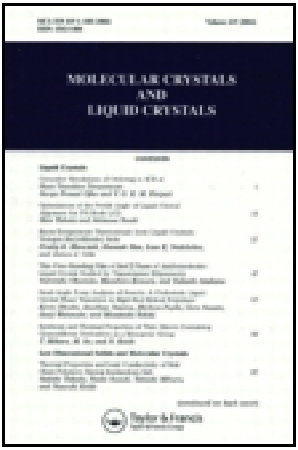

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A new method for the characterization of the kinetics of rotational mobility of chromophores embedded in a polymer matrix is proposed. The method is applied and checked with two different systems consisting of a solid solution of Disperse Red 1 chromophore (DR1) either in PMMA or in bisphenol A thermally reticulating resine.

Keywords: electro-optic Kerr effect; nonlinear optics; polymer blends

INTRODUCTION

At present the blend materials containing optically active molecules (referred also as dyes or chromophores), confined in an optically inert polymer matrix are often exploited in different fields of both basic and applied research [1]. Thermal kinetics and temporal stability are very often the key features concerning such materials and their practical applications. Standard investigation tools like differential scanning calorimetry (DSC) [2] or dielectric spectroscopy [3], give information only on the average properties of bulk material consisting of the inert matrix and the active doping chromophores. Since typical doping chromophore content is rarely bigger then a few weight percent, it hardly modifies the signal originating from the matrix.

The quadratic electro-optic Kerr effect owes its origin to the occurence of optical birefringence induced by an applied external electric

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field. The field direction defines the principal axis of the induced birefringence. If a probing beam of light, initially polarized at 45° azimuth to the electric field direction, is passed through the sample, its polarisation changes to an elliptical one. It means that the light intensity recorded at the exit should be different with and without the applied electric field. In the case of plane parallel electrodes, an initially isotropic medium and the probing beam propagation direction perpendicular to the applied field, the induced optical birefringence is given by

$$\Delta n = n_{\parallel} - n_{\perp} = \lambda B E^2 \tag{1}$$

where B is the Kerr constant, $n_{\parallel}$, $n_{\perp}$ are, respectively, the refractive indices parallel and perpendicular to the applied electric field E and λ is the wavelength of incident light. It can be shown, that the Kerr constant B is proportional to $\chi^{(3)}_{3333}(-\omega;\omega,0,0)$ NLO susceptibility tensor component [4,5] in the case of initially homogenous systems. Due to this fact that the NLO push-pull type components, as it is case for DR1, are strongly anisotropic with a large dipole moment, they contribute at first to the induced birefringence. In this way its magnitude is a fingerprint of thermal kinetics of NLO components in the studied system. Also the NLO components are much more mobile than the polymer chains, which contributes to the Kerr signal principally at low frequency due to their limited mobility.

The values of Kerr constant for common materials are relatively small. Thus it is necessary to apply a very strong static electric field to the sample in order to induce measurable changes of probing light intensity due to the induced birefringence.

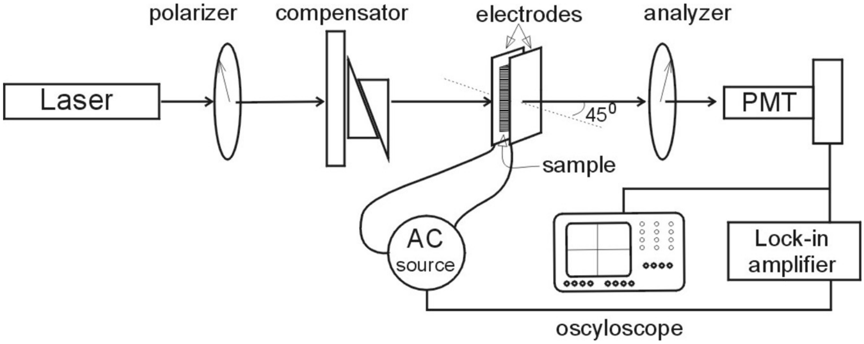

FIGURE 1 Experimental setup for electro-optic Kerr effect measurements.

