Cross-Linked Polymer Materials for Nonlinear Optics. 2. Polyurethanes Bearing Azobenzene Dyes

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ABSTRACT: A cross-linked nonlinear optical urethane polymer is prepared from 4-[(2-hydroxyethyl)sulfonyl]-4′-[*N*,*N*-bis(2-hydroxyethyl)amino]azobenzene (1) and toluene diisocyanate by simultaneously corona poling and cross-linking at 145 °C for only 30 min. This material shows very promising results as NLO material: SHG measurements show a resonantly enhanced d_{33} value of 60 pm/V at 1064 nm 1 day after poling and a 34% decrease after 800 h at 70 °C. Moreover, electrooptic measurements on contact poled samples at 175 °C result in a value of the pockels constant r_{33} of 12.3 pm/V. Poling at 190 °C results in a decrease of less than 40% after 100 h at 150 °C. Additional measurements show a linear interrelation between the electrooptic and the pyroelectric constant, as well as between the electrooptic constant and the dielectric polarization.

Introduction

In the near future there is a definite need for second-order nonlinear optical (NLO) materials for, among others, very fast information transmission. Compared to other materials, NLO polymers offer many advantages, for instance, a high nonlinear optical activity and a good processability.[1] However, the stability of the NLO activity of the present NLO polymers is still a problem, especially when the materials have to be integrated in hybrid electronic and optical devices where short excursions to high temperatures are necessary.[2] The stability of the NLO activity can be much improved by using cross-linked polymers.[3] In the preceding paper we have shown that incorporation of a D-π-A NLO chromophore into a cross-linked polymer by covalent fixation of both the donor and acceptor side to the polymeric matrix leads to materials having stable NLO coefficients.[4] The NLO material consisted of a UV-cured polymethacrylate with a 4-amino-4′-sulfonylazobenzene as a chromophore. However, the rather low absolute values of the NLO coefficients obtained were most likely caused by degradation of the chromophore by the UV light during the polymerization step.

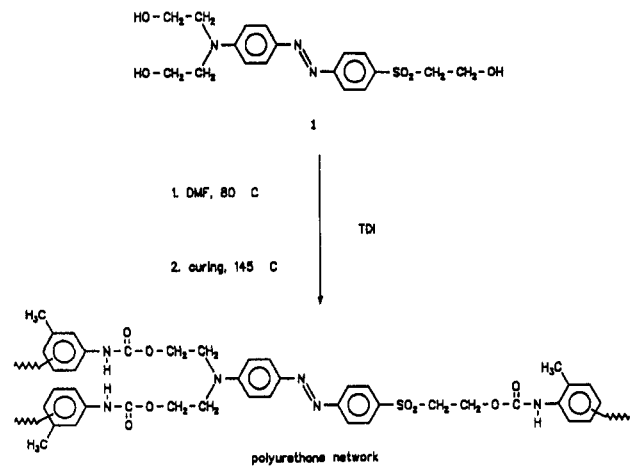
In this paper results are presented on the chromophore 4-[(2-hydroxyethyl)sulfonyl]-4′-[*N*,*N*-bis(2-hydroxyethyl)amino]azobenzene (1) of which both the donor and acceptor groups have been covalently fixed into a polyurethane network by a thermal reaction with toluene diisocyanate (TDI).

Experimental Section

General Procedures. NMR spectra were recorded on a Varian VXR400 spectrometer (^{1}H resonance frequency 400 MHz, ^{13}C resonance frequency 100 MHz) using a 5-mm switchable probe and a VXR 5000 data system. As a reference, the chemical shifts of deuterated DMSO were taken at 2.49 ppm for the proton spectrum and at 39.5 ppm for the ^{13}C spectrum.

Synthesis. 4-[(2-Hydroxyethyl)sulfonyl]-4′-[*N*,*N*-bis(2-hydroxyethyl)amino]azobenzene (1). To a solution of 6.4 g (31.8 mmol) of 1-[(2-hydroxyethyl)sulfonyl]-4-aminobenzene[4,5] in 14 mL of 6 M HCl was added dropwise a solution of 2.4 g (34.8 mmol) of $NaNO_2$ in 15 mL of water at such a rate that the temperature did not exceed 5 °C. To the resulting diazonium salt solution was added a solution of 5.7 g (31.45 mmol) of *N*-phenyldiethanolamine (Janssen Chimica) in 315 mL of 0.1 M HCl, while maintaining the temperature between 0 and 5 °C.

