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### Stable Electrooptical Guest-Host Polymers Based on Crosslinked Allyl Compounds

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## STABLE ELECTROOPTICAL GUEST-HOST POLYMERS BASED ON CROSSLINKED ALLYL COMPOUNDS

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### ABSTRACT

Novel nonlinear optical (NLO) guest-host polymers were prepared by means of a two-step polymerization of multifunctional aromatic allylic monomers. A soluble prepolymer obtained in the first step was doped with the NLO-azo dye 2-((4-(2-hydroxyethyl)-ethylamino)-phenylazo)-3,5-dicyano-4-methylthiophene and aligned by means of corona poling while the polymer network was formed via thermal polymerization in the second step. The crosslinking reaction was followed by film thickness measurements. For example, in a 6 hours' polymerization at 140°C a long-term stable material based on poly(triallyl isocyanurate) was obtained. An order parameter of  $\Phi \approx 0.3$  was deduced from ab-

sorption measurements. An electrooptical coefficient of  $r_{33} \approx 10$  pm/V (at a wavelength of 785 nm) was determined.

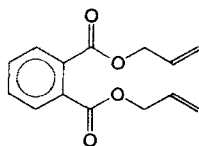
## INTRODUCTION

Future development of optical communications technologies offers chemists major challenges with the design of nonlinear optical (NLO) polymers. Properties inherent to polymers such as low levels of absorption and scattering, ease of preparation and processing, and the possibility of tailoring make them attractive materials for integrated optics. Many original papers and a number of review articles published in recent years [1–11] reflect the great potential of polymers for nonlinear optics. Sufficiently high macroscopic nonlinearity has been achieved in NLO dye-polymer composites by electric field or corona poling. But, in order to produce reliable devices from these materials, an enhanced thermal stability of the polymers is necessary. Orientational relaxation processes leading to a decrease in nonlinear optical coefficients have to be prevented. A promising approach to thermal stability is crosslinking the macromolecules during poling in order to link the chain segments through covalent bonding and lock the aligned dye molecules in the polymer network. The dye molecules can simply be dissolved in the polymer matrix or attached to the macromolecules. Various NLO network polymers have been obtained by free-radical, thermal, or photochemical crosslinking including epoxy resins [12–21], polymers based on acrylic or methacrylic acid esters [22–28], polymers bearing the cinnamic acid moiety [29–38], polyurethanes [39–47], polyamides [48], polyimides [49], or polysiloxanes [50–52].

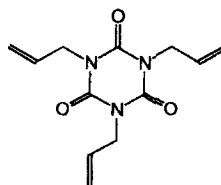
To our knowledge, multifunctional allyl compounds have not been used in this field yet, although, as will be shown, they are qualified as excellent matrices for NLO materials. The allylic double bond has a low reactivity and exhibits a strong tendency toward chain termination through transfer of the hydrogen atom of the  $\alpha$ -carbon in the allyl monomer to the propagating chain radical. The allyl radical formed in this reaction is stabilized by resonance and is usually not capable of initiating a new polymer chain [53]. Hence, in contrast to vinyl and acrylic monomers, multifunctional allylic compounds can be polymerized to considerably higher conversions before the formation of a macromolecular network, and, as a consequence, gelation occurs [54–59]. It is possible to interrupt the allyl polymerization and to isolate a still soluble but highly branched prepolymer. The prepolymer can be processed easily from solution into thin films and can then be crosslinked into a three-dimensional polymer network. Some allyl compounds containing two or three double bonds yield polymers with extremely low optical losses, excellent heat resistance, and good mechanical properties, which have found technical application, e.g., as high quality transparent cast sheets and optical lenses [60]. Here we report the two-stage polymerization and poling of a crosslinked guest–host system based on a multifunctional allyl monomer. Aromatic benzenedicarboxylic acid esters and triallyl isocyanurate were supposed to give good compatibility with the nonlinear optical azo dye, since both polymer and dye are aromatic compounds so that high amounts of the dye could be incorporated into the polymer films.

## EXPERIMENTAL

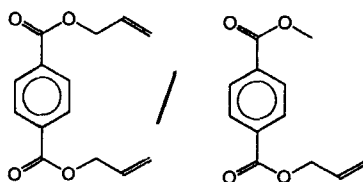
## Substances



DAP



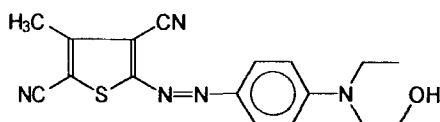
TAIC



AMTP

Diallyl phthalate (DAP) and triallyl isocyanurate (TAIC) were purchased from Aldrich Chemical Co. and freed from inhibitor by vacuum distillation before use. Allyl methyl terephthalate (AMTP) was obtained by transesterification of the dimethyl ester of terephthalic acid with allyl alcohol in the presence of 1 wt% magnesium methylate. It is a mixture of 85 wt% diallyl phthalate and 15 wt% allyl methyl terephthalate. Benzoyl peroxide was purified by reprecipitation from chloroform and methanol. Azo dye 2-((4-(2-hydroxyethyl)-ethylamino)-phenylazo)-3,5-dicyano-4-methylthiophene (HEPCMT) was prepared by azo coupling of 2-amino-3,5-dicyano-4-methylthiophene and *N*-ethyl-*N*-(2-hydroxyethyl) aniline [61].

