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Study of the cross-linking mechanism of a copolymer containing an electrooptic chromophore

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ABSTRACT: The mechanism of the cross-linking reaction occuring between an NLO chromophore copolymerized with a glycidyl epoxide unit (polymer PIII) was rationalized using magic angle spinning (MAS) NMR spectroscopy. A first study conducted on a system composed of a model chromophore and a simple epoxy molecule enabled us to attribute the NMR changes that accompany the epoxy ring opening. Further, the use of a guest–host system made of an azo chromophore dispersed in an MMA–GMA copolymer matrix indicated a quantitative yield of the carboxyl/epoxy anchorage reaction after 30 min of heating at 140 °C. The ^{13}C cross polarization (CP)/MAS NMR spectroscopic study showed unambiguously that the cross-linking reaction in polymer PIII is due to a nucleophilic opening of the epoxy rings by the carboxylic groups of the chromophores resulting in carboxylic ester bond formation. Finally, the blue shift of the ca 500 nm absorption band was modeled with a computational study. It is concluded that the esterification of the acid carboxylic group of the chromophore causes the torsion of the azo molecule. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: second order non-linear optic; cross-linking; polymer; disperse red 1; magic angle spinning NMR spectrometry; quantum chemistry; epoxy

INTRODUCTION

The increasing need for high-speed electrooptic modulators with large bandwidth, low driving voltage and especially long-term stability has led to tremendous research efforts in the area of non-linear optic (NLO) materials.[1,2] Inorganic materials such as lithium niobate have now reached their limits in terms of both efficiency (electrooptic coefficient) and practical use (processability and cost). On the other hand, organic materials are particularly promising for this type of development, because they display high NLO properties, good filmability and high tailoring possibilities.[1–4]

The key issue with organic materials is the lack of temporal stability of the macroscopic electrooptic coefficient (r_{33}) due to the slow relaxation of the field-induced alignment of the chromophores.[2,5] Stabilization of the non-linear response is of paramount importance for commercial applications of this type of material. Two strategies are generally used to maintain the orientation of the chromophores. The first consists in grafting or doping a high glass transition temperature (T_g) polymer with electrooptic chromophores.[2,5,6] However, processability of a high-T_g polymer involves strong heating during the poling process and can therefore cause thermal decomposition of the chromophores. The second strategy relies on using a cross-linkable polymer, in which the mobility of the chromophores is reduced after cross-linking reaction thanks to the formation of new inter- and intrachain chemical bonds between the chromophore and the polymer matrix.[2,5,7–11] As a result, the chromophores are locked in the orientation adopted during the poling process.

The structure of the studied polymer PIII is depicted in Fig. 1 and consists in a methacrylate-based copolymer containing cross-linkable epoxy chains and pendant NLO chromophores bearing a carboxylic acid group (Fig. 1).

It was shown previously that the thermal cross-linking reaction in polymer PIII was an efficient strategy to maintain the orientation of the chromophores after poling, since the electrooptic coefficient of polymer PIII remained stable during several weeks at 85 °C.[12–14] Information on the exact cross-linking mechanism occurring in polymer PIII is therefore of great importance, because this strategy could be certainly advantageously duplicated using a chromophore of higher

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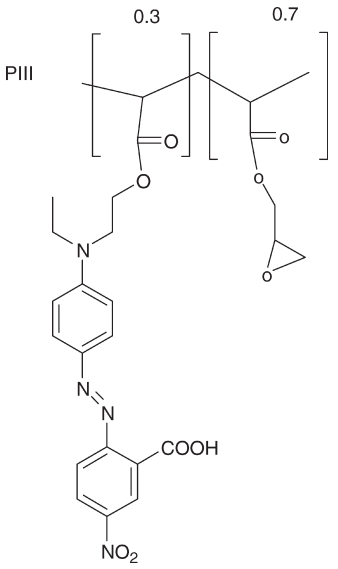


Figure 1. Structure of the studied polymer PIII

hyperpolarizability than disperse red 1 (DR1) and copolymerized within the same glycidyl–methacrylate polymer backbone.[15,16]

The crosslinking of polymer PIII was characterized analytically by an attenuation of the epoxide ν asymmetric IR band located around 903 cm^{-1}.[12–14] The postulated cross-linking was the nucleophilic opening of the epoxy rings by the carboxylic groups of the chromophores (mechanism 1 in Fig. 2), although the self-polymerization of the epoxy groups could also cause hardening of the matrix as well as the depletion of the 903 cm^{-1} IR band (mechanism 2 in Fig. 2). The latter cross-linking mechanism indeed occurs in the hardening process of thermoset epoxy resins.[17] In polymer PIII, such a mechanism would certainly restrict the mobility of the entrapped chromophores and result in a decrease in the epoxy IR band, but the orientational stability of the chromophores would be less than that obtained by their covalent attachments through the carboxylic acid.

The demonstrated efficiency of such a cross-linking reaction to stabilize the orientation of the chromophores,[12–14] but the absence of a systematic study of the mechanism of this reaction, prompted us to investigate in detail the cross-linking reaction of polymer PIII. To this end, solid-state magic angle spinning (MAS) NMR represents a powerful tool because during the cross-linking process the polymer loses its solubility, thus preventing its characterizations by other techniques. Furthermore, a blue shift of the visible charge-transfer band was also observed consecutively to the cross-linking process,[12–14] but an interpretation of this phenomenon has not been given so far. Owing to the strong charge-transfer character of this electronic transition, the hypsochromic nature of this shift does not agree with the logically increased electron-withdrawing effect of the resulting ester group compared with the initial carboxylic acid. Furthermore, it is well documented that the nonlinear optical properties of polarizable push–pull chromophores depend on the $D(\pi) \rightarrow A(\pi^*)$ charge-transfer transition.[18] It was therefore useful to rationalize this observation. A theoretical study was also carried out and it enabled us to interpret satisfactorily the blue shift of the visible absorption band upon cross-linking.

