New Polyamides with Large Second-Order Nonlinear Optical Properties

Christoph Weder, Peter Neuenschwander, and Ulrich W. Suter*

Institut für Polymere, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland

Philippe Prêtre, Philip Kaatz, and Peter Günter

Institut für Quantenelektronik, Eidgenössische Technische Hochschule, CH-8093 Zürich, Switzerland

Received September 28, 1993; Revised Manuscript Received January 19, 1994®

ABSTRACT: A series of NLO polyamides based on the new monomer 2′,5′-diamino-4-(dimethylamino)-4′-nitrostilbene (DDANS) has been synthesized. The polymers are amorphous and show glass transition temperatures up to 206 °C. They can easily be processed by spin-coating into thin films of optical quality. These films have been oriented by a corona discharge poling process. Second-order nonlinear optical coefficients (d_{33}) of up to approximately 40 pm/V at a fundamental wavelength of 1542 nm have been measured. Preliminary results indicate that the orientation of the dipoles shows no significant relaxation at ambient conditions in 120 days after poling. These polymers represent a new approach to the design of polymers with large and stable second-order nonlinear optical properties, where the nonlinear optical units are fixed in the polymer backbone with their dipole moments oriented transverse to the main chain.

I. Introduction

There has been considerable interest in organic nonlinear optical (NLO) materials, because of their potential application in integrated electrooptical devices.[1] A promising approach to the development of new second-order NLO materials is that of poled polymers. The advantages of poled polymers are large susceptibilities, fast response times, easy processability, and high physical and mechanical stability, but their NLO properties are usually not stable, due to the thermal relaxation of the NLO phore orientation.[1]

Different design strategies have been worked out to synthesize polymers with desirable NLO properties. Typically the NLO phores have been incorporated by doping[2-4] (guest–host systems) or attaching them covalently[4-6] (side-chain systems) into amorphous or liquid-crystalline polymers. To enhance the orientational stability of the NLO phores, cross-linked polymers[7,8] or polymers which incorporate the NLO phores with their dipole moments head-to-tail in the main chain[9,10] have been synthesized. However, problems such as relaxation of the NLO phores' orientation, optical losses, or intractability still exist.[1] In this paper, we present a new approach to the design of amorphous polymers with large and stable second-order nonlinear optical properties.

To reach a maximum of NLO phore concentration, the bulky nonlinear optically active units should be linked with small spacer units to or in the polymer main chain. In our approach, the NLO phores are placed into the main chain, and their dipole moments are fixed transverse to it, based on the assumption that in this arrangement the NLO phores are easier to orient by an external field than in structures where their dipole moments are pointing along the polymer main chain. We further surmise that the local chain mobility is predominantly governed and limited by the bulkiness of the NLO phores and that mobility can be influenced by the chain length of flexible spacer units, similar to the behavior observed in liquid-crystal polymers.[11] Hence, we hope to obtain systems with high NLO phore concentration, good orientability, and adjustable stability of properties.

The chosen NLO phore is based on DANS[2,3,12-14] [4-(dimethylamino)-4′-nitrostilbene]. It was modified by the introduction of two amino groups into one of the aromatic rings to achieve the new bifunctional NLO phore DDANS [2′,5′-diamino-4-(dimethylamino)-4′-nitrostilbene] (**4**). We report the synthesis of DDANS (**4**) and the preparation and properties of a series of polyamides made of DDANS (**4**) and aliphatic diacid chlorides.

II. Results and Discussion

Monomer Synthesis. DANS is known to have a large first-order nonlinear hyperpolarizability β;[12-14] the new NLO phore monomer DDANS (**4**) was obtained by the introduction of two amino groups according to the synthetic approach shown in Scheme 1. The four-step synthesis started from 2,5-diaminotoluene that was acylated and nitrated by slightly modified, published procedures.[15] The resulting compound **2** and 4-(dimethylamino)benzaldehyde were employed in a Knoevenagel condensation in dry pyridine in the presence of piperidine to give the stilbene **3** in high yield. After refluxing the crude compound **3** in hydrochloric acid, the free diamine **4** could be isolated. Recrystallization from toluene and acetone/water gave the pure DDANS in violet to black, air stable crystals. The yield of polycondensation quality DDANS over all four steps is 15%.

Synthesis and Characterization of Polymers. Polymers **P1–P5** were prepared by low-temperature polycondensations of DDANS (**4**) with different linear aliphatic diacid chlorides of an even number of methylene groups in 1-methyl-2-pyrrolidone (NMP) as shown in Scheme 2. The number of the diacid's methylene groups was varied from 12 (tetradecanedioyl dichloride, **P1**) to 4 (adipoyl chloride, **P5**).

The condensations proceeded slowly; the increase of the reaction mixtures' viscosity was taken as an indication of the progress of polycondensation. Typical reaction times were in the range of 48 h. In the case of **P2** and **P4**, trimethylchlorosilane was added to the reaction mixture in order to activate the diamine **4** in situ, as proposed by Imai et al.[16] All polymers remained soluble in the reaction mixture. The polymers obtained were characterized by NMR spectroscopy and elemental analysis. Figure 1 shows

® Abstract published in *Advance ACS Abstracts*, March 1, 1994.