Scheme 1



After stirring for 3 h at room temperature, the solution was neutralized with saturated sodium bicarbonate, the precipitate was taken up in ethanol, and the insoluble material left was removed by filtration. After removal of the solvent, purification was performed by repeated crystallization from water/ethanol (1/9, v/v) to produce 7.3 g (58%) of 1 as red crystals: mp 175 °C; ^{1}H NMR (DMSO-d_6) δ 3.41 (t, 2H), 3.52 (t, 2H), 3.62 (t, 2H), 3.65 (m, 2NCH_2), 3.76 (m, CH_2OH), 4.88 (t, O*H*), 4.91 (t, O*H*), 6.91 and 7.83 (AA′BB′, 4H), 7.94 and 8.04 (AA′BB′, 4H); ^{13}C NMR (DMSO-d_6) δ 53.3, 55.9, 57.8, 58.2, 111.5 (*C*(3,Ar′)), 122.0, 125 .6, 129.0, 139.4, 142.5, 152.0, 155.4.

Second Harmonic Generation Experiments. Processing, Corona Poling, and Cross-Linking. In a typical procedure a 20 wt % solution of 19 mg (0.145 mmol of OH) of 1 and 14 mg (0.159 mmol of NCO ≡ 10% excess) of TDI in dry DMF was heated for 10 min at 80 °C. The resulting prepolymeric solution of 1 was used to spin-coat (Convac. Type ST 145) over different substrates (2.5 × 2.5 cm^2) such as glass, indium tin oxide (ITO)-glass, etc.

The substrate was placed on the ground electrode of the poling equipment which had been built in a thermostated oven at 145 °C. Next, a voltage on the corona wires (ϕ = 100 μm, approximately 1 cm above the film surface) was applied, varying from 8 to 10 kV depending on the thickness of the film, the concentration of nonlinear optical molecules, and the temperature selected for poling, while the corona current was established in the range of 5 μA. After 15–30 min, the oven was cooled to about 60 °C (10–15 min) while proceeding with poling. Subsequently, the applied voltage was turned off, and the substrates were further cooled to ambient temperature.

Second Harmonic Measurements. Second harmonic measurements were done in transmission according to Singer et al.[6,7]

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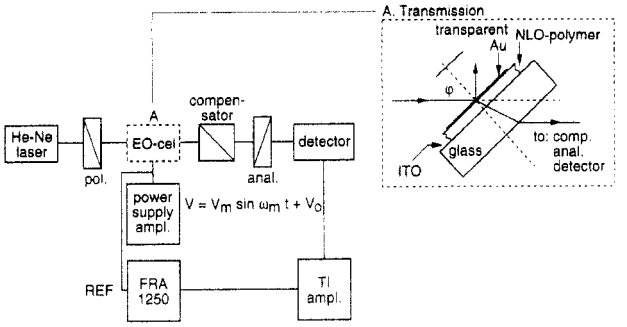

Figure 1. Setup for electrooptic characterization.

with the 1064-nm wavelength of a Nd:YAG laser (pulse length 10 ns, 10 Hz, 10–20 mJ/pulse) and quartz as a reference material. The refractive index of the films on glass was measured by ellipsometry at 633 nm. With this value the refractive indices at 532 and 1064 nm were estimated as $n_{532} = n_{633} + 0.05$ and $n_{1064} = n_{633} - 0.05$ to take account of the dispersion of the refractive index. The resonantly enhanced d_{33} value was calculated according to Singer et al.,[6,7] assuming $d_{13} = 1/3d_{33}$ and accounting for the absorption at 532 nm similar to Mortazavi et al.[8]

Electrooptic, Pyroelectric, and Thermally Stimulated Discharge (TSD) Experiments. Poling. Spin-coated samples were processed as described. After drying in vacuum for at least 24 h at room temperature, a semitransparent Au-electrode was vacuum deposited on top of the polymer layer, thus forming an ITO–polymer–Au sandwich. The samples were protected from moisture by storing them either in vacuum or above P_2O_5.

In a typical experiment the ITO–polymer–Au sandwich was poled at successively higher temperature levels. Next to poling for 30 min at each temperature level, the sample was cooled to room temperature and mounted for a first electrooptic measurement with the poling field still applied. Immediately after switching off the poling voltage, a second measurement was carried out, and by subsequent measurements the short-term decay of the pockels constant $r_{33}(t)$ was studied.