RESULTS AND DISCUSSION

Model compound of the cross-linked chromophore

Spectra recorded by solid-state MAS NMR give signals that are generally much broadened compared with those

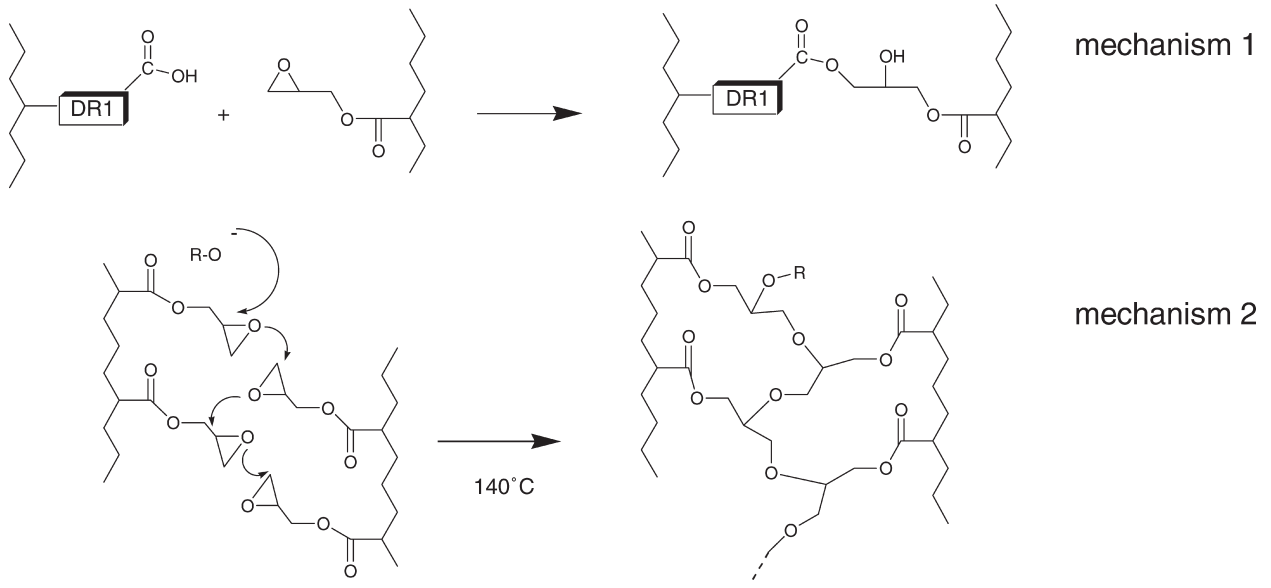


Figure 2. Illustration of the two possible mechanisms that could occur during curing

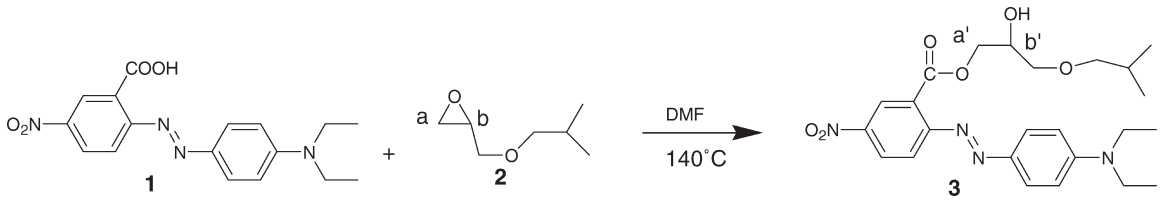


Figure 3. Reaction between compounds **1** and **2** for the preparation of the model compound **3**

recorded in solution. Therefore, we decided to determine, accurately on model compounds, the chemical shift changes that result from the opening of the epoxy rings by an acid carboxylic group. For this purpose, the azo chromophore **1** was chosen for its structural proximity with the chromophore grafted in the polymer PIII (Figs 1 and 3). Compound **1** does not contain the methacrylate group, because it could spontaneously polymerize during heating at 140 °C. Chromophore **1** was synthesized by an azo coupling between the diazonium salt of the commercially available 2-amino-5-nitrobenzoic acid with *N*,*N*-diethylamine, following classical literature conditions.

The reaction between the carboxylic acid and the epoxy group occurred, as expected, in DMF solution at 140 °C (Fig. 3). The product **3** exhibited a blue shift of the intense absorption band in the visible region relative to the starting chromophore **1** (from 558 to 510 nm). The NMR spectra of compounds **2** and **3** enabled us to attribute the pertinent chemical shift changes (both for the carbon and for the proton) that arose after the opening of the epoxy rings (Figs 4 and 5). The assignements of ^{13}C signals were made according to a ^{1}H–^{13}C correlation (HMQC).