Far more convenient measurements can be performed by applying, instead of static, an alternating field with frequency f. In that case, and for a centrosymmetric medium, the probing light intensity is modulated at double frequency 2f [6]. This modulated component can be easily separated by lock-in detection and recorded.

EXPERIMENTAL

A schematic representation of the experimental setup used to measure the electrically induced light intensity modulation, is shown in Figure 1. It consists of a cw laser as the source of monochromatic collimated light, polarizer, Soleil-Babinet compensator, thermo-stated sample holder, analyzer, photomultiplier (PMT), alternating voltage source, lock-in amplifier and oscilloscope. The sample is placed between two ITO coated glasses (semi transparent electrodes).

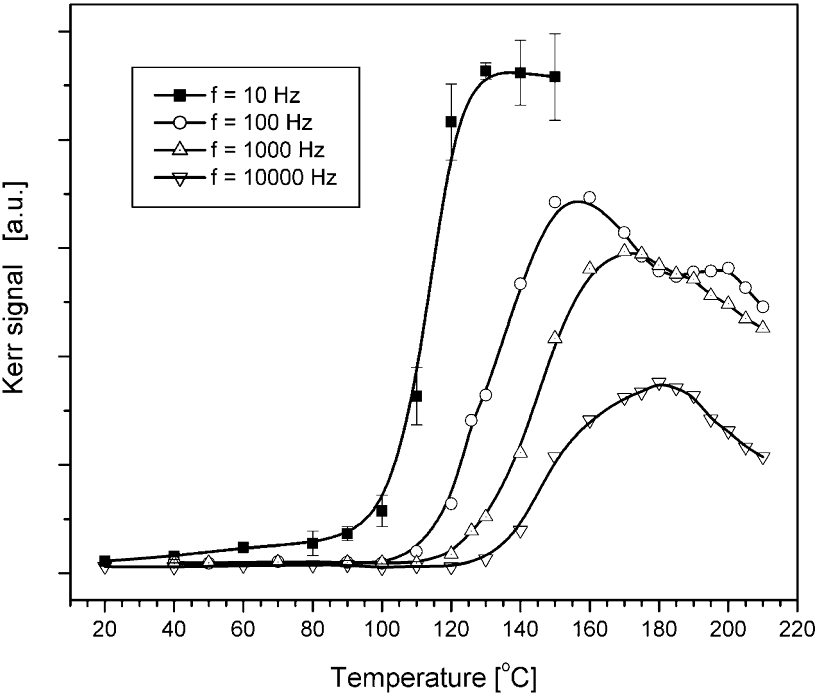

FIGURE 2 Kerr signal of PMMA/DR1 blend measured at different frequencies in function of temperature.

Polarization planes of the polarizer and the analyzer are orthogonal and make an angle of 45° with the vertical direction.

The Soleil-Babinet compensator introduces a phase shift between components of the optical electric field of probing laser beam parallel and perpendicular to the applied electric field. To break the symmetry, the sample is twisted vertically by 45°. The largest modulation signal is observed when the convenient phase difference between these components is $\pi/2$ or $3\pi/2$ [7]. Such choice offers also a simple dependence between the AC field amplitude, the induced phase difference and the modulation amplitude at 2f frequency of the probing beam intensity (further referred as the Kerr signal). It simplifies significantly the determination of the Kerr constant.

In the present study we use the electro-optic Kerr effect only as a diagnostic tool to study mobility of NLO chromophores in the polymer matrix. Therefore the knowledge of exact value of the Kerr constant is not as important as we are interested only in its relative variations as function of temperature. For this reason and for the sake of simplicity we use only the raw data of Kerr signal to illustrate thermal processes present in the studied samples.

