Highly Cross-Linked Polyurethane with Enhanced Stability of Second-Order Nonlinear Optical Properties

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ABSTRACT: A new material processing approach yielding a thermally curable, optically active second-order material, based on a polyurethane derived from poly[(phenyl isocyanate)-*co*-formaldehyde] and 4-[[*N*-(2-hydroxyethyl)-*N*-methylamino]phenyl]-4′-[(6-hydroxyhexyl)sulfonyl]azobenzene is presented. In this procedure a liquid polymer, poly[(phenyl isocyanate)-*co*-formaldehyde], containing one isocyanate group on each of the phenyl rings was selected in order to increase both the efficiency and the uniformity of the cross-linking reaction between polymer chains during the thermal curing process. The cross-linking reaction carried out for a period of 30 min at 160 °C produces a rigid polymeric structure with a glass transition temperature of 142 °C. The presented approach has been applied for preparation of high optical quality films for nonlinear optical (NLO) applications which, when corona poled and thermally cured, reveal a strong optically nonlinear second-order activity with a macroscopic second-order susceptibility $\chi^{(2)}$ of 3×10^{-7} esu. The NLO activity of this material was monitored at 100 °C for a period of 1200 h without showing detectable changes in the $\chi^{(2)}$ value.

Introduction

Second-order nonlinear optical (NLO) materials based on organic compounds have been receiving great attention because of their potential applications in the field of telecommunication, optical signal processing, optical switching, optical sensing, etc.[1] The organic materials appear to be superior because of their larger optical nonlinearity and faster response time than the inorganic ones. Among the organic systems the NLO polymers are of considerable interest, mainly because of their mechanical endurance and easy processability to form desirable optical devices.[2,3] Although the advantage of second-order nonlinear optical polymers was recognized early and extensive research has been focused on this field,[4–9] the stability of the molecular dipole alignment induced by an electric field, particularly at elevated temperatures, is still one of the most critical problems in the design of second-order active polymers for NLO application.

Recently, a high glass transition temperature polyimide doped with NLO molecules[10] (guest–host systems) and cross-linkable polymers with covalently linked, optically active, second-order moieties based on chemical or photochemical reactions have been investigated in order to enhance the temporal stability of poled structures.[11–16] These materials show significant improvement in their performance and are reported to be temporally stable at temperatures around 90 °C. However, these systems seem, until now, to have their restrictions which are the limited doping level in the case of high-T_g guest–host systems and an increase in the optical losses due to the light scattering introduced by the formation of unevenly cross-linked domains.

In the present work, we have investigated the basic chemical properties of a thermosetting polyurethane which was synthesized by the reaction between poly[phenyl isocyanate)-*co*-formaldehyde], a liquid polymer, and 4-[[*N*-(2-hydroxyethyl)-*N*-methylamino]phenyl]-4′-[(6-hydroxyhexyl)sulfonyl]azobenzene and its applicability as an optically nonlinear second-order material.

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So far there has not been any reported cross-linkable polymeric system between a fully amorphous liquid polymer and NLO chromophores. The approach presented here uses poly[(phenyl isocyanate)-*co*-formaldehyde] which can be described as the precursor for the final polymeric structure, containing one isocyanate group on each phenylene ring, and which can be cross-linked with the hydroxy groups of the NLO chromophore across the neighboring polymer chains to prevent the relaxation of its molecular dipole alignment. The NLO chromophore, 4-[[*N*-(2-hydroxyethyl)-*N*-methylamino]-phenyl]-4′-[(6-hydroxyhexyl)sulfonyl]azobenzene, was chosen because of the two highly reactive hydroxy groups terminating the molecule along its molecular dipole axis and its very high second-order activity.[17,18] The design of this system was driven by a few promises. We expected that an amorphous liquid polymer can undergo, efficiently and uniformly, a cross-linking reaction without affecting the optical quality of the final rigid structure. Furthermore, a polymer with one cross-linking site located on every phenylene group should allow a very high doping level with the second-order chromophore which, in turn, is expected, after the cross-linking, to increase the glass transition temperature and thus the rigidity of the final material. This is expected to improve the temporal stability, even at elevated temperatures, of the electrically induced orientation of the NLO chromophores.