The protons designated H_a and H_b on the starting epoxyde **2**, located at 2.72 and 3.12 ppm, respectively, were shifted to 4.37 and 4.07 ppm ($H_{a'}$ and $H_{b'}$) on opening of the epoxy ring. In addition, this was followed by the appearance of a broad doublet signal at 2.46 ppm, attributed to the formation of the hydroxy group (Figs 4 and 5). Similarly in the carbon NMR spectra a downshift

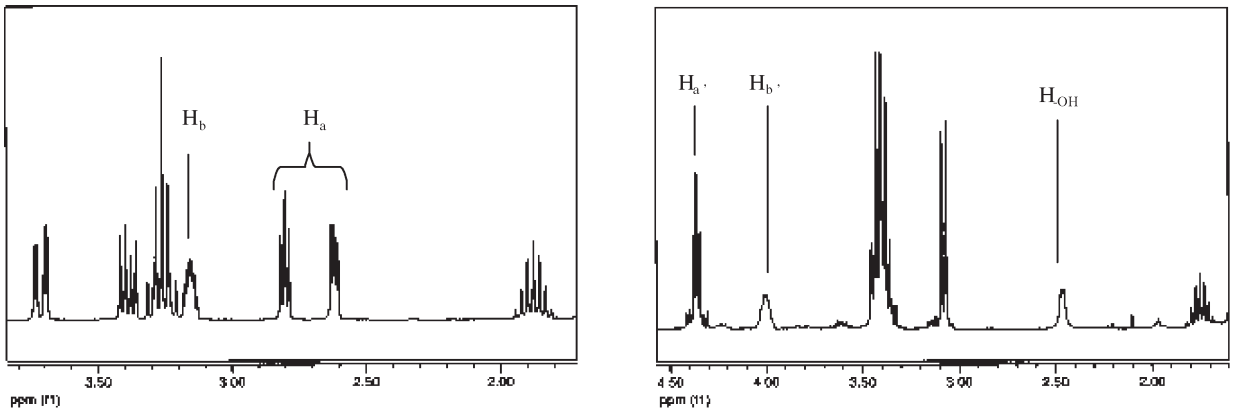


Figure 4. ^{1}H NMR spectra of the epoxy-containing starting material **2** and of the cross-linked product **3** recorded in $CDCl_3$

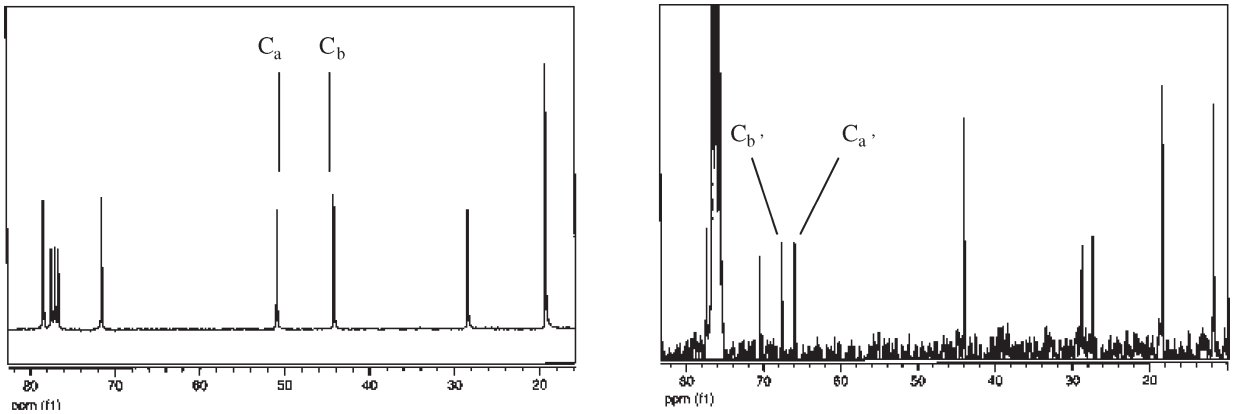


Figure 5. ^{13}C NMR spectra of the epoxy-containing starting material **2** and of the cross-linked product **3** recorded in $CDCl_3$

field can be observed, since the signals of the initial C_a and C_b (located respectively at 51 and 44 ppm) led to $C_{a'}$ and $C_{b'}$ (66 and 67.5 ppm).

Quantification of the yield of the cross-linking reaction

The next step consisted in determining the yield of the cross-linking reaction. This is of great importance for the macroscopic stability of the orientation, which depends strongly on the number of chromophores that have reacted with an epoxy side-chain. To assess this value, a copolymer (molar ratio MMA/GMA = 1) **4** of methyl methacrylate (MMA) and glycidyl methacrylate (GMA) was doped with the chromophore **1** to mimic the polymer PIII. The ratio between **1** and the glycidyl groups of **4** was analogous to that encountered in PIII (molar ratio 3/7). The advantage of this host–guest system compared with polymer PIII is that it enabled us to measure the unreacted chromophore by a simple washing, thus providing immediate access to the yield of the cross-linking reaction. Good film quality (transparency and thickness) were obtained by spin coating from a dichloromethane solution of the mixture of copolymer **4** and chromophore **1** on a glass substrate. In parallel, a MMA/GMA copolymer film with a catalytic amount of **1** (1% molar) was used as a reference, and was submitted to an analogous heating treatment.