HEPCMT



## Methods

The monomers were bulk polymerized at 80°C under nitrogen atmosphere initiated by 0.5% benzoyl peroxide. The prepolymerization process was monitored with refractive index measurements in the batch. Before the gel point was reached the reaction mixture was cooled to ambient temperature and poured into methanol in order to terminate the polymerization and precipitate the prepolymer. Pure prepolymer was obtained after threefold reprecipitation from acetone and methanol.

The monomer conversions were calculated from the iodine number of the prepolymers. Defined as g iodine bound per 100 g of the unsaturated compounds, it was determined by applying the iodine monochloride method [55].

For preparing thin films, solutions containing 20–25 wt% prepolymer and the required dye concentration in cyclohexanone were passed through a 0.5- $\mu\text{m}$  filter, spun at 3000 rpm for 30 seconds onto 2.5 mm  $\times$  2.5 mm microscope glass slides or on quartz slides coated with indium tin oxide (ITO). The samples were dried, first at room temperature for 2 hours, then at 40°C for 48 hours in vacuo to remove residual solvent.

The film thickness was measured interferometrically. To this purpose the samples were scratched with a razor blade and metallized with aluminum.

The dye molecules in the polymer films were aligned in a corona poling setup with a needle. The needle-to-plate distance was 22 mm. The samples were heated on a heating plate to the desired temperature, then the high voltage was applied and adjusted to 5–6 kV so that the corona current amounted to 1–2  $\mu\text{A}$ . After a given time the heating was terminated, the films were cooled to ambient temperature within 1 hour, and then the corona voltage was turned off. All experiments were carried out in air.

Absorption spectra were measured in a Perkin-Elmer UV-VIS spectrophotometer Lambda 19. Dye concentration in the films was taken from the peak absorbance of the spectra normalized to 1000 nm film thickness.

For the thermomechanical analysis an apparatus was used to record the penetration  $s$  of a loaded sphere-shaped head attached to a quartz stick into the sample as a function of temperature. Simultaneously, the derivative  $ds/dT$  was calculated. Experimental parameters were: load 100 g, sphere diameter 6 mm, heating rate 12 K/min.

Differential scanning calorimetric curves were recorded in a Perkin-Elmer calorimeter DSC-7 with a heating rate of 20 K/min.

The extraction of the dye from the polymer-dye films was achieved by means of a simple procedure. The coated glass slides were dipped into methanol at 25°C for 10 minutes and then dried at 40°C for 6 hours. The dye concentration in the films was determined photometrically.

The electrooptical coefficient  $r_{33}$  at  $\lambda = 780$  nm was determined with a setup similar to the scanning electrooptical microscope described elsewhere [62].

## RESULTS AND DISCUSSION

### Preparation and Properties of the Prepolymers

Under uniform conditions as applied here, the three monomers polymerize with different rates. In all cases the conversion of the double bonds in the polymerizing batches increases linearly with the reaction time, whereas it reaches a virtually constant value soon after its beginning in the isolated prepolymers. In Fig. 1 this is demonstrated for TAIC. The molar volume shrinkage of the monomers during prepolymerization is comparable with that of monofunctional allyl compounds [63, 64]. The glass temperatures were found between 60 and 105°C. The prepolymerization data and prepolymer properties are summarized in Table 1.

### Crosslinking of the Prepolymers

The magnitude of bulk second-order nonlinear optical effects of doped polymers depends on the dye concentration in the system and on the orientation degree of the dye molecules. In order to attain a large nonlinear response, high dye concen-

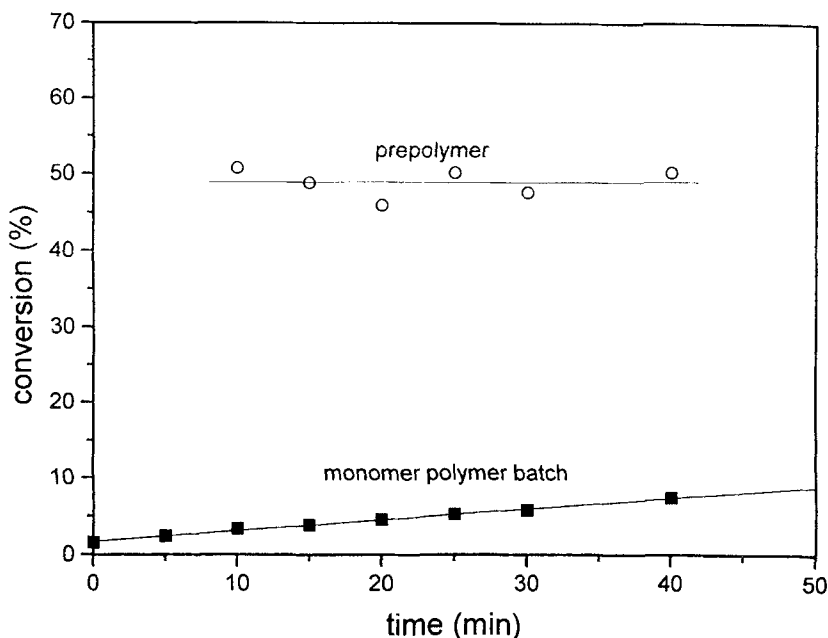


FIG. 1. Prepolymerization of triallyl isocyanurate. Conversion versus time curves.

trations are necessary [65]. At large dye concentrations, however, incompatibility between polymer and dye can lead to undesired phase segregation and crystallization of the dye molecules. The absorbance of poly-TAIC-dye films obeys the Lambert-Beer rule up to about 30 wt% dye concentration, indicating the absence of optical scattering and good compatibility between the two constituents of the composite in this range.