Experimental Section

Materials. 4-[[*N*-(2-Hydroxyethyl)-*N*-methylamino]phenyl]-4′-[(6-hydroxyhexyl)sulfonyl]azobenzene was prepared according to the published procedure.[17] Poly[(phenyl isocyanate)-*co*-formaldehyde], cyclopentanone, toluene (anhydrous), and *N*,*N*-dimethylformamide (DMF, anhydrous) were purchased from Aldrich Chemicals and used as received.

Poly[(phenyl isocyanate)-*co*-formaldehyde] (100 mg, 0.70 mM) and 4-[[*N*-(2-hydroxyethyl)-*N*-methylamino]phenyl]-4′-[(6-hydroxyhexyl)sulfonyl]azobenzene (156 mg, 0.35 mM) were dissolved, prior to the casting of the films, in 1 g of a mixture

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of solvents (toluene:cyclopentaneone:DMF = 5:4:1 by weight). This solution was stirred for 5 min before spin coating. The solution was then filtered through a 0.45-μm Teflon membrane filter (Aldrich) and spun-cast onto glass substrates with an indium tin oxide (ITO) conductive layer, producing extremely transparent reddish films. After spin-coating the films were placed in a dessicator directly and dried in vacuum (10^{-2} Torr) at ambient temperature for 3 h. The thickness of the polymer films was determined after the electric poling and curing processes by using a Tencor Alpha Step 100 surface profilometer. The thicknesses of the films ranged between 0.5 and 5 μm, depending upon the viscosity of the solution and the spinning rate. The refractive indices at the fundamental (1064 nm) and second harmonic (532 nm) wavelengths for the poled films were obtained by combining the prism coupling technique, which was used for measuring two refractive index values at 823 and 632.8 nm, and the interference fringe method, which was used to determine the spectral dispersion of refractive indices in the range between 600 and 1800 nm. The refractive index at 1064 nm was 1.651, and it could be obtained directly from the spectral dispersion curve. The refractive index of 1.773 at 532 nm was obtained by extrapolation of the spectral dispersion curve, but it has a limited accuracy because of the relatively strong absorption of the chromophore at this wavelength.

In order to fabricate the optically active, second-order films, a corona discharge introduced electrical poling was used. The poling was performed in a wire-to-plane geometry[19,20] under in situ conditions which allows one to optimize the poling efficiency by screening the influence of the poling process parameters (such as the intensity of corona discharge, the distance between the film surface and the corona wire, temperature, and poling time) on the second harmonic generation signal obtained from the film being poled. We used the positive polarity of the 25-μm-thick tungsten corona wire which has proven to be more effective than the negative one. During the poling process the strength of the external electric field imposed across the NLO layer was monitored by using an electrostatic voltameter (Model 344, from TREK Inc.). In order to prevent the occurrence of a discharge from the wire, directly to the voltameter sensor head, its distance from the corona wire had to be bigger than the air gap between the wire and sample surface. Depending upon the ambient air humidity in our poling setup, the value of the effective poling field varied between 2.3×10^8 and 4.5×10^8 V m^{-1}. Our attempts to increase the poling field and improve further the poling efficiency produced an uncontrolled corona discharge, resulting in deterioration of the optical quality of our films. The poling process was started at room temperature, and the sample temperature was increased up to 160 °C with a heating rate of 10 °C/m. Then the sample was cured at this temperature for 30 min with the electric field still on. The curing procedure was the same as described for the reactions between isocyanate and hydroxyl groups.[12] In the next step the sample was cooled down to room temperature. The electric field was removed when the temperature of the sample reached 100 °C. This was followed by a rapid drop in the SHG signal intensity to the level of 65−70% of its maximum value.

