Maleimide-Based Cross-Linkable Electrooptic Polymers with Excellent Thermal Stability Characteristics

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Introduction. A key point for the development of devices based on poled electrooptic (EO) polymers is the thermal stability of the orientation of nonlinear optic (NLO) chromophores at elevated temperatures.[1] Integrated optic devices should indeed fulfill manufacturing thermal requirements. Ermet *et al.* have stated that long-term stability of the orientation at 125 °C and short-term stability during brief excursions up to 250 °C are required.[2] Even if promising polymers, thermoplastics, or cross-linked matrices[3–14] with improved thermal characteristics have been published, there is still the need for polymers with the appropriate characteristics. Different approaches have been proposed to overcome the relaxation of NLO units at high temperatures.

One possible approach is to develop linear thermoplastic polymers with high T_g. Promising results have already been published. Dorsch *et al.* have developed a linear polyimide polymer.[3] Dai *et al* have published a polyether side chain whose T_g is close to 205 °C but which has a relatively fast relaxation time.[4] Yoon *et al.* have synthesized a linear epoxy-based polymer showing good stability of orientation at 100 °C.[5]

The use of cross-linkable host matrices in guest/host composites has also been investigated. Epoxy, imide, ether imide, or siloxane matrices have been used and encouraging results obtained.[6] However, relaxation is still fast, and guest/host composites have well-known intrinsic limitations forbidding a potential use in EO devices (small concentration of chromophores, sublimation at high temperatures, faster relaxation decays when compared to functionalized polymers...).[7]

Then, to increase the concentration of NLO units and decrease the relaxation time, Eich *et al.* have proposed to obtain the cross-linked matrix from functionalized NLO units reacted with appropriate coreactants.[8a] They have described the first thermally cross-linked system based on epoxy chemistry with a good stability of orientation at 85 °C. Other epoxy-based cross-linked networks with similar characteristics[8] as well as acrylic-based networks have been published.[9] Quite recently, Lin *et al.* have published a high T_g polyimide matrix with good stability at 85 °C.[10] Using the photoreactive cinnamic group, Chen *et al.* developed photo-cross-linkable EO polymers.[11]

Finally, several groups have recently published thermoplastic polymers bearing, either in the polymeric backbone or on the chromophores, cross-linkable groups. Yu *et al.* have synthesized a polyacrylamide with ethynyl functions attached to the polymeric backbone.[12] The resulting cross-linked network shows good characteristics, as long-term stability is observed at 90 °C. Dalton *et al* have also published different examples of side-chain polymers. These are cross-linked either using the adjunction of another component[13a] or using the unreacted function of trifunctional chromophores.[13]

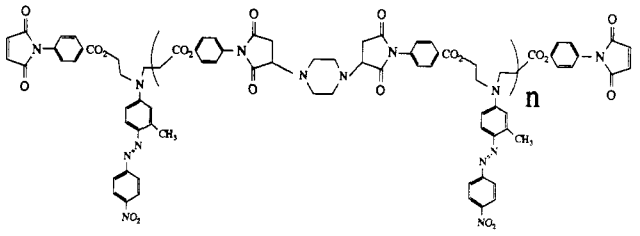

Figure 1. Cross-linkable electrooptical maleimide-based polymer.

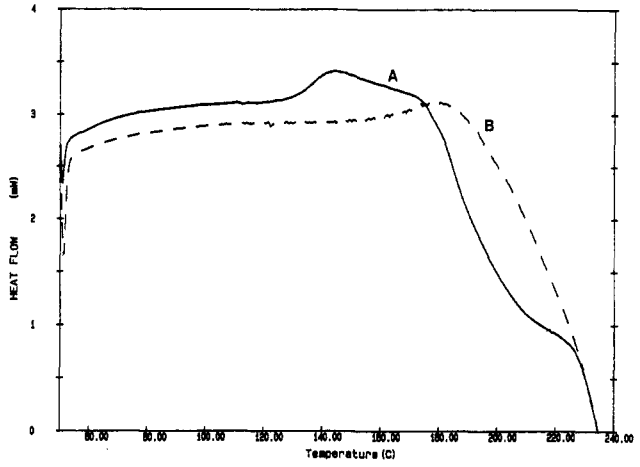

Figure 2. DSC curves obtained under N_2 at 10 °C/min with a DSC 7 Perkin-Elmer: (A) before curing; (B) after curing the sample for 2 min at 200 °C.

One may notice that EO polymers reported until now have excellent long-term stability at room temperature or at 85 °C. Nevertheless, they suffer from rapid relaxation at high temperatures (typically above 100 °C).[2] We report in this paper the thermal characteristics and EO properties of a novel class of EO cross-linkable maleimide-based thermoplastic polymers. The well-known dye DR 17 is reacted with maleimideobenzoyl chloride to obtain a dimaleimide functionalized chromophore. Polymerization is performed in *m*-cresol with nucleophilic addition of primary or secondary diamines on the maleimide double bond. The polymer is recovered by precipitation and purified. The structure of the polymer obtained using the piperazine is illustrated in Figure 1. Other primary or secondary diamines as well as chromophores have been used. Synthesis and properties of this novel class of polymers will be fully discussed in a later publication.[14] The polymer described above is obtained as a red powder. It is readily soluble in common organic solvents and is handled as a classic EO thermoplastic polymer. It can be cross-linked due to the unreacted maleimide functions which are well-known to spontaneously undergo homopolymerization upon heating.[15] Thus, the cross-linked matrix is obtained when the polymer is cured above its glass transition temperature. The cross-linked network is insoluble in organic solvents, and, as we will discuss below, excellent stability of oriented chromophores up to 200 °C may be achieved.