After 30 min of curing in an oven at 140 °C, each film was washed thoroughly with dichloromethane. In the host–guest system, only a small amount of the starting chromophore (1% by weight) was recovered and characterized by ^{1}H NMR, while the remaining part, which had become completly insoluble, showed a strong attenuation of the epoxy band at 903 cm^{-1} and a color change from purple to reddish. The liquid NMR spectrum of the reference MMA/GMA copolymer showed no significant change compared with that of the starting material, indicating that no chemical change had occurred during the heating. The IR analysis confirmed that the material remained unchanged, in particular the epoxy band at 903 cm^{-1} was still present and intense.

From the above experiments, two conclusions could be drawn. First, the cross-linking reaction requires the presence of both a carboxylic acid functionality and an epoxy group and the self-polymerization of the epoxy groups does not occur under our curing conditions. Second, in both the solid state and solution, the cross-linking reaction proceeds with an almost quantitative yield since 99% of the loaded chromophores **1** have been covalently attached to the polymer backbone after heating.

Solid-state NMR of polymer PIII

Three films of the polymer PIII were prepared by spin coating from a trichloroethane solution. One film was heated at 140 °C for 15 min (to induce partial cross-linking), the second for 30 min (for complete cross-linking) and the third was not heated and constituted the reference system. The films were scratched out of the glass substrate and the ^{1}H MAS NMR and ^{13}C cross polarization (CP)/MAS NMR spectra were recorded. The ^{1}H MAS NMR spectra were not exploited because of the line broadening due to the homonuclear dipolar interaction between ^{1}H making the analysis of the cross-linking reaction unreliable. The assignments of the ^{13}C spectra

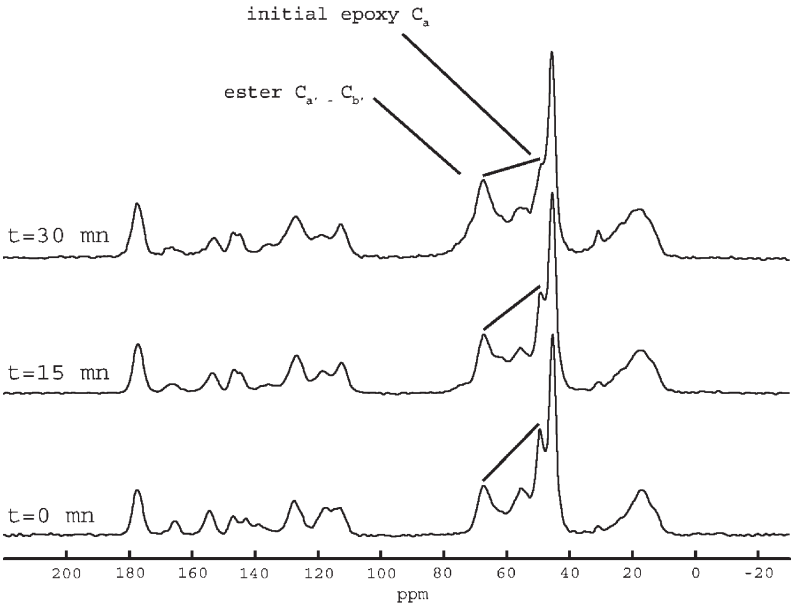


Figure 6. Evolution of the ^{13}C CP/MAS NMR spectrum of the polymer PIII with heating time

were made according to a liquid NMR study on compounds **2** and **3** (Fig. 6). The signal located at 49–50 ppm is assigned to the carbon C_a of the epoxy ring, and the signal around 67 ppm is that of the ester chain ($C_{a'}$ and $C_{b'}$) formed after cross-linking.

Spectra acquired under CP conditions are not quantitative. Nevertheless, considering the spectra of quasi-identical samples acquired under the same experimental conditions as in the present stage, it is still possible to compare the intensity ratio between two lines. Figure 6 clearly shows an increase of the 67 ppm line to the 49–50 ppm line intensity ratio with heating time in accordance with the expected changes from the cross-linking reaction.

These changes agree very well with those observed on the model compounds **1** and **3**, and they clearly indicated that the epoxy groups were opened by a nucleophilic attack of the carboxylic acid. To the best of our knowledge, this is the first NMR-based characterization of the cross-linking reaction in a polymeric system.

Quantum chemistry calculations

Although observed and reported previously,[12–14] the counterintuitive blue shift of the cross-linked polymer has never really been explained. This noteworthy phenomenon was also observed after the cross-linking of our model compound **1**, therefore this shift can be logically assigned to the formation of an ester bond. This hypothesis was further confirmed by preparing the methyl ester of the chromophore **5** (the synthesis of **5** has been described in a previous paper[12] (Fig. 7). Knowing that the ester group displays a stronger electron-withdrawing effect than the carboxylic acid, a red shift of the charge-transfer transition would have been expected to occur upon cross-linking.

The electronic transition responsible for the visible absorption of push–pull azo dyes is attributed to the vibronically coupled π–π^* and n–π^* electronic transitions which display a strong charge-transfer character.[19,20] The degree of frontier orbital overlap between the electron-rich phenylamine moiety and the electron-deficient nitrophenyl moiety is therefore of great importance for this transition (energy and probability). In order to shed some light on this phenomenon, we performed semiempirical quantum calculations on compounds very similar to DR1 carboxylate derivatives, the free carboxylic group **7** and its methyl-esterified analog **8** (Fig. 8).