The stabilizing efficacy of the polymer network is expected to be more effective the more densely the polymer chains are crosslinked with each other. We there-

TABLE 1. Prepolymerization of the Allyl Monomers under Study

	DAP	AMTP	TAIC
Prepolymerization time (min)	290	120	25
Volume shrinkage of the monomer-polymer batch per 1 mole reacted double bonds (mL/mol)	22.4	21.6	21.2
Percentage of reacted double bonds in the batch at the gel point (%)	21	13	12
Percentage of reacted double bonds in the isolated prepolymer (%)	72	58	48
Unreacted allyl groups in the prepolymer per monomeric unit	0.6	0.8	1.6
Glass temperature of the prepolymers (°C)	63	106	75

fore aimed at realizing high monomer conversions. Conditions worked out for bulk polymerizations of allyl compounds found in the literature cannot be applied here, since oxygen, which is supposed to influence the crosslinking process, was present in our experiments. Moreover, it was not clear at the beginning of our experiments if the nitro or thiophene group in the dye, known to inhibit free-radical polymerization, influences the crosslinking reaction. The crosslinking rate increases with increasing temperature, but, simultaneously, the decreasing molecular mobility reduces the achievable dye orientation; in addition, thermal degradation of the dye can arise. Thus, favorable crosslinking and poling conditions are inevitably trade-offs between an appropriately fast crosslinking process on the one hand and the mobility of polymer and dye molecules and thermal stability of the dye on the other hand.

Polymerization reactions are accompanied, as a rule, by a volume shrinkage of the polymerizing system which varies directly with the number of reacted double bonds. In crosslinked polymers the linear relationship between conversion and volume shrinkage is also true beyond the gel point [66]. Since length and width exceed the thickness by orders of magnitude in thin films, the changing film thickness reflects the volume shrinkage reliably so that in the following equations the volume can be replaced by film thickness. For pure polymer the conversion  $C$  is

$$C = 100 \frac{\Delta V}{KV_0} \quad (1)$$

where  $\Delta V$  = volume contraction at conversion  $C$ ,  $C$  (%)

$V_0$  = initial (monomer) volume (mL)

$K$  = contraction coefficient =  $\frac{v_{s,m} - v_{s,p}}{v_{s,m}}$

$v_{s,m}$  = specific monomer volume (mL/g)

$v_{s,p}$  = specific polymer volume (mL/g)

$v_{s,p} = v_{s,m} - \Delta v_s$  (mL/g)

$\Delta v_s$  = decrease in specific volume at 100% conversion of the allyl double bonds (mL/g)

After normalizing the measured volume to the initial volume, the monomer conversion is

$$C = \frac{100}{K} - \frac{100}{K} V_{\text{norm}} \quad (2)$$

The volume  $V_{\text{film}}$  of polymer-dye films is composed of the volume of the shrinking polymer  $V_p$  and the constant volume of the dye  $V_{\text{dye}}$ :

$$\begin{aligned} V_{\text{film}} &= V_p + V_{\text{dye}} \\ &= (1 - p)m_{\text{film}}v_{s,p} + pv_{s,\text{dye}} \end{aligned} \quad (3)$$

where  $p$  = weight portion of the dye in the film (dimensionless)

$v_{s,\text{dye}}$  = specific volume of the dye (mL/g)

$$C = \frac{100[(1 - p)v_{s,m} + pv_{s,\text{dye}}]}{(1 - p)v_{s,m}K} - \frac{100[(1 - p)v_{s,m} + pv_{s,\text{dye}}]}{(1 - p)v_{s,m}K} V_{\text{norm}} \quad (4)$$

The specific volume of the azo dye is  $(0.7936 \pm 0.014)$  mL/g.  $\Delta v_s$  was calculated from the experimental volume shrinkage of the prepolymers (Table 1). The

TABLE 2. Shrinkage Data of the Allyl Compounds Studied

	DAP	AMTP	TAIC
$v_{s,m}$ (mL/g)	0.8921	0.8888	0.8628
$\Delta v_s$ (mL/g)	0.182	0.165	0.256
$v_{s,p}$ (mL/g)	0.7101	0.7239	0.6068
$K$	0.2040	0.1856	0.2967
$V_{\text{norm,pre}}$	0.853	0.892	0.858

volume  $V_{\text{norm,pre}}$  represents the normalized volume of the prepolymers which was used as the initial value of the conversion versus time curves. The data are summarized in Table 2.