Results and Discussion. DSC measurements performed on a DSC 7 Perkin-Elmer setup allow us to observe the T_g as well as the exothermic reticulation peak as illustrated in the DSC traces shown in Figure 2. The T_g is close to 140 °C, while the spontaneous reticulation of the maleimide function starts around 160 °C, giving an exothermic peak around 215 °C, characteristic of the maleimide group.[15] As illustrated in Figure 2, modification of the T_g with curing is noticeable.

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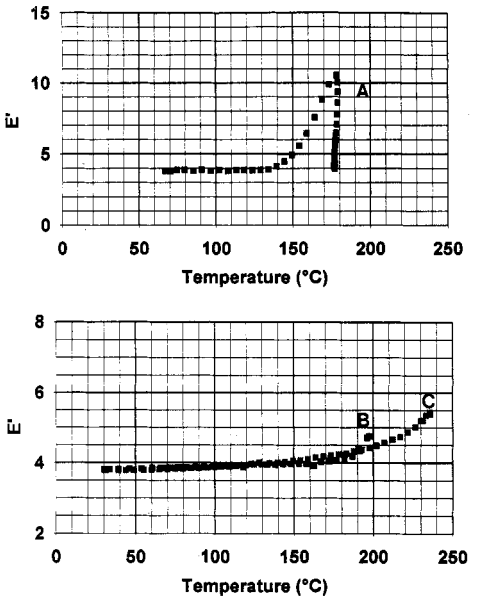

Figure 3. Evolution of the real part of the dielectric constant *vs* temperature (at 20 Hz): (A) before curing; (B) after curing the sample for 5 h at 175 °C; (C) after curing the sample for 2 h at 215 °C.

Thin films of the polymer are obtained by spin-coating dimethylacetamide solutions in a class 100 laminar-flow dust-free room onto Corning 7059 glass substrates covered with a thin gold layer (200-Å thickness). Solvent is removed by drying the films for 16 h at 100 °C under vacuum. Film thicknesses are measured by interferometry, and typical values are 1.8 ± 0.1 μm. A second semitransparent gold electrode of about 200-Å thickness is sputtered on the top surface. Dielectric and electrooptic properties of samples are characterized under vacuum or a nitrogen atmosphere in a custom-made temperature-controlled chamber equipped with fused silica windows. Electrooptic measurements are performed using a Fabry–Perot interferometric technique described previously.[16]

The cross-linking of the matrix is evidenced by dielectric spectroscopy.[16-18] At low frequency (20 Hz), the dielectric constant remains low for temperatures below T^* and increases rapidly at higher temperatures. This threshold temperature, T^*_{20}, may be defined as a dielectric T_g.[17,18] In Figure 3, the real part of the dielectric constant of the film before and after curing is plotted versus temperature. Before curing, T^*_{20} is 145 °C and is close to the T_g measured by DSC (Figure 3A). After the film has been cured for 5 h at 175 °C under vacuum, the T^*_{20} increases to 190 °C as shown in Figure 3B. Subsequent curing of the sample for 2 h at 215 °C results in a T^*_{20} of 220 °C (Figure 3C).

As mentioned by other groups, the DR 17 used in this study is not thermally stable.[6e] Therefore, curing at elevated temperatures degrades some of the chromophores.[19] Nonetheless, the electrooptic coefficients of the cross-linked films have been measured. Moreover, it is preferable to measure the nonzero r_{13} and r_{33} electrooptic coefficients when the film is poled before curing. Thus, we have used the following cycle. After drying the sample 16 h at 160 °C under vacuum, the temperature is raised up to 200 °C under a dc poling field of 25–140 V/μm. After 2 h at 200 °C, the film is cooled down with the poling field still applied. When the temperature is stabilized at room temperature, the poling field is removed. Finally, the EO coefficients are measured at room temperature at λ = 830 nm and 517 Hz. Results are shown in Figure 4. One can notice that the ratio $R = r_{13}/r_{33} = 6.5$ is quite different from the predicted value $R = 3$.[20a] It has been suggested

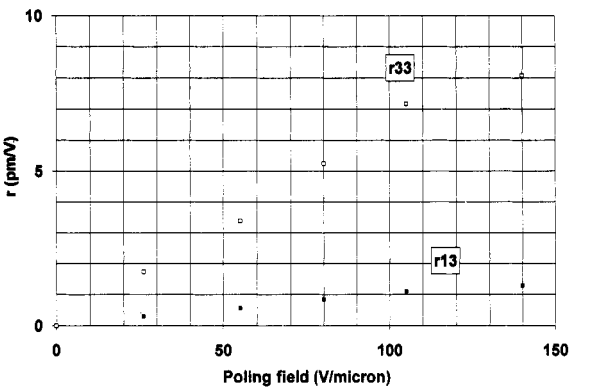

Figure 4. r_{13} and r_{33} coefficients at 830 nm *vs* poling field (see text for details).