Electrooptic Measurements. A transmission-modulated technique[9] (see Figure 1) was used to determine the linear electrooptic coefficient at 633 nm.

A modulating voltage is applied to two parallel electrodes. One electrode is a transparent ITO layer on glass, and the other electrode is a semitransparent Au layer. The input beam polarized at 45° to the plane of incidence is transmitted through the sample at a fixed angle of incidence and passes through an analyzer. A Soleil–Babinet compensator is adjusted to bias the optical system at half-maximum intensity output which is measured with a photodetector. A sinusoidal modulating voltage at 110 Hz and variable amplitude from a frequency response analyzer (FRA; Solartron 1250) in combination with a programmable power supply[10] is applied across the ITO–polymer–Au sandwich. The combined power supply permits the superposition of the modulating voltage to a variable dc bias serving as a poling voltage during electrooptic measurements. The modulation of the output intensity is detected by the same frequency response analyzer. Spurious modulation contributions from interference effects are minimized by subtraction of the output signals at two optical bias positions.[11]

The electrooptical constant r_{33} was calculated according to eq 1[9,10]

$$r_{33} = \frac{3}{n^2}\Gamma_c\frac{V}{V_m}\frac{(n^2 - \sin^2\phi)^{1/2}}{\sin^2\phi} \qquad (1)$$

with approximations $n_x = n_y \approx n_z = n$ and $r_{31} = (1/3)r_{33}$ and with V_m the driving modulating voltage amplitude at frequency ω_m measured by FRA, Γ_c the calibration factor for optical pathlength equivalence per unit of detector response measured by means of the compensator, n the index of refraction, and ϕ the angle of incidence.

Pyroelectric and TSD Measurements. All measurements were performed in a programmable oven, permitting adjustable heating rate, temperature level, and isothermal heating time. An electrometer (Keithley instruments 610B) permitted the monitoring and measurement of poling, pyroelectric, and TSD discharge current.

The intermediate pyroelectric constant of a sample poled at one temperature level was obtained by slowly heating and cooling (0.3 °C/min) around 30 °C and measuring the generated current. Prior to this temperature cycling, the specimen was kept short circuited for some time at 40 °C to eliminate a possible current component stemming from TSD. The dc conduction current levels, which typically are on the picoampere scale, were measured after letting the current come to its equilibrium value at the turning points of temperature. Assuming the dc conduction current to depend approximately linearly on temperature in this small interval, its contribution could be extracted from the current due to the change in temperature, leaving the current component for the calculation of the pyroelectric constant. The maximum admissible heating rate was stated as the rate at which the calculated pyroelectric constant became independent of the rate of change of temperature. Subsequently, further poling was done by heating the sample linearly to a higher temperature level with the poling voltage reapplied, and the sequence of measurements was repeated as described above.

Additionally, the samples were carefully weighed after each cycle to get information about loss of volatile components from the polymer. No such loss was detected up to 190 °C. Alternatively, the poling was done in a single run during linear heating at a rate of 0.5–2 °C/min. After reaching a final temperature, the sample was quenched to room temperature in the poling field. One sample poled in this way was set aside to study long-term stability at 100 °C. Another such sample was subjected to a series of partial TSD measurements. By this we mean the discharge of the specimen in steps by repeated TSD heating runs to higher top temperatures while measuring the current, in a way that part of the dipole polarization is broken down which is unstable up to the respective top temperature at the time scale set by the linear heating rate (1 °C/min). After each heating–cooling cycle, the residual part of the pockels constant was measured.

Results and Discussion

Syntheses and Film Preparation. Azo compound 1 was prepared by the diazo coupling of 1-[(2-hydroxyethyl)-sulfonyl]-4-aminobenzene with *N*-phenyldiethanolamine. A polyurethane prepolymer was made from the triol 1 by reaction with toluene diisocyanate (TDI) in dimethylformamide (DMF) at 80 °C for 10 min. No catalyst was used in order to avoid electrical conduction of the finally cured film. A NCO/OH molar ratio of 1.10/1.00 was chosen in order to be sure of complete reaction of all hydroxyl groups. The remaining isocyanate groups may react with each other to form isocyanurates or may first react with water and subsequently with another isocyanate to give a urea cross-link.