The crosslinking density  $d$  illustrates how densely the polymer chains are linked with each other. At high conversions of multifunctional monomers most of the double bonds function as network crosslinking sites. In this case, by simplifying, the crosslinking density can be expressed as the molar number of polymerized double bonds per unit volume of the polymer.

$$d = n/V_p$$

where  $n$  = molar number of reacted double bonds

$V_p$  = molar polymer volume at conversion  $C$  (mL/mol)

$$d = \frac{n_m C}{v_{s,p} M_m} \quad (5)$$

where  $n_m$  = number of double bonds in the monomer

$v_{s,p}$  = specific polymer volume at conversion  $C$  (mL/g)

$M_m$  = molecular weight of the monomer unit (g/mol)

In general, monomer conversions up to 70–80% are obtained in the bulk polymerization of multifunctional allyl monomers. Crosslinking densities calculated under the assumption of 80% conversion are shown in Table 3 for the three polymers.

TABLE 3. Calculated Crosslinking Density of Allyl Polymers at 80% Monomer Conversion

	DAP	AMTP	TAIC
$M_m$	246	242.1	249
$n_m$	2.0	1.85	3.0
$v_{s,p}$ (mL/g)	0.7465	0.7560	0.6580
$d$ (mmol/mL)	8.7	8.1	14.6



Because of the three double bonds in the monomer unit, a network with remarkably higher crosslinking density than in the other two polymers is predicted for poly-TAIC. Therefore, we conducted polymerization experiments with NLO dye and TAIC polymer alone.

At higher temperatures the polymerization of allyl monomers does not need to be initiated with peroxide since oxygen takes the role of the initiator as was shown with DAP [67]. We decided to use thermal initiation to avoid interfering reactions between initiator radicals and dye molecules.

At a conversion of the available double bonds,  $C = 48 \text{ wt}\%$ , the normalized volume shrinkage of the prepolymer  $\Delta V/V_0$  was as high as 0.142, so the crosslinking of the polymer films consequently begins at  $V_{\text{norm,pre}} = 1.0 - 0.142 = 0.858$ . The polymerization reaction reaches an appreciable rate at temperatures higher than  $120^\circ\text{C}$  (Fig. 2). Monomer conversion does not increase significantly above  $180^\circ\text{C}$ . Polymerization temperatures of  $180^\circ\text{C}$  or higher would be favorable for crosslinking, but to prevent dye damage (see below) all crosslinking and poling experiments were conducted at  $140^\circ\text{C}$ . In pure poly-TAIC and films containing 9% dye (related to the total weight of the film), the polymerizations are characterized by comparable rates. Although 25% of the dye appears to cause a slight delay of the reaction, an ultimate conversion near 90% is nevertheless gained after 24 hours (Fig. 3). We conclude from the curves in Fig. 3 that a polymerization time of 6 hours is satisfactory to build the spatial network stabilizing the dye orientation.

A practical question is how the corona discharge influences the crosslinking reaction. Prepolymer films without and with dye were heated at  $140^\circ\text{C}$  for 120

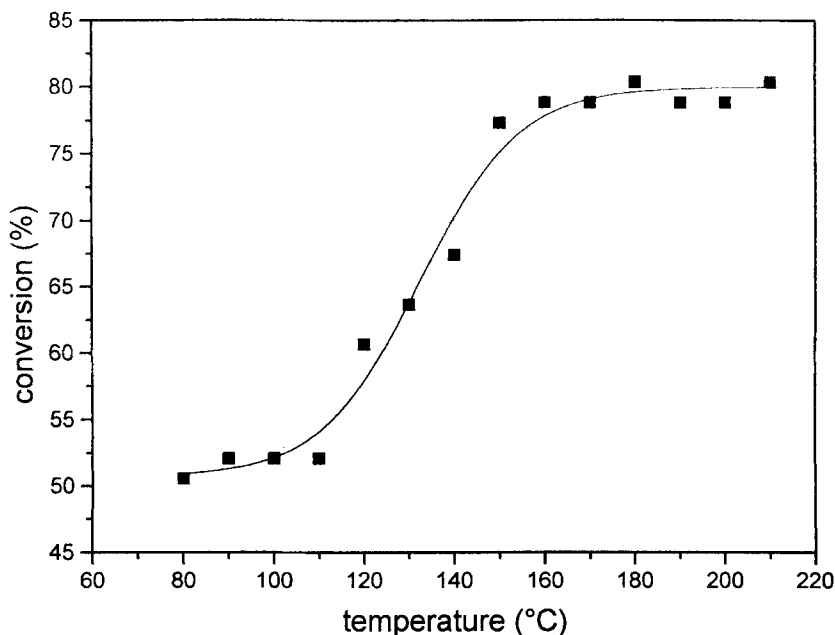


FIG. 2. Crosslinking of TAIC prepolymers. Conversion as a function of the polymerization temperature. Polymerization time 15 minutes.