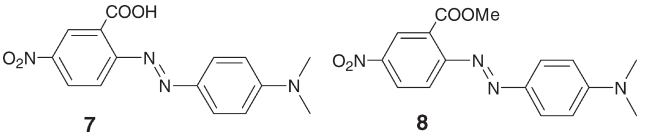


Figure 8. Structures of the molecules **7** and 8 used in the quantum chemistry calculations

The PM3 optimized structure of **7** is almost planar and evidences an intramolecular hydrogen bond between the N ('diazo') and the hydrogen of the—COOH group (Fig. 9). In contrast, the methyl-esterified **8** shows a dihedral angle value of 55° between the phenyl rings and a dihedral angle value closed to 74° between a phenyl ring and the plane define by the O—C═O atoms of the linked COOMe group (Fig. 9 and Table 1).

Therefore, **8** is clearly less conjugated than **7**. The UV–visible electronic spectra were simulated by the ZINDO-CI method.[27] The highest occupied molecular orbital (HOMO) and the two lowest unoccupied molecular orbitals (LUMO and LUMO + 1) are sketched in Table 1.

We have also gathered in Table 1 the characteristics of the first lowest electronic transition with an oscillator strength higher than 0.005 [e.g. transition energy (ΔE), oscillator strength (f), difference between excited- and ground-state dipole moments ($\Delta\mu$), character and weight of the main monoexcitations]. As expected, the energy differences between LUMO and HOMO or LUMO + 1 and HOMO are always higher for the less conjugated

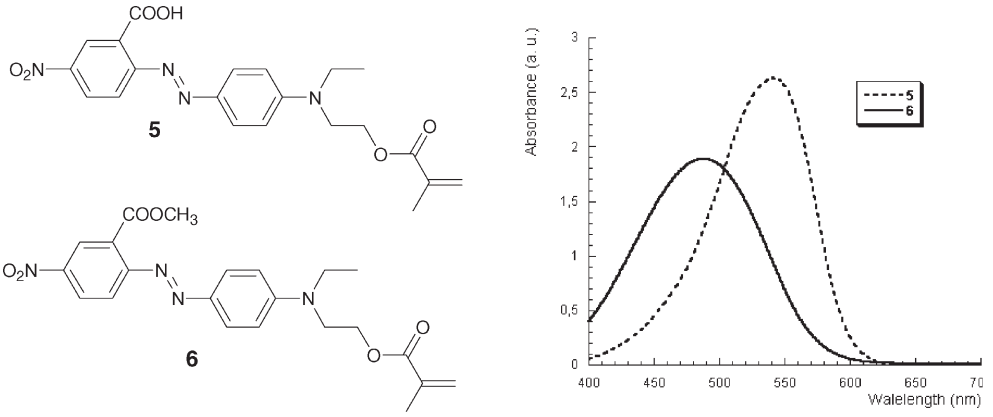


Figure 7. UV–visible absorption spectra of the acid **5** (doted line) and the esterified **6** derivatives (straight line) of a DR1 analog in dichloromethane solution

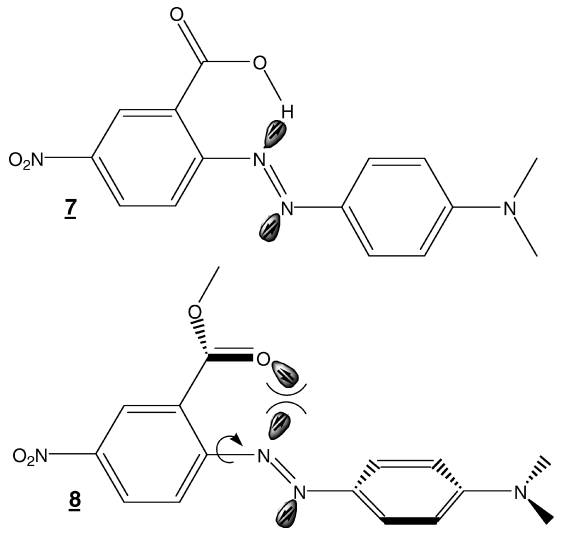


Figure 9. Dihedral twisting explaining the blue shift that occurs during the cross-linking reaction of polymer PIII

molecule **8**. Moreover, the analysis of the lowest electronic transition with a high oscillator strength value evidences a band for which the $\pi \rightarrow \pi^*$ character is unambiguously defined: for both compounds this transition is a mix of HOMO $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO + 1 monoexcitations. However, for **7**, the HOMO $\rightarrow$ LUMO monoexcitation has the major weight (64%) whereas for **8** this is the HOMO $\rightarrow$ LUMO + 1 which has the higher weight (48%). Therefore, the wavelength of the $\pi \rightarrow \pi^*$ transition for **8** is blue shifted relative to that of **7** by 47 nm. This value is similar to the experimental $\Delta\lambda_{max}$ value of 54 nm.