Analysis. The differential scanning calorimetry (DSC) and the thermogravimetry (TG) were performed under an air atmosphere on a thermal analysis system consisting of Shimadzu DSC-50 and Shimadzu TGA-50 units. A heating rate of 10 °C/min was applied for the two methods. IR spectra were obtained from a Mattson Alpha Centauri FT-IR instrument. The IR spectra of the polymeric system before and after the cross-linking reaction were obtained by using sodium chloride disks which were spin-coated with the polymer solution used for the preparation of films for optical measurements. UV−vis spectra of the precursor polymer and the cross-linked polymer were recorded on a Shimadzu UV-3101PC spectrophotometer.

Optical Measurements. The second harmonic generation (SHG) measurements of the poled and cured polymer films were performed on the experimental setup described earlier.[21] The macroscopic second harmonic susceptibility $\chi^{(2)}$ has been measured using the angular dependence method. The results have been obtained by comparing the SHG intensity produced by the poled polymeric film to that from a Y-cut quartz crystal. We assumed the second harmonic coefficient d_{11} of a Y-cut quartz crystal to be equal to 0.81×10^{-10} esu[22] as the value which appears to be more consistent with the data we obtained from electrooptic measurements than the most frequently used $d_{11} = 1.17 \times 10^{-9}$ esu.[21] The electrooptic coefficient r of the poled film was determined using the ellipsometric technique by measuring the relative amplitude and phase changes of the reflected 632.8-nm He−Ne laser beam with p and s polarizations.[23,24]