0024-9297/94/2227-2181$04.50/0

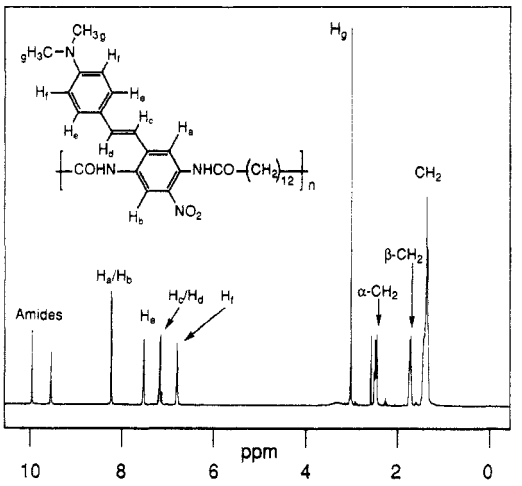
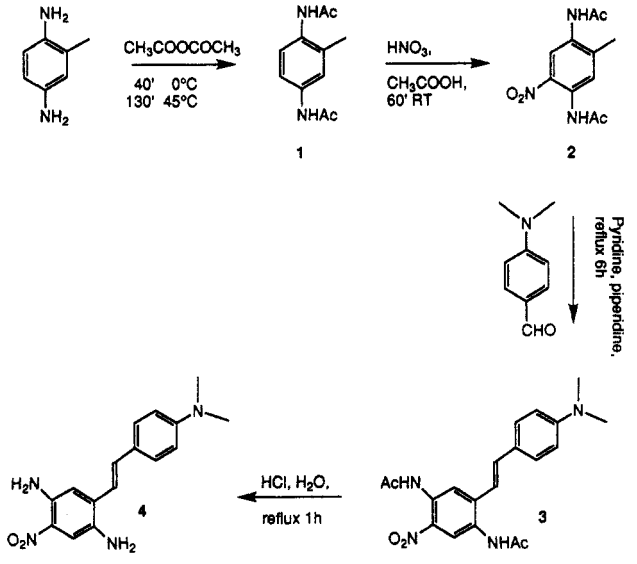
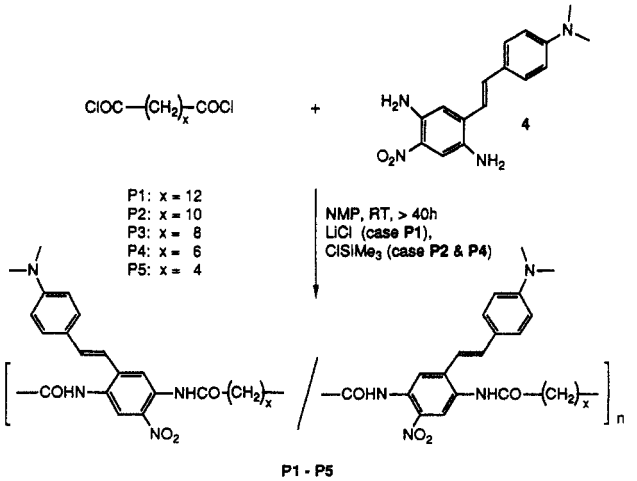


Figure 1. ^{1}H NMR of polymer **P1** in DMSO. Indexing corresponds to a hypothetical, constitutionally regular isomer (see legend to Figure 2).

Scheme 1. Synthesis of DDANS



Scheme 2. Synthesis of Polymers P1–P5 from DDANS and Aliphatic Diacid Chlorides



the ^{1}H NMR spectrum of **P1**; the signals are consistent with the expected structure. This spectrum is representative for all other polymers except that the aliphatic region changes with the number of methylene groups in the diacid.

A measurement of the reactivity of the functional groups of DDANS was carried out following the method proposed by Meyer et al. using ^{1}H NMR spectroscopy.[17] The

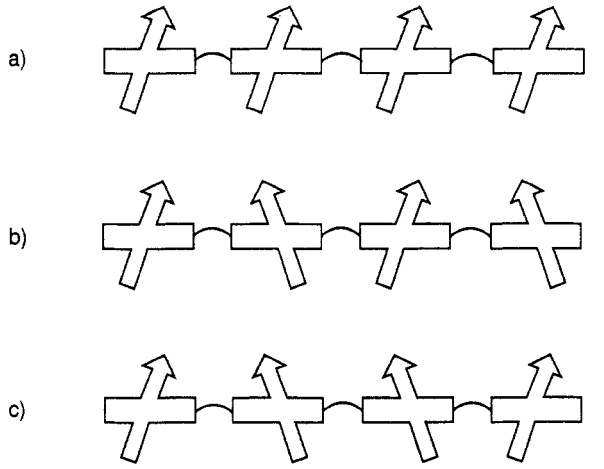


Figure 2. Schematic representation of different constitutional cases of polymers consisting of a nonsymmetric NLO phore and a symmetric spacer: (a) "head-to-tail", (b) "head-to-head/tail-to-tail", and (c) "nonregular" arrangement.

