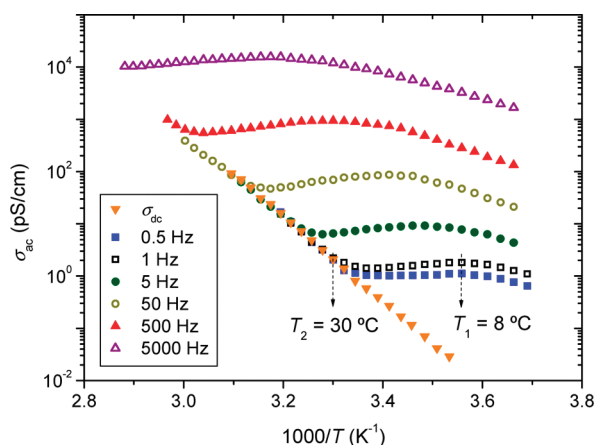
Figure 2. Temperature dependence of ac conductivity (σ_{ac}) for a PVK/PDCST/BBP/C$_{60}$ (49.5:35:15:0.5 wt %) composite at various frequencies. Temperatures T_1 and T_2 correspond to the 1 Hz frequency curve (see text).

Figure 3. Conductivity contrast (M) at 20 V/μm as a function of temperature for PVK/PDCST/BBP/C$_{60}$. Temperature T_2 is indicated.

versus real impedance, as illustrated for 70 °C in the inset of Figure 1. The Nyquist plot gives information about the volume resistance, R, of the composite and the capacitance, C, of the parallel condenser that orients the NLOs. The constant phase element is necessary to model the diffusion effects related to the straight line observed at very low frequencies. The vertex of the semicircle corresponds to the frequency that satisfies the relation $\omega CR = 1$.

Figure 2 shows the temperature dependence of σ_{ac} plotted in an Arrhenius representation at various frequencies. Results obtained under a dc field (σ_{dc}) are also included. Above 0.5 Hz three different behaviors can be distinguished corresponding to low, high, and intermediate temperatures. These regimes are delimited by the experimentally determined temperatures T_1 and T_2. T_1 is obtained from the maximum of the σ_{ac} curve, and T_2 is the temperature at which σ_{ac} reaches the σ_{dc} value. In the low-temperature regime ($T < T_1$), the conductivity depends strongly on frequency, its temperature dependence is weak, and the activation energy is about 0.5 eV. In the high-temperature regime ($T > T_2$), the conduction mechanism, with a larger activation energy (1.6 eV), is dominated by temperature and is not frequency-dependent. In the intermediate regime ($T_1 < T < T_2$), the activation energy is slightly negative, that is, the conductivity decreases with temperature. This anomalous behavior might be due to the increase in the movement of the carbazole units above T_g, which would disturb the charge transport through PVK, thus decreasing σ_{ac}. According to this hypothesis, the temperature T_1 would be the T_g. Its value decreases with frequency and tends to the value obtained by DSC for low frequencies. When T_g is measured by dielectric spectroscopy, the value is usually obtained from the response of an increase in the permittivity signal or a peak in the loss factor under a field of frequency 1 Hz as the onset.[19] We have checked that the analysis using those magnitudes leads to the same value as that obtained from the maximum of the σ_{ac} curve. With these criteria, the value of T_1 is 8 °C (see Figure 2), which is near the T_g obtained by DSC (12 °C). In the intermediate regime, the activation energy below 1 Hz increases, and the maximum disappears.
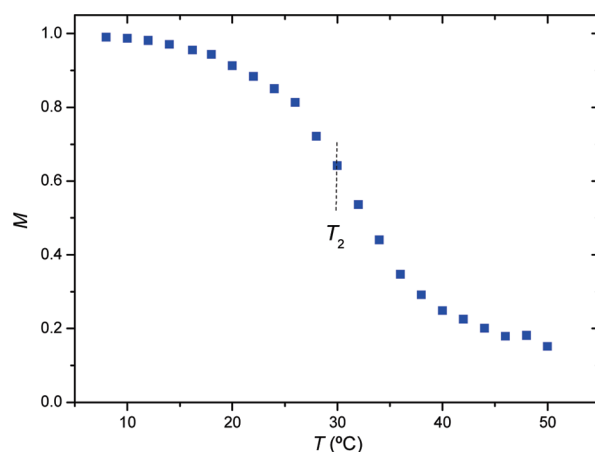
In the limit, the response would be the straight line corresponding to σ_{dc}. Similar results were obtained with composites containing different amounts of plasticizer, varying between 0 and 15 wt %. In all cases, the temperature T_1, obtained from the maximum of the σ_{ac} curve at 1 Hz, was similar (differences less than 5 °C) to that obtained by DSC. Hence, it is concluded that T_1(1 Hz) $\approx T_g$. Concerning T_2, it constitutes the level above which conduction mechanisms become dominated by temperature. The T_2 value for the standard composite (containing 15 wt % of BBP), obtained from the 1 Hz curve, is around 30 °C (see Figure 2), that is, 22 °C above T_1. Additional experiments showed that the change in the plasticizer, with the concentration ranging between 0 and 15 wt %, affects T_2 in a similar way as it does to T_1. The difference between T_2 and T_1 is approximately constant (24 °C), independent of the amount of plasticizer. Given that the T_g(ph) parameter (approximately 26 °C above T_g) determined in a previous work[5] represents the temperature at which photoconductivity becomes dominated by temperature, its correlation with T_2 is evident. Thus, it can be concluded that T_2(1 Hz) $\approx T_g$(ph). Since the difference is independent of the amount of plasticizer, these results indicate that, even though T_2 and, consequently, T_g(ph) are different than the calorimetric T_g, there is a close relationship between them.