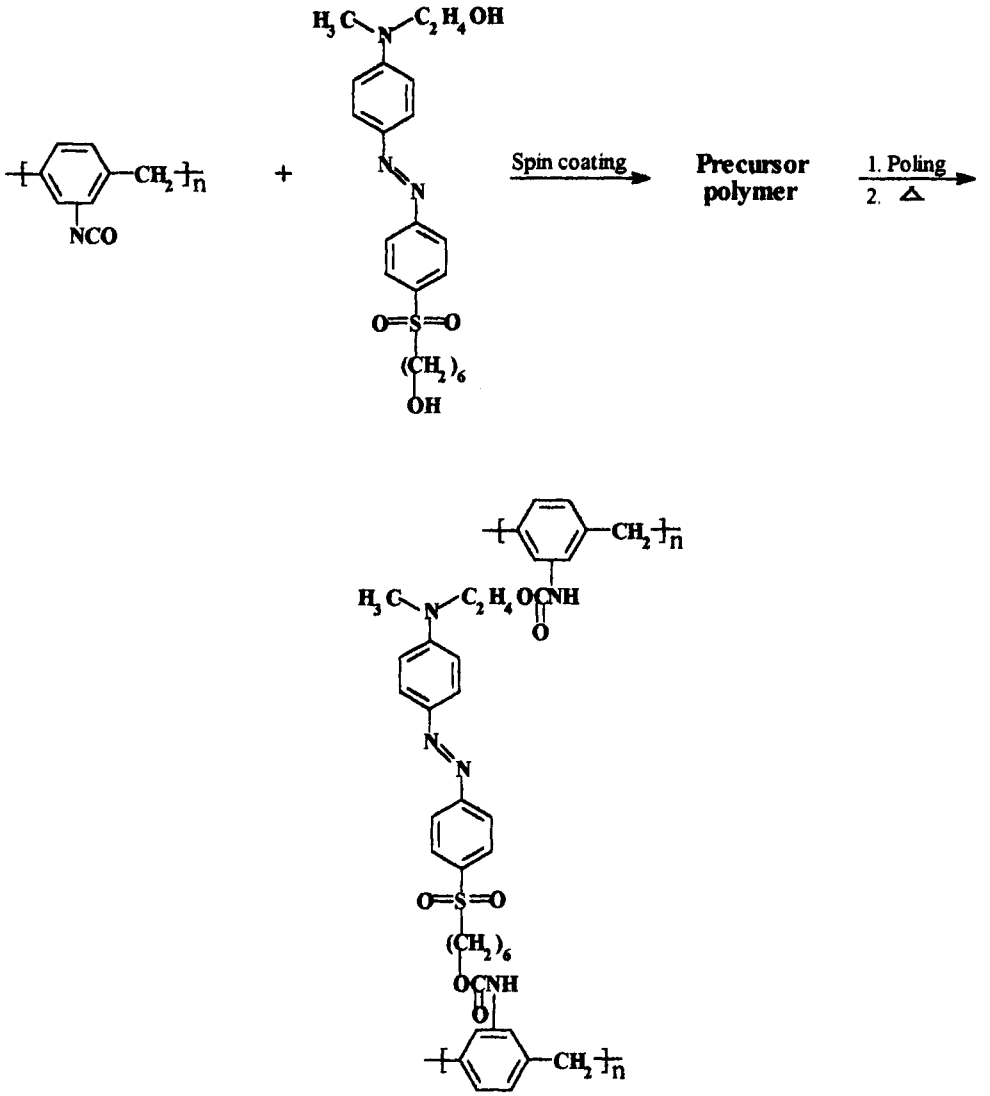
Results and Discussion

The formation of the cross-linked polymer is shown in Scheme 1. As mentioned before, the curing process was carried out at a temperature of 160 °C for 30 min. After the curing process was accomplished, a solubility test was performed in which the films were dipped into a mixture of cyclopentanone and DMF (50:50 by weight). In contrast to the starting system which was soluble in many organic solvents, such as ketones (cyclopentanone, cyclohexanone, acetone), chlorinated hydrocarbons (chloroform, methylene chloride, dichloroethane), DMF, and their mixtures, the cross-linked structure does not dissolve or even swell when exposed to the solvent for 30 min. This fact indicates the high efficiency of a thermally induced cross-linking reaction between poly[(phenyl isocyanate)-*co*-formaldehyde] and 4-[[*N*-(2-hydroxyethyl)-*N*-methylamino]phenyl]-4′-[(6-hydroxyhexyl)sulfonyl]azobenzene. The solubility test was performed for samples cured for 30 min at temperatures ranging between 100 and 200 °C. The samples cured at temperatures below 125 °C show more or less solubility in the solvents specified above. The samples reacted at temperatures between 125 and 150 °C cannot be dissolved, but they exhibit clearly some swelling effects because of the solvent intake by the polymeric layers. The swelling is more pronounced for the samples cured between 125 and 145 °C than for that treated at 150 °C. At the curing temperature of 160 °C no traces of material swelling could be observed. Any further increase in the curing temperature above 160 °C did not appear to have any influence on the properties of the final polymeric structure, except that curing time could be reduced to just 5 min when a temperature of 200 °C is applied. In addition, a mechanical abrasion test was performed in order to verify the curing parameters. When the material remains un-cross-linked or cross-linking is far from being complete, the surface of the polymeric film is soft, and it can be scratched easily. When the degree of cross-linking reaction increases, the polymeric layers become more and more rigid, resisting scratching by sharp tips. Similarly as in the solubility test, also in the abrasion test the curing temperature of 160 °C has proven to be sufficient to complete the cross-linking reaction.

The DSC and TGA of the cross-linked polymer are given in Figure 1. These thermograms were obtained after thermal treatment of the precursor polymer for 30 min at 160 °C. As shown in Figure 1, the glass transition temperature of the cross-linked polymer appears at 142 °C. The same value of T_g was obtained when higher temperatures were used to introduce the cross-linking. When samples cured at temperatures below 160 °C were scanned, we observed a gradual shift of T_g to lower temperatures.

A second characteristic point on the DSC curve, common for all our samples, is the temperature of 258 °C, when thermal degradation of the polymer sets in. A same threshold temperature for the thermal decomposition was obtained from TGA in Figure 1.