CONCLUSIONS

This contribution provides a full understanding of the thermal cross-linking mechanism of polymer PIII. Our approach was based on the study of the model compounds **1** and **3** and a ^{13}C solid-state MAS NMR investigation of polymer PIII. The locking of the orientation of chromophores in polymer PIII is attributed to the formation of new covalent ester-type bonds between the carboxylic acid group attached to the chromophores and the epoxy side-chains of the polymer. It is worth noting that the systematic blue shift observed upon esterification of the chromophore (**1**, **5**, **7** and in polymer PIII) is supplementary convincing evidence that the cross-linking reaction occurring in polymer PIII is due to the esterification of the carboxylic acid group and not the self-polymerization of the epoxides. The experiments indicated that this cross-linking reaction is quasi-quantitative and is completely finished after 30 min of heating at 140 °C. Furthermore, the results of a theoretical quantum chemistry study explained the blue shift of the visible absorption band that occurred with the cross-linking reaction. This shift is ascribed to the torsion of the chromophores induced by steric strains created by the formation of ester bonds. The distortion of the molecule arose from the loss of hydrogen bond with the carboxylic acid and the nitrogen lone pair of the azo group and the simultaneous repulsion between nitrogen and oxygen lone pairs consecutive to the ester bond formation (Fig. 9). As a consequence, the maximum absorbance of the ca 500 nm electronic absorption band was shifted to shorter wavelengths and its intensity was decreased owing to the lower strength of the dipolar transition. In the context of the two-state model of Oudar and coworkers,[18,21] the magnitude of the hyperpolarizability coefficient is known to be proportional to the square of the transition oscillator strength and inversely proportional to the square of the energy of the charge-transfer transition. According to this law, the torsion of the azoic chromophore must induce a decrease of the molecular first hyperpolarizability (β) and is therefore at the expense of the level of the overall electrooptic coefficient of the polymer (r_{33}). As such, moving the carboxylic acid group to another position (*meta* position of the nitrophenyl ring or reversing the positions of CO_2H and NO_2, for example) could certainly be advantageous for the overall electrooptic performance of the cross-linked polymer without affecting the stability of the dipole orientations. Finally, knowing that this type of cross-linking reaction is particularly efficient in decreasing the relaxation of chromophores, we believe that it can be used advantageously with other NLO chromophores grafted on methacrylate monomer copolymerized with GMA.

EXPERIMENTAL

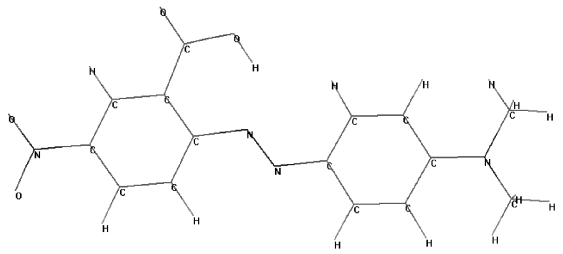
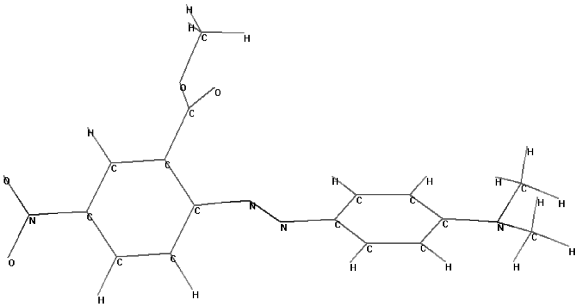
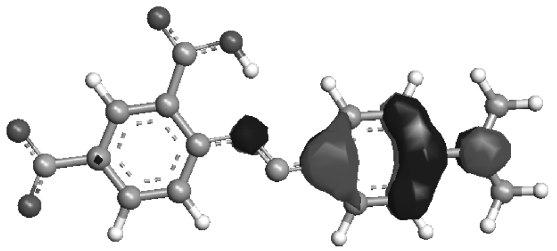
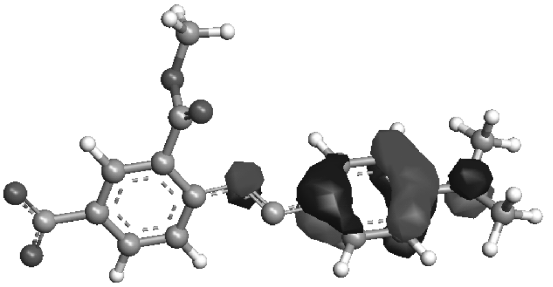
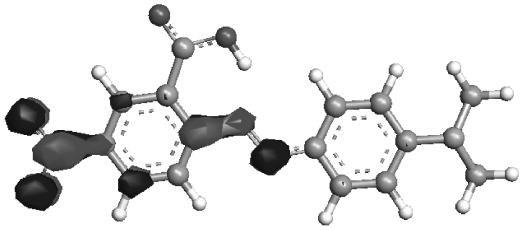
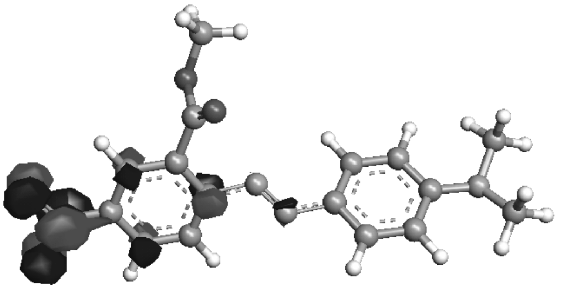
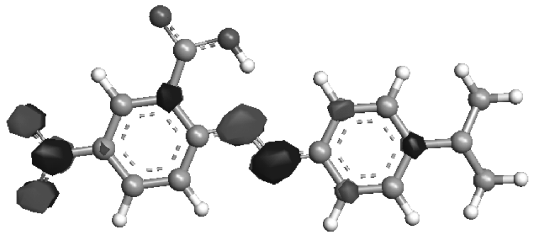
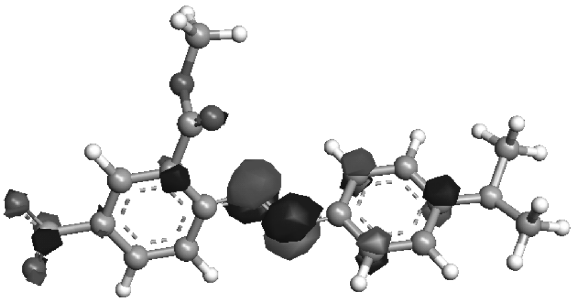
General methods

^1H NMR spectra were recorded on a Bruker ARX 400 MHz spectrometer. Chemical shifts for ^1H NMR spectra are referenced relative to residual ^1H in the deuterated solvent ($CDCl_3$, $\delta = 7.26$ ppm).