The relevance of considering the critical temperature T_2 to optimize the PR performance of polymer composites is illustrated in Figure 3, where the conductivity contrast M is represented as a function of temperature. Here, M is defined as the ratio between the photoconductivity (σ_{ph}) and the conductivity in the presence of light (σ_{light}), with $\sigma_{ph} = \sigma_{light} - \sigma_{dc}$ and σ_{dc} as the dc dark conductivity. Results show that T_2 (generally different than T_g) sets the temperature above which M and hence the PR effect become drastically reduced. Therefore, in order to optimize M, the parameter to be considered is T_2 and not T_g, as generally believed. On the other hand, T_g is the temperature that plays an important role in optimizing the birefringence[2−4] since below its value, chromophore orientation and therefore the PR speed become drastically

reduced. In this respect, we did not find changes in the behavior at temperatures close to T_2. It should be noted that M is particularly important when working at low fields.[11] That is probably one of the reasons why, in many studies, this parameter has not been considered.

In conclusion, we have reported a useful method based on the temperature dependence of the ac conductivity to determine, from a single experiment, two temperatures, T_1 and T_2, that limit the range of the photorefractive (PR) response of polymer composites. T_1 represents the calorimetric T_g. T_2, which coincides with the previously reported T_g(ph) and generally differs from T_g, sets the level above which conduction mechanisms become dominated by temperature. Beyond this temperature, the conductivity contrast and, consequently, the PR effect are drastically reduced. In addition, ionic impurity diffusion processes, which play an important role in PR property optimization, have been clearly identified from the frequency dependence of the ac conductivity at high temperatures.

PR samples were prepared as previously described.[20] PVK (secondary standard), BBP, and C_{60} were supplied by Aldrich and used as received. PDCST was synthesized according to the literature.[21] Complex impedance measurements were carried out by using an oscillator (Hameg HM8030) that supplies a sinusoidal voltage of amplitude 10 V in a frequency range between 0.05 Hz and 5 MHz and a digital oscilloscope (Tektronix TDS3012) to measure current and phase shift. For the experiments at high fields, a signal of amplitude 200 V at 50 Hz, provided by a variable transformer connected to the main line of the laboratory, was used. Samples were placed in a temperature-controlled (between −5 and 80 °C) system. In the experiments in which conductivity was studied as a function of temperature, data were acquired every 2 °C while the temperature varied at a rate of 0.5 °C/min. From the experimentally measured complex impedance, σ_{ac} was calculated from $\sigma_{ac} = Gd/S$, where G is the conductance, d is the thickness of the sample ($\sim$10 μm), and S is the area of each electrode ($\sim$1.0 cm^2). The error in the σ_{ac} values was about 10%, which arises mainly from the difficulty of measuring accurately the effective surface (common area of both electrodes) and the film thickness. Photoconductivity measurements were performed by a simple dc technique at a field of 20 V/μm. The current through the sample was measured with a Keithley 600B electrometer in the dark and under illumination at the 633 nm light provided by a 35 mW Melles Griot He−Ne laser with an intensity of 50 mW/cm^2.

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