Scheme 1



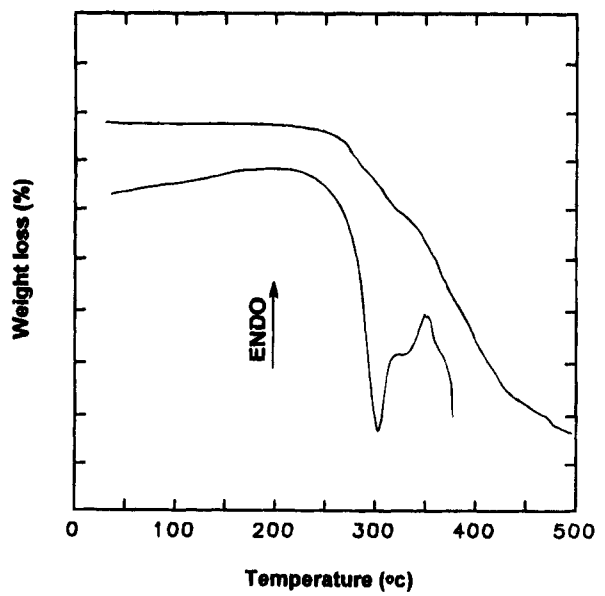


Figure 1. DSC and TGA thermograms of cross-linked polyurethane.

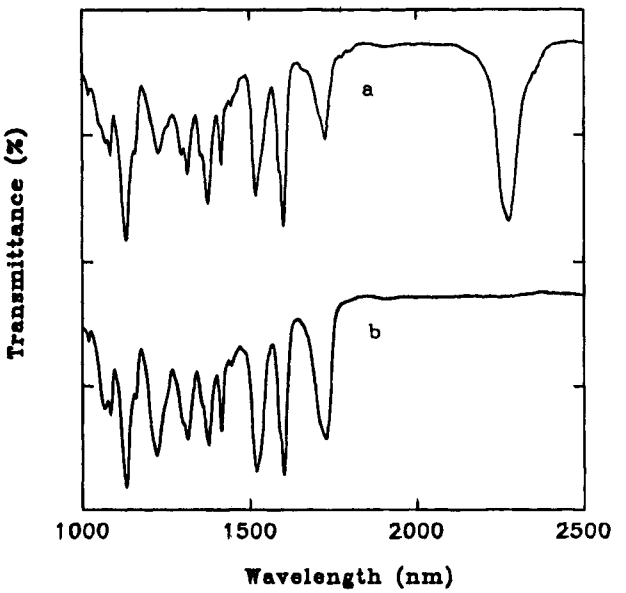


Figure 2. IR spectra of (a) the precursor polymer and (b) the cross-linked polymer.

In Figure 2 the FT-IR spectrum of the cross-linked polymer is compared with that of the precursor polymer.

As known, the −C=N− stretching of the isocyanate group has a well-resolved absorption peak at 2270

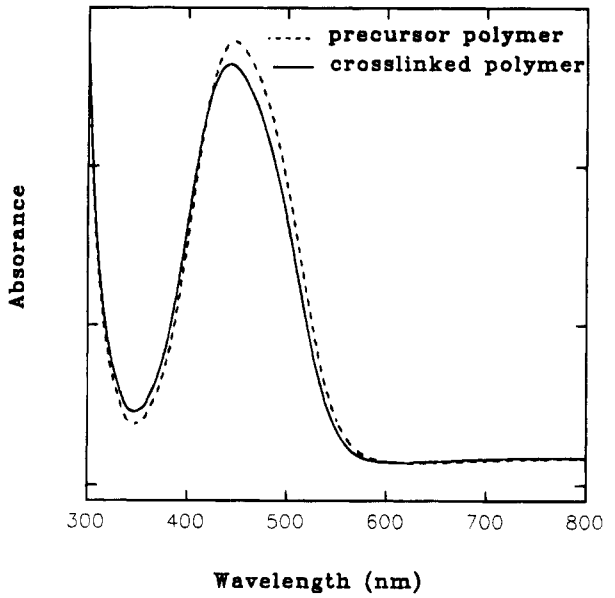


Figure 3. UV–vis spectra of the precursor polymer and the cross-linked polymer.

cm^{-1}.[24] The pristine material exhibits a sharp absorption peak at 2276 cm^{-1} of the isocyanate group of the poly[(phenyl isocyanate)-*co*-formaldehyde] (Figure 2a). After cross-linking at 160 °C for 30 min the band of the isocyanate group disappears completely from the spectrum. These IR data provide strong evidence for the very high degree of the thermally induced cross-linking reaction between poly[(phenyl isocyanate)-*co*-formaldehyde] and 4-[[*N*-(2-hydroxyethyl)-*N*-methylamino]phenyl]-4′-[(6-hydroxyhexyl)sulfonyl]azobenzene.