Solid-state NMR spectra were acquired at room temperature using a Bruker Avance 500 MHz spectrometer operating at 125.7 MHz for ^{13}C and using a Bruker 4 mm double-bearing probehead. ^{13}C spectra were referenced to TMS using adamantane as a secondary reference. $\{^1H\}$–^{13}C CP/MAS spectra were acquired using a ramp–amplitude sequence,[22] a 15 kHz MAS spinning rate, a 2 ms contact time and a repetition time of 2 s. ^1H decoupling during acquisition was achieved using the TPPM method[23] with an r.f. field of $\sim$60 kHz.

UV–visible absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. Fourier transform IR spectra were recorded on pressed KBr pellets on a Bruker Vector 22 spectrometer. Mass spectra were recorded on an HP 5989A EI-MS spectrometer or on a JMS-700 double-focusing mass spectrometer of reversed geometry equipped with electrospray ionization (ESI)

Table 1. HOMO, LUMO, LUMO + 1 sketches and energies, characteristics of the lowest electronic transition with an oscillator strength higher than 0.005: transition energy (ΔE), oscillator strength (f), difference between excited-and ground-state dipole moments ($\Delta\mu$), character and weight of the main monoexcitations calculated by the ZINDO/S-CI method

	
ΔE =3.07 eV f=1.14 $\Delta\mu$=14.0 D 64% (HOMO $\rightarrow$ LUMO) $\pi \rightarrow \pi^*$ 27% (HOMO $\rightarrow$ LUMO+1) $\pi \rightarrow \pi^*$	ΔE =3.47 eV f=1.01 $\Delta\mu$=15.4 D 36% (HOMO $\rightarrow$ LUMO) $\pi \rightarrow \pi^*$ 48% (HOMO $\rightarrow$ LUMO+1) $\pi \rightarrow \pi^*$
HOMO = –8.36 eV 	HOMO = –8.24 eV 
LUMO = –2.48 eV 	LUMO = –2.22 eV 
LUMO+1 = –1.73 eV 	LUMO+1 = –1.28 eV 
Chromophore **7**	Chromophore **8**

source (JEOL, Akishima, Tokyo, Japan). Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040–0.063 mm mesh) or with SDS neutral alumina (0.05–0.2 mm mesh). Air-sensitive reactions were carried out under argon in dry solvents and glassware. Chemicals were purchased from Aldrich and used as received. 2-({4′-[ethyl(methacryloyloxyethyl)amino]phenyl}diazenyl)-5-nitrobenzoate (**5**) was synthesized according to a previously published method.[12]

Computational methods

The PM3 semi-empirical Hamiltonian[24] was used as implemented in the quantum mechanical programs MOPAC2000.[25] All geometries were completely optimized, i.e. no restrictions on geometry were assumed. In order to limit degrees of freedom for this type of molecule, calculations were performed on less substituted analogs: the EtN–C_2H_4–OC(O)–C(Me)═CH_2 group was replaced by an—NMe_2 group.

Starting from the previous geometry, we selected in the Arguslab program[26] the ZINDO-CI method parameterized to reproduce UV–visible spectroscopic transitions.[27] During these calculations, the following overlap weighting factors were used: 1.267 for π–σ and 0.585 for π–π. Monoexcitations were constructed from a 20 molecular orbital window spanning the frontier orbitals (10 occupied and 10 vacant). Configuration interaction energies were adjusted for first-order solvent effect through the self-consistent reaction field model of Karelson and Zerner:[28] solute was embedded in a spherical cavity of 7.5 Å radius; CH_2Cl_2 solvent is described by its dielectric constant $\varepsilon = 9.08$ and refractive index $n = 1.423$.

Synthesis of the compounds

*2-{[4′-(diethylamino)phenyl]diazenyl}-5-nitrobenzoic acid (**1**).* A solution of 2-amino-5-nitrobenzoic acid (1.5 g, 8 mmol) in 17 ml of 0.5 N NaOH (8.5 mmol) was stirred at 80 °C until complete dissolution of the compound. After cooling to room temperature (r.t.), an aqueous solution of 10 N HCl (8 ml, 80 mmol) was added dropwise, leading to a bright yellow precipitate. The mixture was cooled to 0 °C and $NaNO_2$ (0.552 g, 8 mmol) in 2 ml of H_2O was added. The solution was stirred for 1 h at this temperature. The solution was then filtered and the yellow filtrate was added to *N*,*N*-diethylaniline (1.190 g, 8 mmol). After 12 h of stirring at r.t., dichloromethane and water were added to the mixture. The organic layer was extracted, dried on $MgSO_4$ and evaporated. The residue was chromatographied on silica eluted with CH_2Cl_2–Et_2O (8:2) to give 1.69 g of **1** (60%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 14.25 (s, 1H), 9.12 (d, 1H, $^4J = 2.4$ Hz), 8.36 (dd, 1H, $^4J = 2.4$ Hz, $^3J = 9.0$ Hz), 8.10 (d, 1H, $^3J = 9.0$ Hz), 7.77 (d, 2H, $^3J = 9.0$ Hz), 6.77 (d, 2H, $^3J = 9.0$ Hz), 3.57 (q, 4H, $^3J = 4.8$ Hz), 1.32 (t, 6H, $^3J = 4.8$ Hz). IR (cm^{-1}): 3450 (m, ν_{st}, OH), 2980–2940 (m, ν_{st}, Alk), 1703 (s, ν_{st}, C═O acid), 1605 [s, Ar(ring)], 1518 (s, ν_{asym}, NO_2), 1336 (s, ν_{sym}, NO_2). UV–vis (CH_2Cl_2): λ_{max}, 558 nm.