reactivity ratio of the NLO phore's two amino groups for the reaction with an aliphatic acid chloride (defined as the ratio of the two kinetic reaction constants) was determined to be at least 1:100 for acetyl chloride. Since polycondensate from one symmetric and one nonsymmetric component (as it is the case here) exist in different constitutions, different constitutional regularities are possible and have to be distinguished[17,18] (see Figure 2). The polymers discussed in this paper should have constitutionally nonregular arrangements of the monomeric units (case c in Figure 2), because the nonsymmetric DDANS and the symmetric aliphatic diacid chlorides were mixed "infinitely fast" on the time scale of the condensation reaction (see ref 17 for a detailed explanation). Unfortunately, experimental proof for the constitution of **P1–P5** could not be obtained. (Note that only head/tail-type isomerism is possible; the main chain does not contain centers of configuration and, hence, there is no "tacticity".)

The thermal properties of the polymers have been investigated using DSC and TGA at heating rates of 20 °C/min. TGA and DSC experiments show that for all polymers the first decomposition step sets in at around 210 °C in air and also under nitrogen atmosphere. The temperature of the maximum decomposition rate for this first decomposition step is 300 °C. In addition to these decompositions the DSC curves show "step changes" that arise from the glass transitions of the polymers. The *Tg*'s are found to be linearly dependent on the number of methylene groups of the flexible spacer, ranging from 125 °C for **P1** to 206 °C for **P5**.

All polymers are completely soluble in concentrations of 5% w/w or more in classical amide solvents such as NMP and DMSO and acids such as formic acid or trichloroacetic acid. The weight-average molecular weight (M_w) of **P4** is 116 000 ± 12 000 as determined by static light scattering in NMP. The inherent viscosities measured at a polymer concentration of $c = 0.5$ g/dL at 25 °C range from 0.40 to 0.89 dL/g and prove the polymeric character of all polymers. The physical properties of all polymers are summarized in Table 1.

Preparation of Films. All polymers were amorphous and could be processed into thin, dark red and transparent films by spin coating from NMP solutions on heated substrates. Orientation in the films was induced by corona poling above *Tg*; this process was not optimized but standardized to conditions to yield good and reproducible results for both polymers **P1** and **P4**.

Table 1. Physical Properties of Polymers P1–P5

polymer	chromophore concentration,[a] (%)	η_{inh},[b] dL/g	T_g, °C
P1	67.7	0.40	125
P2	71.5	0.73	144
P3	75.8	0.46	159
P4[c]	80.7	0.82	176
P5	86.3	0.89	206

[a] In percent w/w of the polymer's repeat unit. [b] Determined at 25 °C in NMP at a polymer concentration of 0.5 g/dL. [c] M_w of **P4** is 116 000 ± 12 000 as determined by static light scattering.

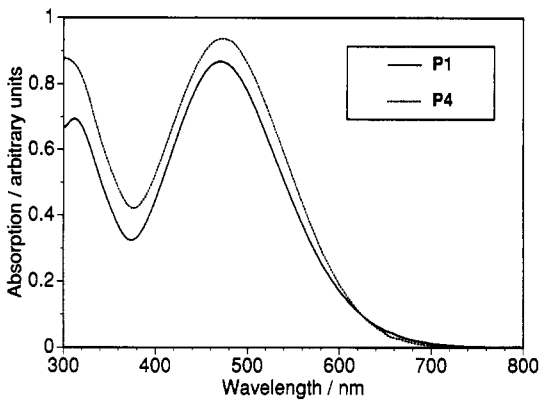


Figure 3. Thin film absorption spectra of polymers **P1** and **P4** on fused silica.

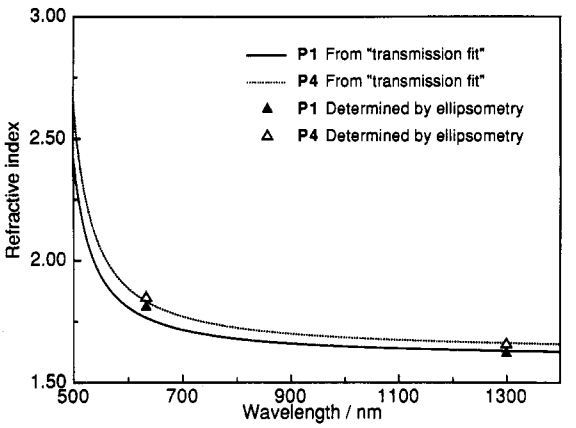


Figure 4. Refractive index dispersion of polymers **P1** and **P4**.

Linear Optical Properties. Polymers **P1** and **P4** were our main points of interest because these are the polymers with the lowest and the highest glass transition temperatures of the prepared series (omitting **P5**, the T_g of which is 206 °C, in the range of thermal decomposition). Therefore the linear and nonlinear optical properties of these two polyamides were examined in greatest detail.

Figure 3 shows the UV–vis spectra of unpoled film samples of **P1** and **P4** that are representative for all other polymers. All polymers show an absorption maximum between 471 and 473 nm and are transparent at wavelengths longer than 700 nm. The extinction coefficients are slightly different due to the different contents of NLO phore of the polymers.