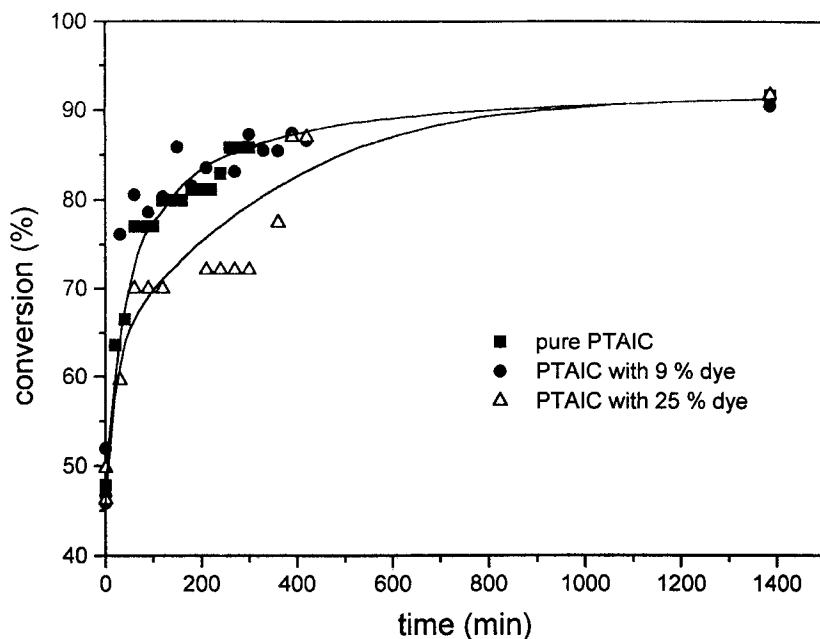


FIG. 3. Crosslinking of TAIC prepolymer and prepolymer-dye composites containing 9 and 25 wt%, respectively, dye at 140°C. Conversion as a function of the polymerization time.

minutes with the corona voltage on for different time periods. The polymerization of allyl double bonds proceeds slightly accelerated in the poled samples, presumably due to the faint UV radiation present in the corona discharge (Fig. 4).

The diffusion of dye out of the polymer film provides a qualitative measure of the polymerization conversion in the film. The dye molecules are supposed to be fixed more effectively in smaller network meshes. Prepolymer films containing 10 wt% dye were polymerized at different temperatures for 1 hour. Then the samples were dipped in methanol, and the loss of dye was determined from the absorption spectra of the films before and after extraction. In all cases the dye is rapidly extracted from the films. But especially at short dipping times, the extraction is slowed down with increases in temperature and conversion of polymerization (Fig. 5).

### Thermal and Thermomechanical Behavior

The glass temperature has a great influence on the orientational stability of NLO polymers. The segmental motion of polymer chains is significantly restrained below this temperature. When the temperature of the polymers is raised, the macromolecules as well as the dye molecules relax in the vicinity of the glass temperature from their state of nonequilibrium and the dye molecules lose their noncentrosymmetric alignment. In order to minimize this relaxation, a glass temperature as high as possible is an important demand in the development of novel NLO polymers so that its difference from the operating temperatures is sufficiently large.

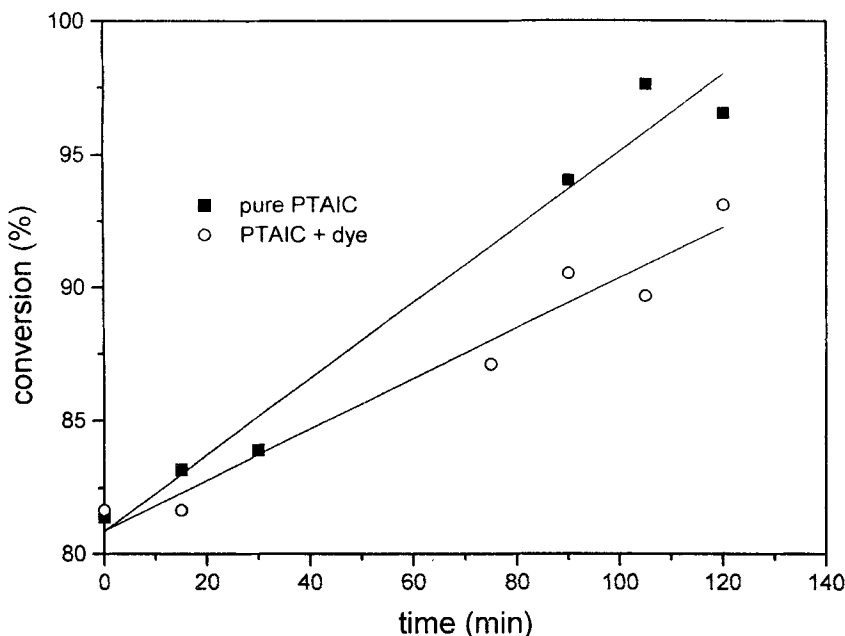


FIG. 4. Influence of corona poling on the crosslinking rate. Conversion as a function of the poling time. All samples were polymerized at 140°C for 120 minutes; only the poling period was varied.