The prepolymer solution was spin-coated into 0.5–1-μm-thick films, on glass, or ITO-coated glass, and the films were cured at 145 °C for 30 min. The concentration of the NLO chromophores was 17.6×10^{20} cm^{-3}.

As shown in Figure 2, the UV–vis absorption spectrum of the cured film has a λ_{max} at 440 nm, whereas no absorption is present at 633 nm, the wavelength used for electrooptic measurements. However, the harmonic frequency at 532 nm produced by the SHG measurement is absorbed in part by the film.

After curing no isocyanate peak could be detected in the FTIR spectrum, as seen from Figure 3, and the films showed a distinct T_g of 155 °C. This distinct T_g in the highly cross-linked material might be explained by assuming that the cross-linking density was not optimal, either because of the chosen NCO/OH ratio or because of the formation of a too rigid network at the curing temperature preventing further cross-linking.

Second Harmonic Generation Experiments. For second harmonic generation (SHG) experiments films were

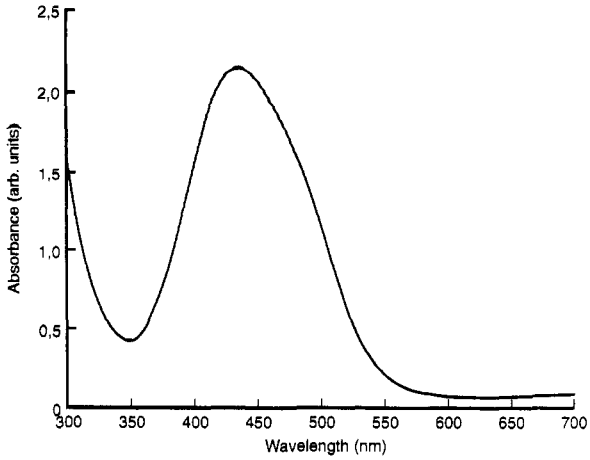

Figure 2. UV–vis absorption spectrum of a spin-coated film of 1 and TDI on glass cured at 145 °C with air as a reference. The residual absorption beyond 600 nm is due to reflections.

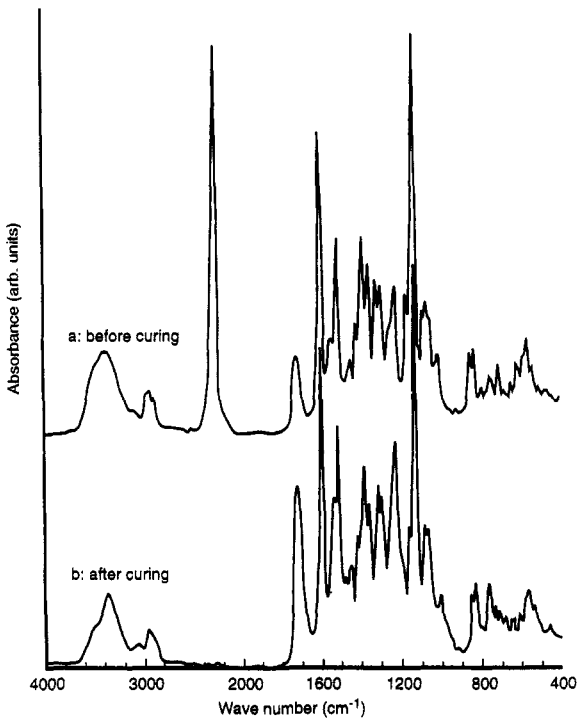

Figure 3. FTIR spectra of a film of 1 and TDI, precured at 80 °C (a) and fully cured at 145 °C (b).

simultaneously cured and corona poled at 145 °C for 30 min and cooled to ambient temperature. The SHG signal of the films was measured 1 day after poling relative to quartz at 1064 nm. This gave an estimation of the resonance-enhanced d_{33} value, *viz.*, 60 pm/V (143 × 10^{-9} esu), taking into account the absorption at 532 nm. The stability of the SHG signal was followed at 70 °C. At this temperature the d_{33} value decreased to 40 pm/V (34% decrease) after ca. 800 h (see Figure 4).