Refractive indices were determined by two different methods. From the interference fringes in the UV–vis transmission spectra of thin polymeric films on fused silica substrates, a one-oscillator Sellmeier dispersion formula could be fitted for each polymer[19] (values from this expression will be labeled below as "transmission fit" values). For two wavelengths (633 and 1300 nm) the refractive indices were determined by ellipsometry. The results from the two methods are found to be comparable as shown in Figure 4 for polymers **P1** and **P4**. The polymers show refractive indices increasing with the content of the NLO phore.

Nonlinear Optical Properties. The appropriate point group for a poled NLO polymer is ∞mm (by definition, the infinite-fold rotation axis is taken to be along the three-direction).[1] The electric field $\mathbf{E}^{\omega} = (E_1^{\omega}, E_2^{\omega}, E_3^{\omega})$ of an incoming laser beam induces a nonlinear polarization $\mathbf{P}^{2\omega}$ in the polymer film, which is proportional to the nonlinear optical coefficients d_{31} and d_{33}:

$$\mathbf{P}^{2\omega} = \epsilon_0 \begin{pmatrix} 2d_{31}E_1^{\omega}E_3^{\omega} \\ 2d_{31}E_2^{\omega}E_3^{\omega} \\ d_{31}(E_1^{\omega})^2 + d_{31}(E_2^{\omega})^2 + d_{33}(E_3^{\omega})^2 \end{pmatrix}$$

This nonlinear polarization generates a second harmonic wave in the polymer film.

The nonlinear optical coefficients d_{33} have been characterized using a standard Maker fringe technique[20] at a fundamental wavelength of 1542 nm. The absorption of the polymers at the second harmonic wavelength (771 nm) is neglectable and therefore the obtained second harmonic generation (SHG) coefficients d_{33}, 40 pm/V for **P1** and 27 pm/V for **P4**, are essentially not resonance enhanced.

The change of the optical indicatrix of a nonlinear optical material due to an applied dc electric field **E** is referred to as the linear electrooptic or Pockels effect:[21]

$$\Delta\left(\frac{1}{n^2}\right)_{ij} = \sum_k r_{ijk}E_k$$

The electrooptic coefficient r_{ijk} is the sum of an electronic contribution (r^e_{ijk}) and the effects from optic (r^o_{ijk}) and acoustic (r^a_{ijk}) phonons. The electrooptic effect for organic materials is assumed to be mainly of electronic origin. It therefore exists a direct relation between electronic electrooptic and nonlinear optical coefficients:[21]

$$r^e_{ijk} = \frac{-4}{n_i^2 n_j^2} d^{EO}_{ijk}$$

where the nonlinear optical coefficient d^{EO}_{ijk} for a static and an optical field at frequency ω is related to the SHG coefficient $d^{-2\omega';\omega',\omega'}_{kij}$ measured at optical frequencies ω' by[22]

$$d^{EO}_{ijk} \equiv d^{-\omega;\omega,0}_{ijk} = \frac{f_i^{\omega} f_j^{\omega} f_k^{0}}{f_k^{2\omega'} f_i^{\omega'} f_j^{\omega'}} \cdot \frac{(3\omega_0^2 - \omega^2)\cdot(\omega_0^2 - \omega'^2)^2\cdot(\omega_0^2 - 4\omega'^2)}{(3\omega_0^2 - 3\omega'^2)\cdot(\omega_0^2 - \omega^2)^2\cdot\omega_0^2} \cdot d^{-2\omega';\omega',\omega'}_{kij}$$

The f are local field factors in the Lorentz approximation, and ω_0 is the resonance frequency for the dominant oscillator. Taking the isotropic refractive indices from the "transmission fit", the electrooptic coefficients r^e_{33} at a fundamental wavelength of 1.3 μm are 16 pm/V for **P1** and 10 pm/V for **P4**.

The measured second-order nonlinear coefficients for **P1** are higher than for **P4**. Because the NLO phore concentration is 13% higher for the latter polymer, this result is initially surprising. The fact that the determined second-order nonlinear optical properties are related to the poling conditions that have not yet been optimized may explain this result.

The electrooptic coefficients r^e_{33} = 16 pm/V for P1 and 10 pm/V for **P4** have to be compared with the value r_{33} = 32 pm/V for $LiNbO_3$.[21] It should be possible to reach