The glass temperature of poly-TAIC and poly-TAIC-dye was determined by means of differential scanning calorimetry and thermomechanical analysis. The prepolymer exhibits a glass temperature near 75°C; a  $T_g$  cannot be observed in crosslinked poly-TAIC (Fig. 6). In crosslinked polymers the thermal effects are often small and the glass transformation extends over a broad temperature range, so a glass temperature cannot always be detected, whereas thermomechanical analysis reflects the transformation. In contrast to pure poly-TAIC, we detected a glass temperature in the crosslinked dye-containing composites (Fig. 7) which decreases linearly with the dye concentration (Fig. 8). Two effects may be considered to account for this. The dye could lead to a decrease in the polymerization conversion compared with the pure polymer, or the dye molecules could act as a plasticizer. The volume contraction measurements seem to exclude decreased conversion, hence the measured glass temperature is due to the latter effect. However, there is no explanation at present for the drastic change in the thermal behavior if only a few percent of the dye are added to the polymer. This issue is the subject of current detailed investigations.

### Poling and Orientational Order [68]

The orientation of dye molecules in poly-TAIC was achieved by corona poling in the usual way without a grid. The samples were heated to 140°C. When this temperature was reached, the corona voltage was turned on. The films were subse-

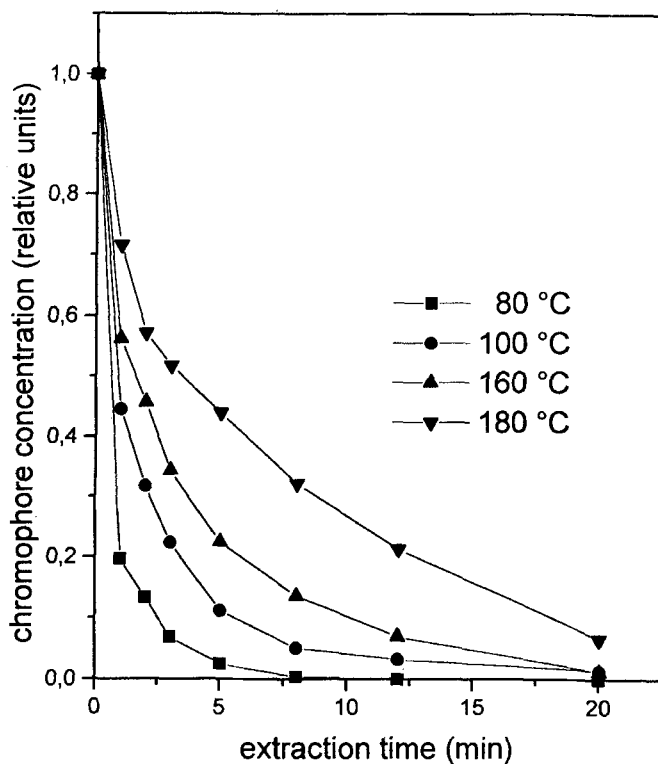


FIG. 5. Dye extraction. Residual dye concentration related to the initial concentration before extraction in the films as a function of the extraction time. Polymerization at 80–180 °C for 1 hour.

quently cooled to ambient temperature with the high voltage still applied in order to freeze the aligned dye molecules in their oriented position. At the beginning of the process, the poling temperature exceeds the glass temperature by at least 65 °C, but, as confirmed by the resulting orientation, the curing procedure obviously leads to a rise of the glass temperature of the system so that an efficient stabilization of dye alignment is accomplished.

The orientation of dye molecules was monitored by measuring the absorption spectra of the samples before and after poling. The orientational arrangement manifests itself in a decrease of the peak absorbance of the polymer films, which was utilized to estimate the order parameter  $\Phi$  [69].

$$\Phi = \frac{A_0 - A_s}{A_0}$$

where  $A_0$  = absorbance of the unpoled sample

$A_s$  = absorbance of the poled sample

As discussed above, high temperature is necessary to attain a convenient polymerization rate. Degradation or loss through sublimation of the dye has to be

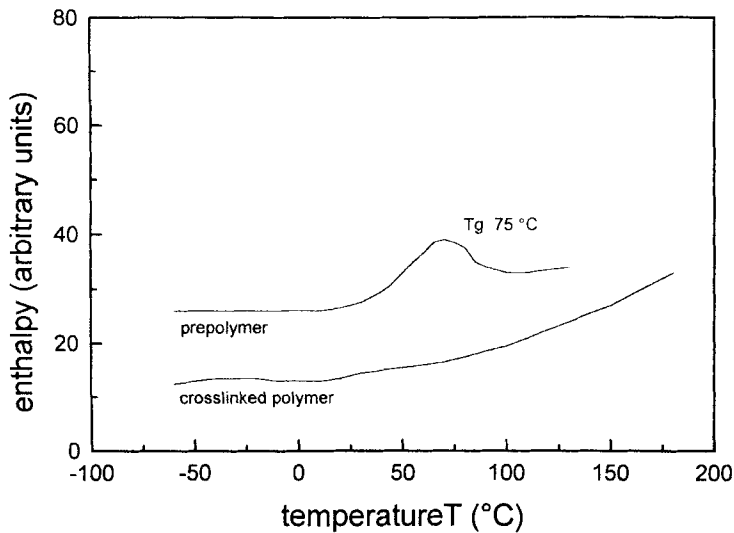


FIG. 6. DSC traces of TAIC prepolymer and crosslinked polymer.