The dielectric measurements, shown for comparison, were done on the same sample in the same termostated holder. This procedure allowed to avoid possible mismatch of actual temperature of the sample. All temperature dependence measurements were done in isothermal mode i.e., before measurement, the sample was first conditioned at a given temperature.

SAMPLE PREPARATION

PMMA powder ($M_w = 25000$) was thoroughly mixed with DR1 polycrystalline powder in proportion 9:1 wt. The mixture was then stirred in a mechanical homogeniser at temperature of 200°C, i.e., well above the temperature of glass transition T_g of PMMA and of melting temperature T_m, of DR1. When homogenized, the blend material was transformed in pellet. Next, the pellet was put in a circle hole punched in a Teflon sheet (0.1 mm thick) stuck on a substrate (ITO covered glass). The Teflon sheet was thinner than the pellet diameter. Then, the substrate was gradually heated and the pellet was covered with a second same substrate, slightly shifted aside to make room for electric leads. After some time the pellet softened and filled entirely the hole in Teflon sheet. After cooling to the ambient, the PMMA:DR1 layer was inspected under optical microscope to check its homogeneity. DSC measurements of the blend material didn't reveal any transition characteristic of melting of crystalline substance like in pristine DR1.

The chromophore was found to work as plasticizer lowering glass transition temperature T_g from 104°C to 91°C. It can be assumed that within the accuracy of used testing methods, the chromophore was homogenously dispersed in the matrix polymer.

Similar procedure was followed in case of bisphenol A epoxy resin. The only difference was that the DR1 was dissolved in the resin prior to the addition of hardener.

RESULTS

Presented below experimental results illustrate fact that Kerr effect can bring some new information on thermal kinetics of NLO polymer blends. Nevertheless, further studies are required for a complete explanation of observed phenomena.

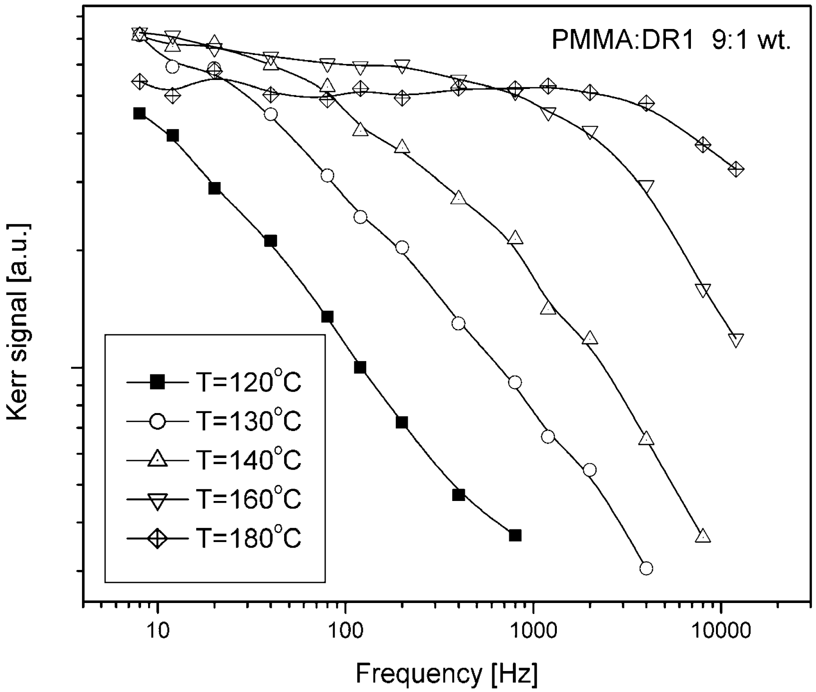

FIGURE 3 Frequency dependence of Kerr signal at different temperatures. Lines are eye guides only. Above the temperature of 180°C signal observed in frequencies lower than 100 Hz was very noisy and for this reason not shown on the figure. Please note the graph was drawn in double log-log scale.