Analogous results have been obtained by Chen et al.,[12] who found a relaxation of 30% after 3000 h at 90 °C for a polyurethane network consisting of a prepolymer of 4-nitro-4′-[*N*,*N*-bis(2-hydroxyethyl)amino]azobenzene (Disperse Red 19) and 4,4′-diisocyanato-3,3′-dimethoxydiphenyl cross-linked with triethanolamine. This polyurethane, however, showed no glass–rubber transition temperature after cross-linking. This suggests that for our system a more stable NLO activity could be obtained in the case of a higher cross-linking density.

Linear and cross-linked polyurethanes were also studied recently by Kitipichai et al.[17] and Francis et al.[18] The

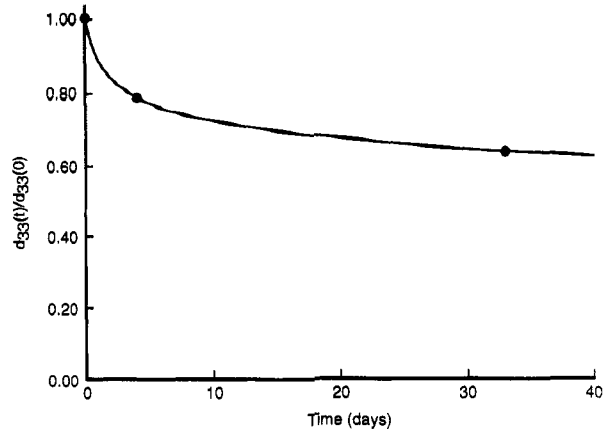

Figure 4. Second-order nonlinear optical coefficient, $d_{33}(t)/d_{33}(0)$, as a function of time at 70 °C. The inserted line is only a guide to the eye.

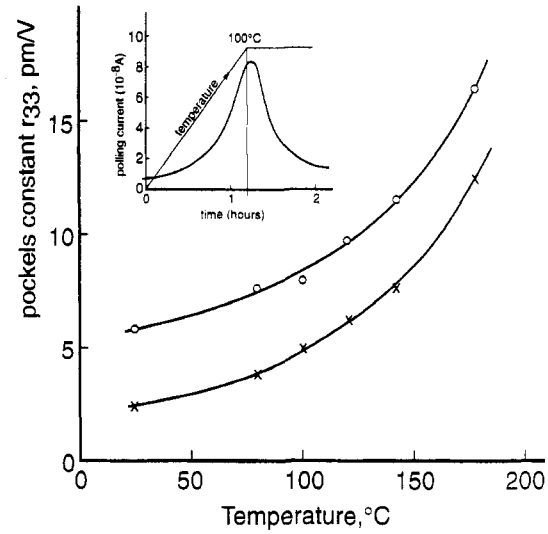

Figure 5. Pockels constant r_{33} as the result of repeated isothermal poling at increasing temperature levels: (○) poling field on; (×) poling field off. Poling field 50 V/μm; poling time 30 min at each temperature level; heating rate between levels 1 °C/min. Inset: typical course of poling current.

former showed that polyurethanes formed by hydroxyaniline derivatives and TDI had good NLO activities. Especially, a cross-linked triol, in which the chromophore was covalently attached to the polymer network with both the electron-donor and -acceptor side, exhibited no decrease in NLO activity during 50 min at 100 °C.

Ulman et al.[13] have measured that for 4-(*N*,*N*-dimethylamino)-4′-(methylsulfonyl)azobenzene $(\mu_g)_z\beta_z$ equals 512 × 10^{-48} esu at 1907 nm, where $(\mu_g)_z$ = molecular ground-state dipole moment and β_z = *z*-component of the vector component of the second-order hyperpolarizability. After correcting for the dispersion in β_z[14] with $(\mu_g)_z \approx 8$ D and λ_{max} = 440 nm, this gives a β_z value of 182 × 10^{-30} esu at 1064 nm. From the equation $d_{33} = {}^1/_2NF\beta\langle\cos^3\phi\rangle$ (where N = number concentration of NLO chromophores (cm^{-3}), F = local field factor = $f_{2\omega}f_\omega f_\omega$, $f_i = ((n_i)^2 + 2)/3$, n_i = refractive index at i, and ϕ = angle between the molecular *z* axis and the poling field), $n_\omega = 1.65$, $n_{2\omega} = 1.75$, and $N \approx 17.6 \times 10^{20}$ cm^{-3}, a d_{33} value of $\approx 280\langle\cos^3\phi\rangle$ pm/V is calculated. So, $\langle\cos^3\phi\rangle$ is about 0.21 after 1 day after poling and 0.14 after 800 h of aging at 70 °C.