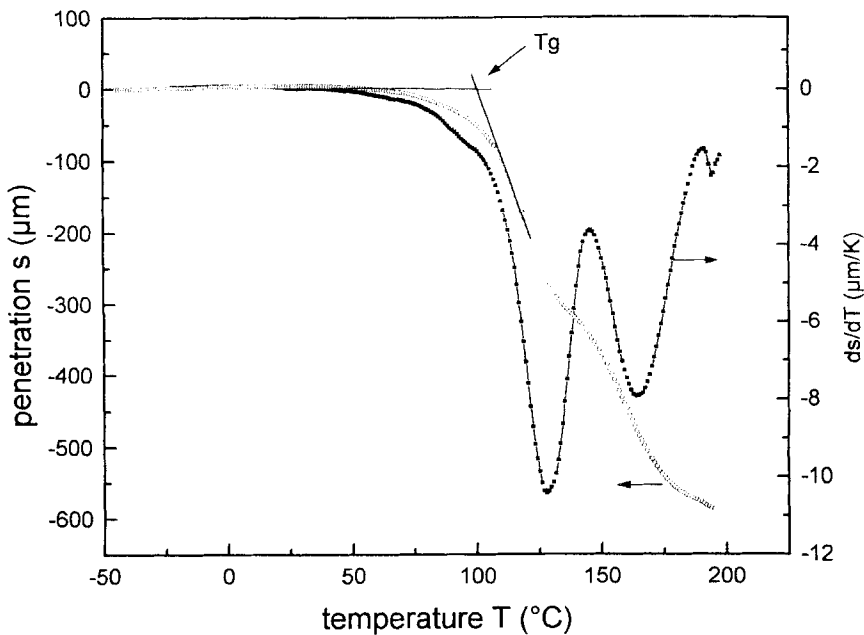


FIG. 7. Thermomechanical curve of a crosslinked TAIC polymer-dye composite containing 10 wt% dye.

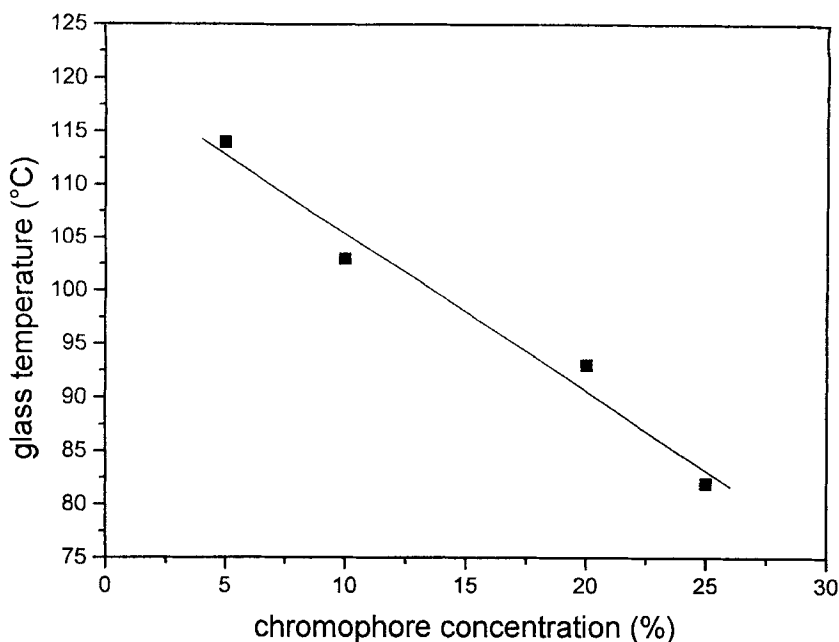


FIG. 8. Glass temperature of crosslinked TAIC polymer-dye composites as a function of the dye concentration derived from thermomechanical analysis.

expected at higher temperatures, and this leads to a decrease in the absorbance and thus to wrong values for the determined order parameter. For avoiding this, the thermal stability of the dye was studied prior to the poling experiments by annealing polymer-dye films at temperatures between 110 and 180°C for 15 hours. Up to 140°C, no change in the absorption spectra is detected (Fig. 9). At higher temperatures, the absorbance of the samples changes severely. The shape of the absorption spectrum does not change, and traces of the dye were precipitated on the heating plate around the samples so that the decrease in dye concentration is obviously associated with sublimation of the dye. Consequently the behavior of the dye controls the thermal stability of the polymer films. On the basis of these results, a poling temperature of 140°C was established.

The success of the crosslinking is demonstrated in the absorption spectra shown in Fig. 10. In uncrosslinked prepolymer films poled at 70°C the poling effect is displayed immediately after applying the high voltage. As the alignment of the dye molecules is not stabilized, the orientation decays at ambient temperature within about 1 week and a pristine spectrum is obtained after reheating the polymer to 70°C. In order to crosslink TAIC, prepolymer-dye films were heated to 140°C according to the protocol elaborated and the corona voltage was applied. The films were kept at this temperature for 6 hours to complete the crosslinking reaction. An order parameter  $\Phi = 0.2 \dots 0.3$  was obtained. At ambient temperature no change of the spectrum was observed during the first week after poling. Subsequent heating at 50, 80, and then 100°C, respectively, yields a slight decrease in the orientation degree of only about 15%.