PMMA/DR1 Blends

The observed dependence of Kerr signal on temperature and frequency is shown in Figure 2. The temperature at which the curve start to diverge from its plateau shifts towards higher values with increasing field frequency. It can be interpreted in terms of damped oscillator – the higher frequency the stronger is damping of molecules reorientation. This assumption is supported by the next figure. Indeed, Figure 3 shows a strong frequency dependence of Kerr signal on temperature. It is seen that at a given temperature the magnitude of Kerr signal depends on frequency like $\approx f^{a}$ unless the plateau value is attained. Lower is the tempreraturе at lower frequency the Kerr signal decreases. This is a finger print of the temperature dependence mobility of chromophores. Figure 4 compares the temperature dependencies of ε' of PMMA and PMMA:DR1 blend and of Kerr. One can see

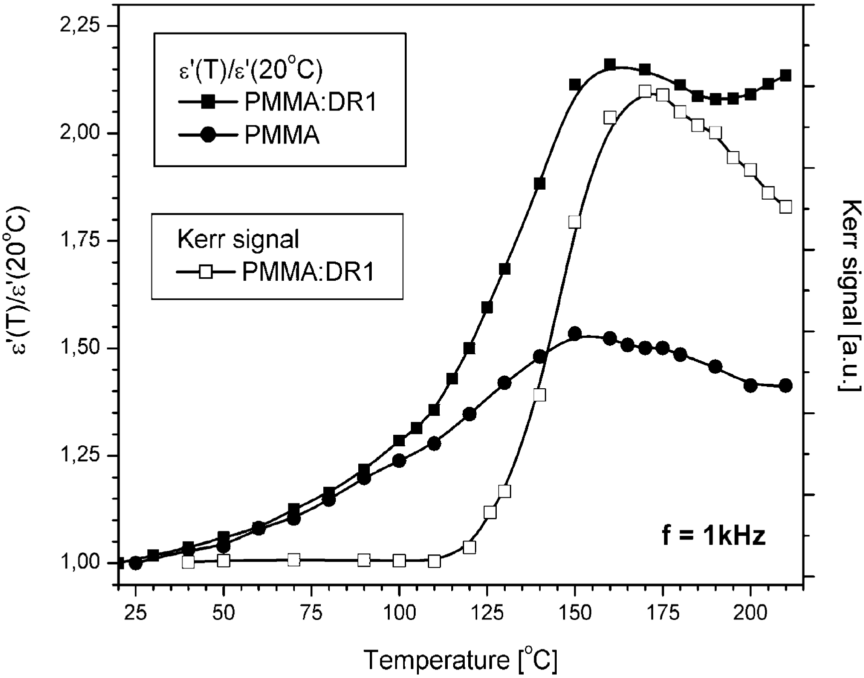

FIGURE 4 Temperature dependences of dielectric constant ε' (T) of PMMA:DR1 blend (full squares), pristine PMMA matrix (full circles) and Kerr signal in PMMA:DR1 (empty squares) taken at 1 kHz. The dielectric constants are normalized to the room temperature values.

that the Kerr signal doesn't follow closely the ε' curves. Firstly, at low temperature the Kerr signal is almost constant and practically negligible. It starts to increase abruptly at about 115°C (temperature about 15°C higher than the glass transition temperature of PMMA), reaches a maximum at 160°C and thereafter decreases. In contrary, the dielectric constant ε' (T) dependence on temperature is much smoother. It starts to increase at 20°C, reaches a maximum at above 150°C, i.e., 10 degrees less than in Kerr signal and thereafter decreases. The data shown in Figure 4 less presume another increase at temperatures higher than 200°C. Thus one can conclude that the temperature induced ability of DR1 to reorient lags behind that of PMMA matrix polymer.