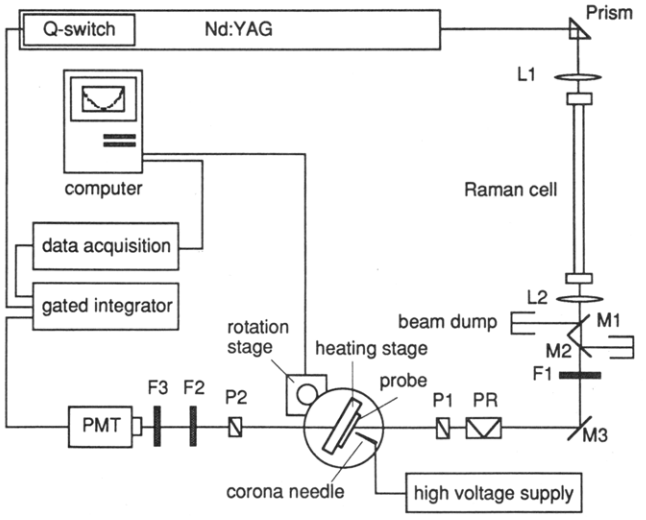


Figure 5. Experimental setup for SHG measurements: The laser beam is focused with lens L1 into a 1-m long Raman cell and recollimated with lens L2. Dielectric mirrors M1 and M2 reflect the fundamental wavelength, λ = 1.06 μm. Filter F1 eliminates residual flashlamp light. PR: polarization rotator; P1, P2: polarizers. Filter F2 blocks the fundamental wave (λ = 1.54 μm), and F3 attenuates the second harmonic signal.

Table 2. Linear and Nonlinear Optical Properties of Polymers P1 and P4

polymer	λ_{max}, nm	n (633 nm)	n (1295 nm)	d_{33}, pm/V (1542 nm)[c]	r^e_{33}, pm/V (1300 nm)[c]
P1	471	1.758[a]	1.627[a]	40	16
		1.808[b]	1.649[b]		
P4	473	1.832[a]	1.663[a]	27	10
		1.847[b]	1.657[b]		

[a] Value taken from the "transmission fit". Uncertainty at least ±0.01. [b] Determined by ellipsometry. [c] Experimental error: ±10%.

this level within our new concept using an improved NLO phore with larger hyperpolarizability and optimized poling conditions.

Preliminary results indicate that the orientation of the NLO phores in **P4** shows no significant relaxation at ambient conditions within 120 days after poling. Detailed relaxation measurements are in progress and will be reported later. All optical properties of **P1** and **P4** are summarized in Table 2.

III. Conclusion

We have presented a new approach to the design of NLO polymers. A novel bifunctional NLO phore was synthesized, and a series of linear polyamides containing the new NLO phore was prepared. These polymers have a high NLO phore density, are amorphous, and have high, adjustable glass transition temperatures. The polymers can easily be processed into thin films of optical quality. Second harmonic generation measurements on poled films showed large second-order nonlinearities. Preliminary results indicate that the second-order nonlinearities of at least one of the polymers show no significant decay at ambient conditions within 120 days.

IV. Experimental Section

Methods. All reagents and solvents were purchased from FLUKA and Aldrich Chemical Co. except sebacoyl dichloride which was obtained from Merck. Only analytical grade quality chemicals were used. Pyridine and 1-methyl-2-pyrrolidone (NMP) were purified by distillation under reduced pressure from calcium hydride. The commercially available sulfate form of 2,5-diaminotoluene was converted into the free diamine by treatment with aqueous sodium hydroxide followed by extraction with methylene chloride. The crude diamine was used without further purification. 4-(Dimethylamino)benzaldehyde was purified by sublimation. The commerically available adipoyl chloride, sebacoyl chloride, and dodecanedioyl dichloride were purified by distillation under reduced pressure. The other diacid dichlorides were prepared by a standard procedure[23] and were purified by at least two distillations under reduced pressure. All other compounds were used as received. All reactions were carried out under dry nitrogen or argon atmosphere using standard vacuum-line and glovebox techniques. ^{1}H NMR and ^{13}C NMR spectral data are expressed as ppm relative to internal TMS and were obtained on different Bruker NMR spectrometers. UV–vis spectra were reecorded on a HP 8452A Diode Array spectrophotometer and a Perkin-Elmer Lambda 9. TGA measurements were carried out on a Perkin-Elmer Series 7 Analysis System, under nitrogen and air at heating rates of 20 °C/min. DSC measurements were performed on a Mettler TA-3000 under nitrogen at a heating rate of 20 °C/min. Melting points were determined by DSC. Inherent viscosities were measured with a Cannon–Fenske type viscosimeter at a polymer concentration of c = 0.5 g/dL at 25 °C. Static light scattering was done in NMP on a modified Sofica 42.000 using a 7 mW He-Ne laser light source (633 nm, vertically polarized). The intensity of scattered light was corrected for the optical absorption of the polymer solution. The refractive index increment at 633 nm was determined using a Brice Phoenix BP-2000-V differential refractometer. Elemental analyses were carried out by the Microanalysis Laboratory of the Department of Chemistry of ETH Zürich.