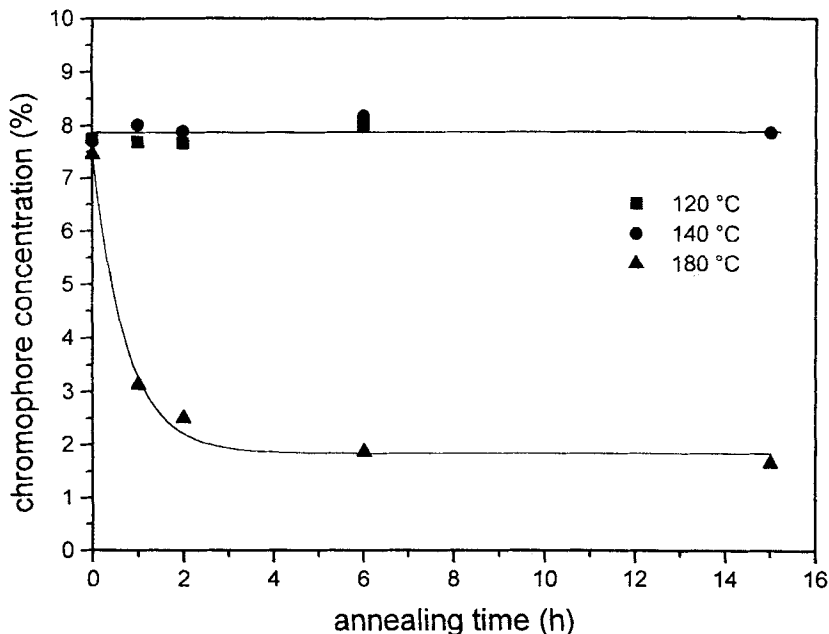


FIG. 9. Thermal stability of the dye in poly-TAIC films. Dye concentration of the films determined photometrically as a function of polymerization time at 120, 140, and 180°C, respectively. Initial dye concentration 7.7 wt%.

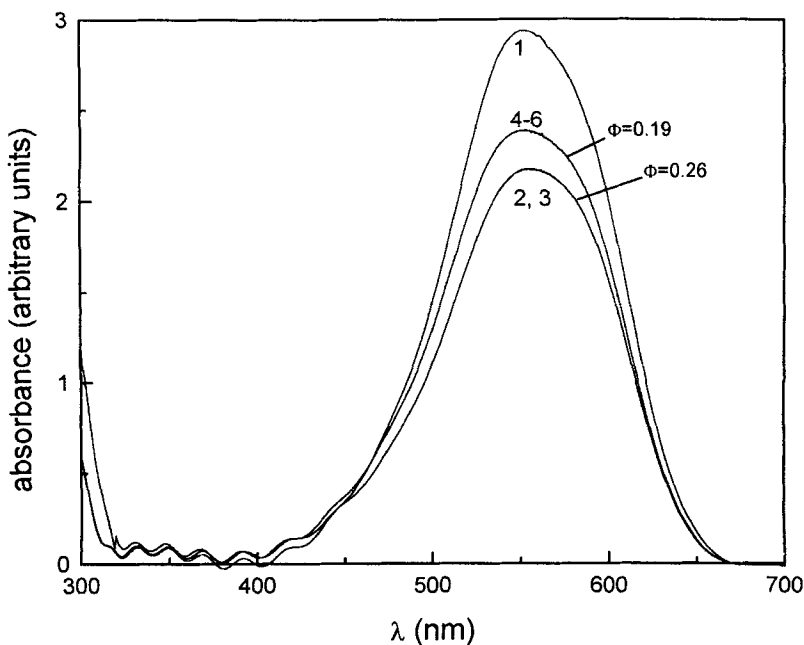


FIG. 10. Absorption spectra of unpoled and (crosslinked) poled poly-TAIC-dye composites. Dye concentration 12 wt%: (1) before poling, (2) immediately after poling, (3) aging 1 week at 25°C, (4) aging 1 week at 25°C and 6 hours at 50°C, (5) aging as for (4) and an additional 6 hours at 80°C, (6) aging as for (5) and an additional 32 hours at 100°C.

As shown above, thermal degradation of the dye does not occur at 140°C. The unchanged shape of the absorption spectrum after poling suggests that the dye is also not degraded by corona poling. To be sure that the spectra really do reflect dye orientation, we determined the electrooptical activity, which is independent of the spectroscopic characterization. An electrooptical coefficient  $r_{33} \sim 10$  pm/V at 785 nm was measured on a polymer sample containing 25 wt% dye.

## CONCLUSIONS

We have introduced a novel, promising matrix for nonlinear optical and electrooptical applications. Besides their excellent optical properties, crosslinked allyl polymer-dye composites exhibit the high thermal and long-term stability required for practical devices. Following the polymerization process by means of volume shrinkage measurements based on the conversion of double bonds has proven to be a successful tool to optimize the crosslinking conditions. The assessment of the crosslinking density can be used for screening different potential NLO network polymers. The degree of orientation and the electrooptical coefficient found in the present crosslinked guest-host system will certainly be improved when the NLO dye is covalently attached to the polymer, which also allows for a higher dye concentration. Such experiments are currently under study.

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