Epoxy Resin Bisphenol A:DR1 Blends

Figure 5 shows the variation of Kerr signal during the curing, at different temperatures, of the epoxy resin containing diluted DR1

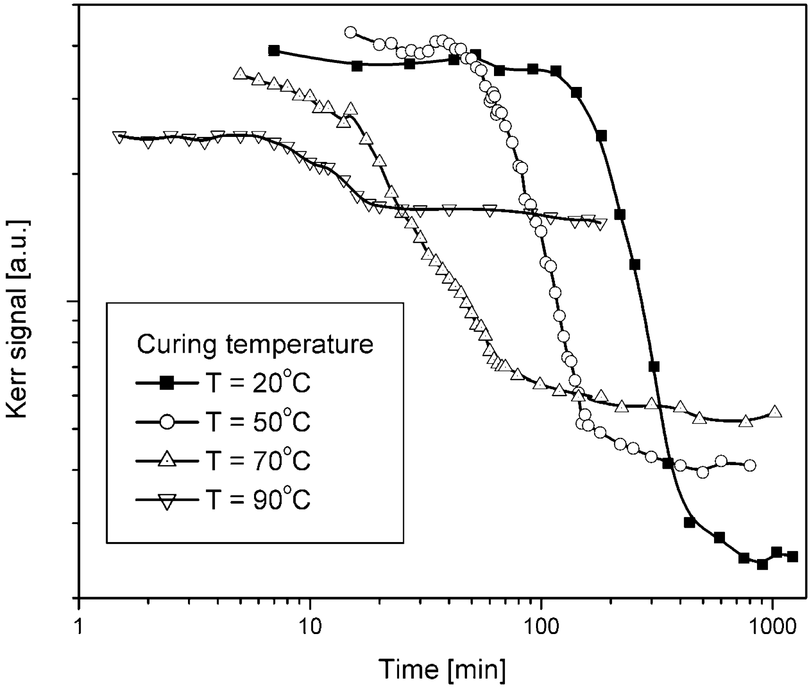

FIGURE 5 Temporal variation of Kerr signal in Bisphenol A:DR1 cured at different temperatures. The measurements are done at 100 Hz.

chromophore. A common feature of all graphs is a strong dependence of the Kerr signal in function of temperature and of curing time. After initially almost constant signal, corresponding to uncured still resin, it starts to decrease fast after a laps time which depends on curing temperature. It corresponds to the final reticulation and immobilization of chromophores. The laps time is shorter for higher temperatures, as expected.

The Kerr signal dependencies on testing frequency during the curing of bisphenol A:DR1 blend at 50°C are shown in Figure 6. One observes some maxima, whose position depends on the frequency of applied field. They occur at shorter curing times when checked with higher frequencies. It can be a proof of increasing viscosity of the sample. Before final setting the sample becomes elastic – already not liquid but not solid yet and confined DR1 molecules act like damped oscillators. It is also possible that that the AC field increase locally the temperature, which takes some time to be evacuated.