In Figure 3, UV–vis absorption spectra of a thin film of the precursor polymer (λ_{max} = 449 nm) and that after its complete cross-linking (λ_{max} = 440 nm) are presented. The λ_{max} of the fully cross-linked system is shifted slightly toward shorter wavelengths, compared with that of the precursor polymer. This behavior is similar to what has been observed in other cross-linked systems[16,17] and what can be explained by some distortion in the geometry of the chromophore caused by partial shrinking of the polymeric matrix during cross-linking.

In our electrical poling experiments we applied the thermal curing conditions (160 °C for 30 min) which appear to introduce to our polymer the highest cross-linking efficiency without causing any deterioration in their optical quality. As mentioned before, the poling field was removed during the cooling down stage of our experiments, when the sample temperature reached 100 °C. Immediately a sharp decay in the second harmonic signal intensity, reaching up to 70% of its value before removal of the poling field, could be seen. This drop in the second harmonic generation signal was followed by a complete disappearance of the corona discharge induced voltage on the surface of the poled sample, which indicates the absence of residual charges on the film surface. We assume that this initial decay is due to the spontaneous randomization of an un-cross-linked fraction of the aligned chromophore which has not been reacted completely between the polymer chains. When the electric field was removed at room temperature, the SHG signal decayed slower, over the first few hours, to reach the same intensity level as was obtained by removing the electric field at 100 °C. The poled and cured polymer films possess a high second-order optical activity with a macroscopic second-order susceptibility $\chi^{(2)}$ of 3 × 10^{-7} esu. The $\chi^{(2)}$ could be obtained at this

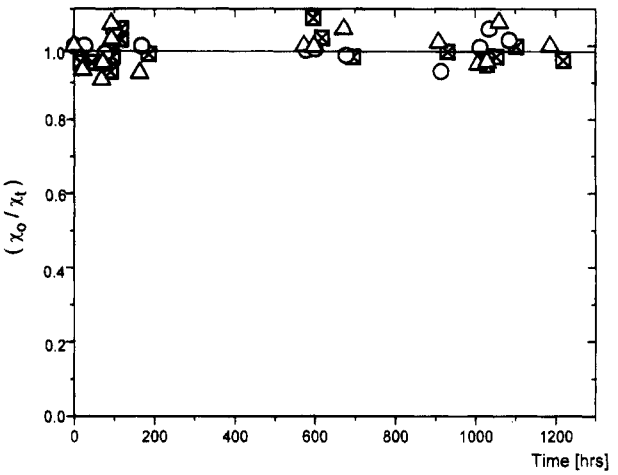


Figure 4. Temporal stability of macroscopic second-order hyperpolarizability at 100 °C.

level because of a very high number density of the NLO chromophore, 4-[[*N*-(2-hydroxyethyl)-*N*-methylamino]-phenyl]-4′-[(6-hydroxyhexyl)sulfonyl]azobenzene, which was estimated to be 10^{21} cm^{-3} (61% of the chromophore by weight). In addition, it should be noted that the $\chi^{(2)}$ value depends strongly upon the poling process parameters such as the poling electric field, the atmosphere the corona discharge is produced in, the poling temperature, and poling time. Therefore, we assume the $\chi^{(2)}$ value reported here may not be optimized completely.