Monomer Synthesis. 2,5-Diacetamidotoluene (1). Acetic anhydride (400 mL) was cooled to 0 °C. 2,5-Diaminotoluene (55.5 g, 0.454 mol) was subsequently added to the stirred and ice cooled anhydride in 10 min. The reaction mixture was then stirred under cooling for 35 min, stirred an additional 130 min at ca. 45 °C, and finally poured into ice water (400 mL). The resulting slightly pink precipitate was collected, washed with water, dried, and recrystallized from ethanol to yield the white compound 1 (58.8 g, 66%): mp 222 °C; ^{1}H NMR (300 MHz, DMSO, 298 K) δ 2.01 (s, 3 H, $COCH_3$), 2.02 (s, 3 H, $COCH_3$), 2.14 (s, 3 H, Ar-CH_3), 7.24 (d, $^3J_{(H,H)}$ = 8.6 Hz, 1 H, Ar), 7.33 (dd, $^4J_{(H,H)}$ = 2.0 Hz, $^3J_{(H,H)}$ = 8.6 Hz, 1 H, Ar), 7.41 (d, $^4J_{(H,H)}$ = 2.0 Hz, 1 H, Ar), 9.20 (s, 1H, NH), 9.83 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO, 298 K) δ 17.97 (Ar-CH_3), 23.03 (CO-CH_3), 23.81 (CO-CH_3), 116.67, 120.62, 125.48, 131.56, 132.12, 136.31 (all Ar), 167.94 (carbonyl), 168.05 (carbonyl); mass spectrum m/e 206 (M^+ parent). Anal. Calcd for $C_{11}H_{14}N_2O_2$: C, 64.06; H 6.84; N 13.58. Found: C, 64.10; H, 6.72; N, 13.41.

2,5-Diacetamido-4-nitrotoluene (2). Compound 1 (66.7 g, 0.323 mol) was dissolved in acetic acid (260 mL) under heating. The clear solution was rapidly cooled to 18 °C, and a mixture of fuming nitric acid (11.3 mL) and 65% nitric acid (11.3 mL) was added dropwise to the ice-cooled reaction mixture at 18–20 °C. After the addition was completed, the mixture was stirred for 50 min at 15–24 °C and finally poured into cooled acetic acid (350 mL). The resulting yellow precipitate was collected, washed with water, dried, and recrystallized from acetic acid to yield the yellow compound 2 (52.9 g, 65%): mp 258 °C; ^{1}H NMR (200 MHz, DMSO, 298 K) δ 2.06 (s, 3 H, $COCH_3$), 2.10 (s, 3 H, $COCH_3$), 2.28 (s, 3 H, Ar-CH_3), 7.49 (s, 1H, Ar), 8.17 (s, 1H, Ar), 9.48 (s, 1H, NH), 10.13 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO, 298 K) δ 17.93 (Ar-CH_3), 23.29 (2 × CO-CH_3), 119.81, 126.65, 127.62, 133.23, 137.78, 139.79 (all Ar), 168.40 (carbonyl), 168.77 (carbonyl); mass spectrum m/e 251 (M^+ parent). Anal. Calcd for $C_{11}H_{13}N_3O_4$: C, 52.59; H, 5.22; N, 16.72. Found: C, 52.61; H, 5.35; N, 16.50.

***trans*-4-(Dimethylamino)-2′,5′-diacetamido-4′-nitrostilbene (3).** Compound 2 (26.5 g, 0.106 mol) and 4-(dimethylamino)-benzaldehyde (23.5 g, 0.157 mol) were dissolved in dry pyridine (270 mL) at reflux. Piperidine (13.5 mL) was added, and the reaction mixture was stirred at reflux for 6 h. Water produced during the condensation was extracted from the reaction mixture by a Soxhlet filled with molecular sieves. The resulting heterogeneous red mixture was cooled to room temperature, allowed to stand for 2 days, and transferred into ice water (1 L). The resulting precipitate was collected, washed with water, and dried to yield the crude red-brown compound 3 (32.7 g, 81%). A sample

of this product (3.6 g) was recrystallized first from cyclohexanone then from pyridine to yield the pure red brown compound **3** (2.3 g, 64%): mp 284 °C dec; ^{1}H NMR (400 MHz, DMSO, 298 K) δ 2.08 (s, 3 H, $COCH_3$), 2.15 (s, 3 H, $COCH_3$), 2.97 (s, 6 H, $N(CH_3)_2$), 6.76 (d, $^3J_{(H,H)}$ = 8.7 Hz AA'BB'-system, 2H, aromatic), 7.11/7.21 (m, $^3J_{(H,H)}$ = 16.1 Hz AB-system, 2 H, trans vinylene), 7.52 (d, $^3J_{(H,H)}$ = 8.7 Hz AA'BB'-system, 2 H, Ar), 7.94 (s, 1 H, Ar), 8.19 (s, 1 H, Ar), 9.82 (s, 1 H, NH), 10.17 (s, 1 H, NH); ^{13}C NMR (100 MHz, DMSO, 298 K) δ 23.36 (2 × CO-CH_3), 39.72 ($N(CH_3)_2$), 111.93 (2 Ar), 116.40 (vinylic), 120.89, 121.55, 124.01, 128.30, 128.52, 131.08 (all Ar), 134.06 (vinylic), 136.98, 139.42, 150.61 (all Ar), 168.51 (carbonyl), 169.02 (carbonyl); mass spectrum *m/e* 382 (M^+ parent). Anal. Calcd for $C_{20}H_{22}N_4O_4$: C, 62.82; H, 5.80; N, 14.65. Found: C, 62.64; H, 6.04; N, 14.50.