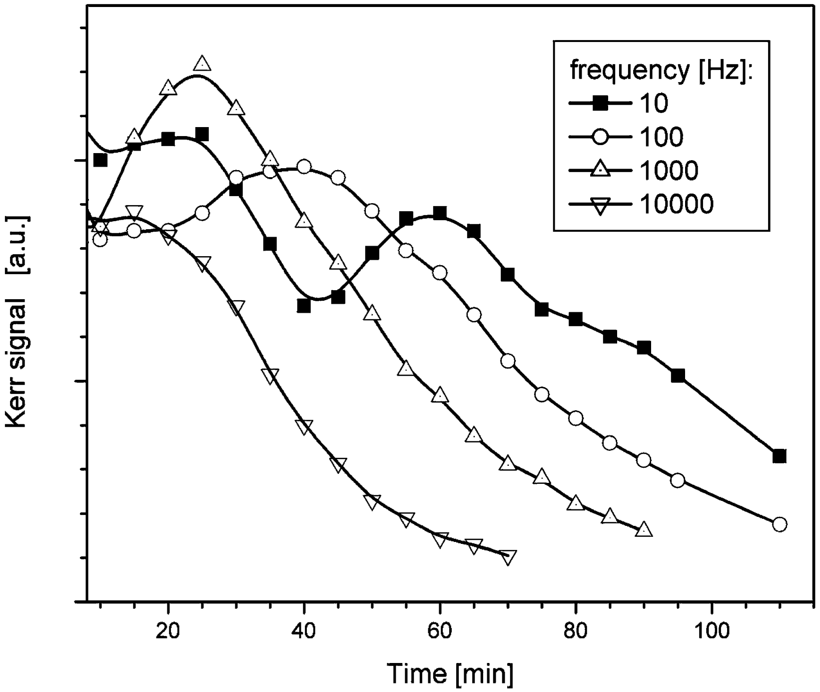

FIGURE 6 Temporal variation of Kerr signal in Bisphenol A:DR1 at different frequencies. The curing temperature is of 50°C.

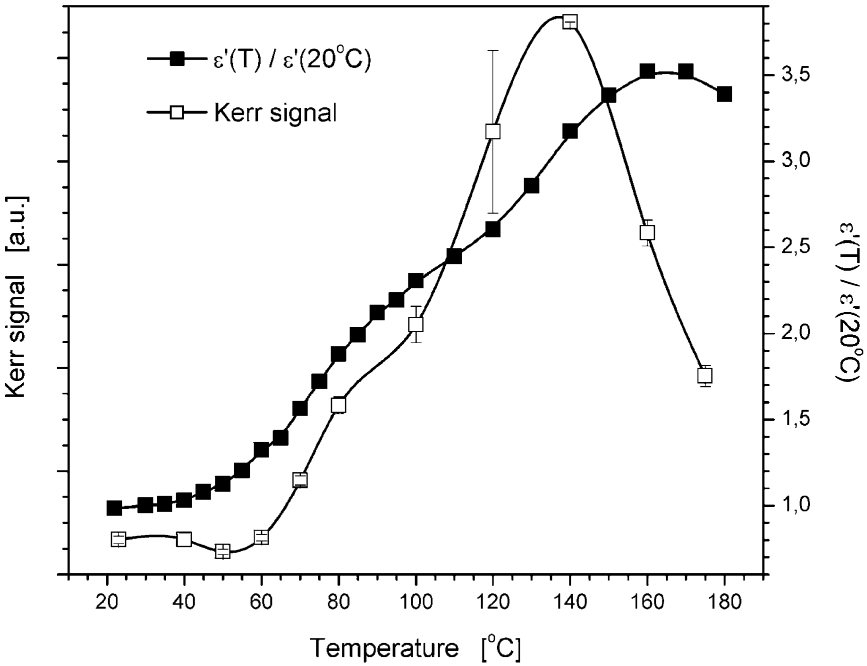

FIGURE 7 Temperature dependence of dielectric constant ε' (T) (open squares) and of Kerr signal (full squares) in Bisphenol A:DR1. The measurements were done with AC field of frequency f = 100 Hz.

Similar comparative EO Kerr effect and dielectric constant studies, like in case of PMMA:DR1 (cf. Fig. 4), were also performed on already cured blends of bisphenol A:DR1. Figure 7 shows the temperature dependence of both dielectric constant ε' (T) and Kerr signal. If at lower temperature the curves representing the Kerr signal dependence lags behind the curve of ε' (T) like in case of PMMA:DR1 blend, at higher we observe an inverse situation. Also both dependences exhibit different shapes. It means that the temperature dependence of Kerr signal is a specific phenomenon, depending on the matrix origin.

CONCLUSIONS

In this paper we have proposed a new method for characterizing blends containing a host polymer and a guest NLO chromophore. It was shown, that by using the quadratic electro-optic effect it is possible to distinguish between the thermal kinetics of the matrix and of the dopant.

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