Electrooptic Experiments. For a stepwise poled sample, as described before, the cumulative building up of the pockels constant is shown in Figure 5.

The result shows an increase of poling effectiveness toward higher temperatures up to 180 °C and probably

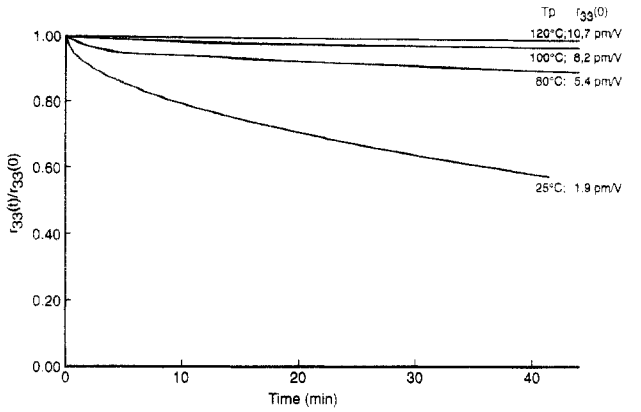

Figure 6. Short-term stability of r_{33} at room temperature for intermediate poling/cross-link histories (T_p, E_p = 500 kV/cm, t_p = 15 min).

beyond. This can be understood in terms of increased mobility at the higher temperature in favor of both the dipole orientation and the progress in network formation. Indeed, on heating to a higher temperature, we pass the T_g of the precedingly formed network, which in turn is further increased by the ongoing isothermal poling.

It should be noted that the cross-linking and the dipole orientation processes obey different time schedules. The orientation of even slowly relaxing dipoles should be maximum before a too fast cross-linking will prevent the dipoles to reach the maximal orientation.

Thus, an ideal route for poling and cross-linking in terms of temperature, time, and poling field may exist to obtain an optimal large and stable orientation of the NLO dipole moiety. In this respect the course of the dc poling current during isothermal poling may be a guide; see the inset in Figure 5.

After a rise during the heating part, the poling current becomes maximum on reaching the level of constant temperature and will subsequently decrease to a stationary value. The decrease is a consequence of both the reduction of orienting dipoles in time and the decrease of charge carrier mobility by the cross-link process. It is seen that these processes may take several hours at 100 °C.

With respect to the electrooptic result in Figure 5, a further note may be given to the almost constant difference between the r_{33} values measured with and without poling field. This points at a constant fraction of fully mobile NLO dipoles, not contributing to r_{33}.

From the increase of T_g of the polymer network by cross-linking at subsequent higher temperature and thus an increase in the difference $T_g - T_r$, T_r being the relaxation temperature, we expect[15] an improved stability over the preceding poling/cross-linking cycle in Figure 5. This is indeed confirmed by Figure 6 for T_r at room temperature.

To study the long-term stability, we subjected a sample, that was poled at 140 °C, to isothermal decay at 100 °C.

The result shown in Figure 7 correlates well with the temporal behavior at 70 °C in Figure 4 for a sample corona poled at 145 °C.

By arguments known from literature[15] we expect a similar temporal behavior at 150 °C for a sample poled at 190 °C. This is indeed confirmed by the additional result in Figure 7. The $r_{33}(0)$ value, 8.5 pm/V, was somewhat lower than the value found at 175 °C in Figure 5, 12.3 pm/V, due to difficulties in poling at 190 °C. However, after extrapolating the results in Figure 5, good poling at 190 °C should result in an electrooptic coefficient of 16 pm/V.

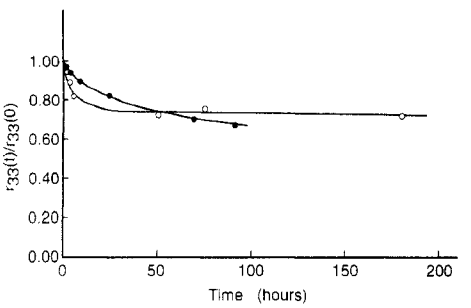

Figure 7. Isothermal stability of the pockels constant $r_{33}(t)/r_{33}(0)$ at 100 (○) and 150 °C (●) poled at 140 and 190 °C, respectively.