***trans*-2',5'-Diamino-4-(dimethylamino)-4'-nitrostilbene (4, DDANS).** The crude compound **3** (37.6 g, ca. 98 mmol) was dissolved in 12% hydrochloric acid (600 mL) and heated to reflux for 1 h to form a yellow precipitate. The reaction mixture was then cooled in an ice bath for 1 h and the precipitate was collected. It was transferred in an aqueous solution of 0.75 N NaOH (400 mL) and stirred for 15 min. The resulting deep purple precipitate was filtered off, washed with 0.75 N NaOH and water, dried, and recrystallized first from toluene then from acetone/water to yield the compound **4** (12.9 g, ca. 44%) as violet-black crystals: mp 222 °C dec; ^{1}H NMR (300 MHz, DMSO, 298 K) δ 2.95 (s, 6 H, $N(CH_3)_2$), 4.97 (s, 2 H, NH_2), 6.73 (d, $^3J_{(H,H)}$ = 8.9 Hz AA'BB'-system, 2H, aromatic), 6.76 (s, 2 H, NH_2), 6.98/7.14 (m, $^3J_{(H,H)}$ = 16.1 Hz AB-system, 2 H, trans vinylene), 7.14 (s, 1 H, Ar), 7.28 (s, 1 H, Ar), 7.52 (d, $^3J_{(H,H)}$ = 8.9 Hz AA'BB'-system, 2 H, Ar); ^{13}C NMR (50 MHz, DMSO, 298 K) δ 39.78 ($N(CH_3)_2$), 107.32 (Ar), 111.96 (2 Ar), 113.55 (Ar), 117.56 (vinylic), 124.48 (Ar), 128.27 (2 Ar), 129.39 (Ar), 132.72 (vinylic), 135.11, 136.74, 139.27, 150.33 (all Ar); mass spectrum *m/e* 298 (M^+ parent). Anal. Calcd for $C_{16}H_{18}N_4O_2$: C, 64.41; H, 6.08; N, 18.78; O, 10.73. Found: C, 64.45; H, 6.01; N, 18.74; O, 10.87.

Polymer Synthesis. Polymer P1. DDANS (**4**) (2.801 g, 9.388 mmol) and LiCl (2.23 g) were weighed into a three-necked flask equipped with a mechanical stirrer, argon inlet, and a septum and dissolved in NMP (19 mL). The solution was cooled for 30 min in a salt–ice bath, and tetradecanedioyl dichloride (2.772 g, 9.388 mmol) and additional NMP (18 mL) were added through a syringe. The system was stirred under further cooling for about 4 h and then at room temperature for another 46 h. Finally the solution was diluted with NMP (30 mL) and poured into water (1300 mL). The precipitated polymer was washed with water until the water was free of chloride ions and dried in vacuum at 65 °C to yield the red brown polymer **P1** (4.55 g, 93%): ^{1}H NMR (500 MHz, DMSO, 353 K) δ 1.30 (m, 16 H, 8 × CH_2), 1.64 (m, 4 H, 2 × β-CH_2), 2.40 (m, 4H, 2 × α-CH_2), 2.95 (s, 6 H, $N(CH_3)_2$), 6.73 (d, $^3J_{(H,H)}$ = 7.8 Hz AA'BB'-system, 2H, aromatic), 7.10 (m, 2 H, vinylene), 7.46 (d, $^3J_{(H,H)}$ = 7.8 Hz AA'BB'-system, 2 H, Ar), 8.17 (s, 1 H, Ar), 8.18 (s, 1 H, Ar), 9.49 (s, 1 H, NH), 9.91 (s, 1 H, NH); ^{13}C NMR (125 MHz, DMSO, 353 K) δ 24.76, 25.16, 28.51, 28.59, 28.67, 28.78, 28.81, 28.83, 28.88, 28.92, 28.95, 28.98, 35.84, 36.42, 112.15, 117.22, 120.38, 121.98, 124.45, 128.40, 129.39, 131.04, 134.14, 138.15, 138.48, 150.80, 171.52, 172.03. Anal. Calcd for $(C_{30}H_{40}N_4O_4)_n$: C, 69.20; H, 7.74; N, 10.76; O, 12.29. Found: C, 69.43; H, 7.54; N, 10.52; O, 12.01.

Polymer P2. DDANS (**4**) (2.937 g, 9.844 mmol) was weighed into a three-necked flask equipped with a mechanical stirrer, argon inlet, and a septum and a dissolved in NMP (15 mL). The solution was cooled for 15 min in a salt–ice bath, and then trimethylchlorosilane (0.5 mL), NMP (10 mL), and after another 10 min cooling dodecanedioyl dichloride (2.632 g, 9.850 mmol) and additional NMP (6 mL) were added through a syringe. The system was stirred under further cooling for about 4 h and then at room temperature for another 44 h. Finally the solution was diluted with NMP (25 mL) and poured into water (2000 mL). The precipitated polymer was washed with water until the water was free of chloride ions and dried in vacuum at 80 °C to yield the red brown polymer **P2** (4.70 g, 97%): ^{1}H NMR (500 MHz, DMSO, 353 K) δ 1.31 (m, 12 H, 6 × CH_2), 1.64 (m, 4 H, 2 × β-CH_2), 2.40 (m, 4 H, 2 × α-CH_2), 2.95 (s, 6 H, $N(CH_3)_2$), 6.73 (d, $^3J_{(H,H)}$ = 7.2 Hz AA'BB'-system, 2H, aromatic), 7.10 (m, 2 H, vinylene), 7.46 (d, $^3J_{(H,H)}$ = 7.6 Hz AA'BB'-system, 2 H, Ar), 8.15 (s, 1 H, Ar), 8.17 (s, 1 H, Ar), 9.49 (s, 1 H, NH), 9.90 (s, 1 H, NH). Anal. Calcd for $(C_{28}H_{36}N_4O_4)_n$: C, 68.27; H, 7.37; N, 11.37; O, 12.99. Found: C, 67.97; H, 7.24; N, 10.58; O, 12.89.