*2″-Hydroxy-3″- isobutoxypropyl - (2 - {[4′-(diethylamino)-phenyl]diazenyl}-5-nitrobenzoate) (**3**).* A solution of **1** (50 mg, 0.15 mmol) and **2** (98 mg, 0.75 mmol) in DMF (2 ml) was stirred at 140 °C in a sealed tube for 2 h. The solvent was then rotary evaporated and the residue, after drying under vacuum, was purified by chromatography on silica gel, eluting with CH_2Cl_2–Et_2O (9:1). An orange solid was recovered (70 mg, 99%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.55 (d, 1H, $^4J = 2.7$ Hz), 8.30 (dd, 1H, $^4J = 2.7$ Hz, $^3J = 9.0$ Hz), 7.80 (d, 2H, $^3J = 9.6$ Hz), 7.66 (d, 1H, $^3J = 9.0$ Hz), 6.64 (d, 2H, $^3J = 9.6$ Hz), 4.37 (m, 2H), 4.07 (m, 1H), 3.40 (m, 6H), 3.07 (d, 2H, $^3J =$ 6.6 Hz), 2.47 [m, 1H (OH)], 1.73 (m, 1H), 1.17 (t, 6H, $^3J = 7.3$ Hz), 0.80 (d, 6H, $^3J = 6.8$ Hz). ^{13}C NMR (300 MHz, $CDCl_3$), δ (ppm): 165.32, 155.10, 146.29, 142.52, 127.55, 127.29, 125.98, 125.71, 124.46, 119.02, 110.13, 77.35, 70.44, 67.55, 65.87, 43.92, 27.30, 18.23, 11.64. IR (cm^{-1}): 3435 [m, ν_{st}, OH (epoxy opening)], 2960–2870 (m, ν_{st}, Alk), 1728 (s, ν_{st}, C═O acid), 1601 [s, Ar(ring)], 1517 (s, ν_{asym}, NO_2), 1331 (s, ν_{sym}, NO_2), 1265 (s, *i*-Bu), 1140 (s, ν_{st}, C–O–C). UV–vis (CH_2Cl_2): λ_{max}, 511 nm MS: *m*/*z* 472 (M^+), 293 (100%).

*Methyl [2-({4′-[ethyl(methacryloyloxyethyl)amino]phenyl} diazenyl)-5-nitro benzoate] (**6**).* To a solution of **5** (1 g, 2.35 mmol) in dry acetone (20 ml) were added potassium carbonate (2 g, 11.7 mmol) and dimethyl sulfate (0.45 ml, 4.7 mmol). The solution was stirred 10 min under argon at r.t. Water was added and the mixture was extracted twice with CH_2Cl_2. The organic layer was dried on $MgSO_4$, filtered and evaporated. The residue was filtered through silica gel using dichloromethane as solvent, affording, after evaporation, a red–orange product (1.06 g, 100%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.63 (d, 1H, $^4J = 2.1$ Hz), 8.36 (dd, 1H, $^4J = 2.1$ Hz, $^3J = 9.0$ Hz), 7.87 (d, 2H, $^3J = 9.3$ Hz), 7.75 (d, 1H, $^3J = 9.0$ Hz), 6.81 (d, 2H, $^3J = 9.3$ Hz), 6.11 (s, 1H), 5.60 (s, 1H), 4.37 (t, 2H, $^3J = 6.0$ Hz), 3.95 (s, 3H, COOMe), 3.74 (t, 2H, $^3J = 6.0$ Hz), 3.55 (q, 2H, $^3J = 7.5$ Hz), 1.95 (s, 3H), 1.27 (t, 3H, $^3J = 7.5$ Hz). ^{13}C NMR (300 MHz, $CDCl_3$), δ (ppm): 178.2, 166.90, 155.99, 152.70, 145.12, 144.11, 135.84, 135.81, 128.70, 126.69, 126.29, 125.44, 120.05, 111.52, 61.62, 52.74, 48.78, 45.71, 18.34, 12.28. IR (cm^{-1}): 2980–2940 (m, ν_{st}, Alk), 1736 (s, ν_{st}, C═O ester), 1724 (s, ν_{st}, C═O ester), 1635 [s, Ar(ring)], 1519 (s, ν_{asym}, NO_2), 1336 (s, ν_{sym}, NO_2), 1164 (m, n_{st}, C–O–C), 832 (m, n_{oop}, CH_2═C). UV–vis (CH_2Cl_2): λ_{max}, 488 nm.

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