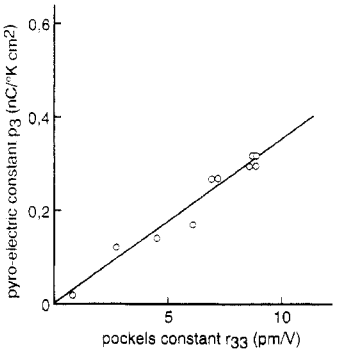

Figure 8. Pyroelectric constant p_3 versus the corresponding pockels constant r_{33}.

Apart from the correspondence of the temporal behavior of corona-poled and contact-poled samples, we surprisingly find reasonable agreement between the respective d_{33} and r_{33} values, after correction for dispersion.[16] Applying the well-known two-level model, with the proper physical constants of the polymer mentioned above, the value of r_{33} = 12.3 pm/V at 633 nm results in a corresponding value of the second-order nonlinear optical coefficient $d_{33} \approx 58$ pm/V at the fundamental wavelength of 1064 nm. This is close to the experimental value of d_{33} = 60 pm/V found for a corona-poled sample. Probably it is the reduced thickness of the polymer layer due to curing shrinkage, resulting in a larger effective poling field strength, that is responsible for this coincidence.

Pyroelectric and TSD Measurements. The pyroelectric property, *i.e.*, a reversible linear relationship between the amount of generated electric charge and a corresponding difference in temperature, could be a useful secondary property of an NLO material.

Moreover, the pyroelectric property offers a convenient way to study the presence and state of dipole orientation, as it is directly related to the polarization P by the average angle of orientation $\langle \cos \phi \rangle$ of dipoles to the direction of the poling field. In contrast, the second nonlinear electrooptical property is related to P by $\langle \cos^3 \phi \rangle$. For $\mu E/kT < 1$ the relation between $\langle \cos \phi \rangle$ and $\langle \cos^3 \phi \rangle$ should be approximately linear.[7]

We investigated this relation on a poled sample (T_p(max) = 150 °C; 50 V/μm) that was subjected to a series of partial TSD runs and measured the pyroelectric constant p_3 around 30 °C after finishing each heating–cooling cycle. In contrast to intermediate pyroelectric measurements during a stepwise poling experiment (*i.e.*, building up of polarization), the partial TSD method (*i.e.*, breaking down of polarization) avoids effects of residual surface and space charge.

We compare the set of p_3 values with the corresponding r_{33} values in Figure 8.

The experimental values are well within limits for linearity. The unique relationship could offer the pos-

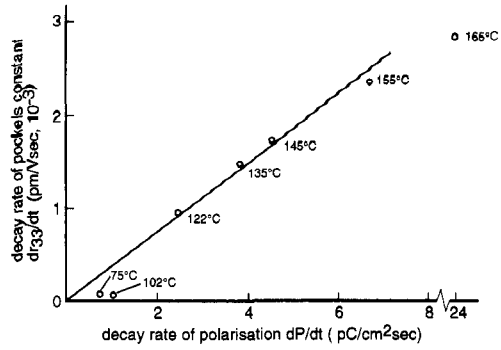

Figure 9. Decay rate of the electric polarization versus the decay rate of the pockels constant obtained by partial TSD; original poling T_p = 150 °C, 50 V/μm, heating rate 1 °C/min.

sibility to study the temporal behavior of r_{33} with pyroelectric measurements.

In the partial TSD experiments we measured the discharge currents during every heating–cooling cycle with increasing top temperature.

From the difference in released charge the decay rate of polarization in the corresponding temperature interval was approximated and compared to the rate of decrease of r_{33} over the same temperature interval.

As shown in Figure 9, both decay rates correlate linearly to a fair degree.

The linear relation is lost above the poling temperature as shown in Figure 9 by the off-scale value. Repoling of a discharged sample at the formerly applied poling temperature results in only half of the original value and shows much poorer temporal stability.

Drastic changes in the network organization could explain these observations.

Conclusions

Azobenzene 1 cross-linked with TDI shows very promising results as an NLO material: a resonantly enhanced d_{33} value of 60 pm/V at 1064 nm 1 day after corona poling and a 34% decrease in 800 h at 70 °C; an electrooptic coefficient r_{33} = 12.3 pm/V. Poling at 190 °C results in a decrease of less than 40% after 100 h at 150 °C.

The results of the electrooptic, pyroelectric, and TSD measurements are in agreement with each other. The combination can be helpful to optimize the cross-linking density which could increase the stability even further.

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