The second-order activity of our material shows a pronounced spectral dispersion. When considering the electrooptic coefficient r_{33}, one can see that its value varies with the operational wavelength. With the 632.8-nm line of a He–Ne laser we determined the r_{33} coefficient of a permanently poled film to be 29.8 pm/V. At 687 nm the value of r dropped to 18.1 pm/V, to retain only 13.2 pm/V at 823 nm. When compared with the intrinsic optical losses at these wavelengths equal to 21.5 dB/cm at 632.8 nm and 3.11 dB/cm at 823 nm, spectral dispersion of the r_{33} coefficient indicates a strong absorption resonance enhancement of the second-order activity at shorter wavelengths. We obtained a constant value of the r_{33} coefficient for our material at modulation ac frequencies ranging between 1 Hz and 100 kHz, which indicates that our electrooptic coefficient does not include any frequency-dependent orientational contribution. The films poled under conditions described in this paper exhibit excellent long-term temporal stability of their nonlinear properties. No decay in the $\chi^{(2)}$ value was observed after a small fraction of the unreacted chromophore molecules is allowed to relax in the short step of the initial decay. After that the material retains its optical activity even at elevated temperatures. We monitored the value of $\chi^{(2)}$ for three samples of poled films which were stored at a temperature of 100 °C over a period of 50 days. As shown in Figure 4 there is, within experimental error, no decay in the second-order nonlinear optical activity of those samples. This excellent stability of the poling-introduced NLO chromophore alignment proves the cross-linking reaction in our system to be the very efficient. This corresponds very well with the disappearance of the isocyanate and hydroxyl groups we discussed above representing the changes in the IR spectrum (Figure 2) introduced by the cross-linking reaction.

In Figure 5 the thermal stability of the $\chi^{(2)}$ value is presented. It can be seen that the main portion of the SHG signal disappears rapidly when the film temperature was increased up to 150 °C. However, there is

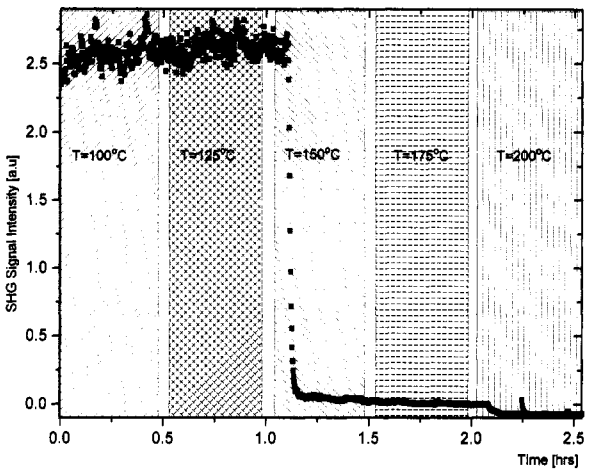


Figure 5. Thermal stability of the SHG signal obtained from poled and cured material.

still a small fraction of the SHG signal remaining. It does not decay further until the sample temperature reaches 200 °C. We can explain the main part of the decay in the SHG signal intensity occurring around 150 °C as a rapid orientational randomization of the NLO chromophore after the glass transition temperature of the polymer has been exceeded. Though we cannot find a feasible mechanism justifying the presence of this high-temperature resistant poled fraction of chromophore in our system, there is no evidence of any other phase transition occurring around 200 °C which could be taken under consideration in regard to this phenomenon.

Conclusion

A highly cross-linked thermally stable electrically aligned polyurethane structure derived from poly[(phenyl isocyanate)-*co*-formaldehyde] and 4-[[*N*-(2-hydroxyethyl)-*N*-methylamino]phenyl]-4′-[(6-hydroxyhexyl)sulfonyl]azobenzene was prepared under *in situ* conditions when simultaneously poled and thermally cross-linked. The optically nonlinear polymeric material exhibits a high second-order activity described by a $\chi^{(2)}$ value of 3×10^{-7} esu and an electrooptic coefficient r_{33} of almost 30 pm/V at 633 nm. The poled and thermally cured polymeric films exhibit excellent temporal stability of their nonlinear properties, retaining their activity even when stored for 50 days at 100 °C.

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