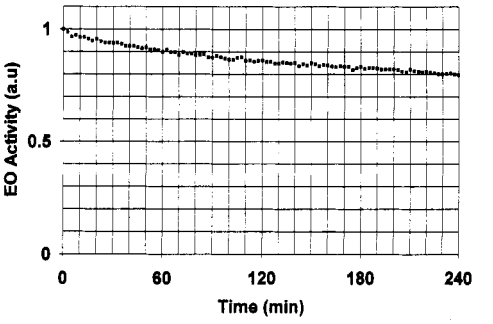

Figure 5. Temporal behavior of the EO signal, $S(t)$, at 175 °C in the matrix cured 2 h at 200 °C.

that this could be due to hindered rotation of the chromophores in highly rigid matrices.[20b] As Disperse Red 17 is known to have a static hyperpolarizability $\beta_0 = 47 \times 10^{-30}$ esu[21] and a dipole moment in the ground state of 8.2 D,[22] the oriented gas model developed by Singer *et al.*[21] and the two-level model[23] give a r_{33} of 9 pm/V at 830 nm under a poling field of 100 V/μm.[24] Therefore, despite an obvious deviation of the orientation from the simple thermodynamic model, the r_{33} is close to the optimal theoretical thermodynamic value.

The stability of the EO coefficients at elevated temperatures is the characteristic that we are focusing on as it is the key for the use of EO polymers in integrated optics devices. The stability of the oriented chromophores with time and temperature is characterized as

$$S(t) = r_{13}(t)/r_{13}(t=0^+)$$

where $t = 0^+$ is the moment immediately following the removal of the poling field (typically 0.1 s after removing the poling field). Therefore, the percentage of the EO signal due to χ^3 is completely relaxed, and only the linear EO effect is taken into account.[25,26]

The short-term temporal behavior of the EO coefficients is studied at different temperatures. As illustrated in Figure 5, a typical deorientation of the chromophores at 175 °C of a network cured following the cycle described previously is about 20% in 4 h and 42% in 15 h. At 150 °C, the decay is within the experimental error. Curing the same sample for 2 h at 215 °C generates a network with *a slow decay even at 200 °C* as illustrated in Figure 6. However, curing and studying the sample at such temperatures degrade the chromophore and cause a decrease in the r coefficient of approximately 40%.

The linear optical properties are estimated at 830 nm with a diffused light technique[27] and at 1300 and 1550 nm using a prism coupling technique.[28] Optical losses depend on the nature of the diamines and the dye.[14] Typically,

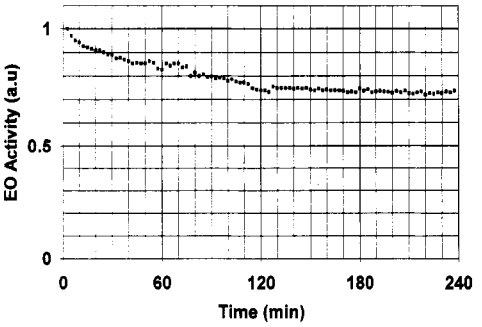

Figure 6. Temporal behavior of the EO signal, $S(t)$, at 200 °C in the matrix cured 2 h at 215 °C.

optical losses are around 4 dB/cm at both 1300 and 1500 nm in the case of the polymer shown in Figure 1, while they are about 2 dB/cm at 830 nm and 0.6 dB/cm at 1300 nm when the diamine is *N,N'*-dimethyl-1,6-hexanediamine and the dye is 3-(dicyanomethylene)-5,5-dimethyl-1-[*p*-[bis(hydroxyethyl)amino]styryl]cyclohexene.[14,29]

Conclusion. We have developed a novel class of EO cross-linkable maleimide-based thermoplastic polymers. The polymers are thermoplastic in nature and may be cross-linked thermally. Due to unreacted maleimide functions, the network is easily obtained by spontaneous homopolymerization during poling. Typically, we obtain an EO coefficient of 8 pm/V at 830 nm. The cross-linked matrix based on these polymers is, to our knowledge, the first system to show simultaneously a high r_{33} EO coefficient and a good stability of the EO activity at 150 °C and up to 200 °C. However, curing the polymer at elevated temperatures partially degrades chromophoric units. Therefore, the search for NLO chromophores with higher stability in temperature as well as higher activity is currently under way.

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(19) We estimate the percentage of degraded dye by UV–visible spectroscopy on thin films before and after curing. Therefore, curing a sample for 5 h at 175 °C degrades around 10% of the chromophore, while curing a sample for 2 h at 215 °C generates a loss close to 25% of dye.
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