Polymer P3. DDANS (**4**) (3.032 g, 10.16 mmol) was weighed into a three-necked flask equipped with a mechanical stirrer, argon inlet, and a septum, and dissolved in NMP (33 mL). The solution was cooled for 45 min in a salt–ice bath, and sebacoyl chloride (2.415 g, 10.10 mmol) and additional NMP (8 mL) were added through a syringe. The system was stirred under further cooling for about 4 h and then at room temperature for another 68 h. Finally the solution was diluted with NMP (40 mL) and poured into water (1000 mL). The precipitated polymer was washed with water until the water was free of chloride ions and dried in vacuum at 70 °C to yield the red brown polymer **P3** (4.35 g, 93%): ^{1}H NMR (500 MHz, DMSO, 353 K) δ 1.37 (m, 8 H, 4 × CH_2), 1.67 (m, 4 H, 2 × β-CH_2), 2.41 (m, 4 H, 2 × α-CH_2), 2.91 (s, 6 H, $N(CH_3)_2$), 6.72 (d, $^3J_{(H,H)}$ = 8.5 Hz AA'BB'-system, 2H, aromatic), 7.10 (m, 2 H, vinylene), 7.46 (d, $^3J_{(H,H)}$ = 8.5 Hz AA'BB'-system, 2 H, Ar), 8.15 (s, 1 H, Ar), 8.18 (s, 1 H, Ar), 9.49 (s, 1 H, NH), 9.91 (s, 1 H, NH). Anal. Calcd for $(C_{26}H_{32}N_4O_4)_n$: C, 67.22; H, 6.94; N, 12.06; O, 13.78. Found: C, 67.34; H, 6.78; N, 11.91; O, 13.87.

Polymer P4. DDANS (**4**) (2.978 g, 9.982 mmol) was weighed into a three-necked flask equipped with a mechanical stirrer, argon inlet, and a septum, and dissolved in NMP (20 mL). The solution was cooled for 45 min in a salt–ice bath, then trimethylchlorosilane (0.5 mL), NMP (2 mL), and after another 10 min cooling suberoyl chloride (2.1062 g, 9.978 mmol) and additional NMP (2 mL) were added through a syringe. The system was stirred under further cooling for about 4 h and then at room temperature for another 92 h. Finally the solution was diluted with NMP (25 mL) and poured into water (1500 mL). The precipitated polymer was washed with water until the water was free of chloride ions and dried in vacuum at 80 °C to yield the red brown polymer **P4** (4.10 g, 94%): ^{1}H NMR (500 MHz, DMSO, 300 K) δ 1.38 (m, 4 H, 2 × CH_2), 1.63 (m, 4 H, 2 × β-CH_2), 2.37 (m, 2 H, 1 × α-CH_2), 2.44 (m, 2 H, 1 × α-CH_2), 2.91 (s, 6 H, $N(CH_3)_2$), 6.71 (m, AA'BB'-system, 2H, aromatic), 7.11 (m, 2 H, vinylene), 7.45 (d, AA'BB'-system, 2 H, Ar), 7.99 (s, 1 H, Ar), 8.13 (s, 1 H, Ar), 9.76 (s, 1 H, NH), 10.13 (s, 1 H, NH). Anal. Calcd for $(C_{24}H_{28}N_4O_4)_n$: C, 66.04, H, 6.47; N, 12.84; O, 14.66. Found: C, 65.86; H, 6.54; N, 12.72; O, 14.89.

Polymer P5. DDANS (**4**) (2.402 g, 8.051 mmol) was weighed into a three-necked flask equipped with a mechanical stirrer, argon inlet, and a septum and dissolved in NMP (20 mL). The solution was cooled for 30 min in a salt–ice bath, and adipoyl chloride (1.4735 g, 8.050 mmol) and additional NMP (6 mL) were added through a syringe. The system was stirred under further cooling for about 2 h and then at room temperature for another 41 h. Finally the solution was diluted with NMP (20 mL) and poured into water (1100 mL). The precipitated polymer was washed with water until the water was free of chloride ions and dried in vacuum at 60 °C to yield the red brown polymer **P5** (3.11 g, 90%): ^{1}H NMR (400 MHz, DMSO, 353 K) δ 1.76 (m, 4 H, 2 × β-CH_2), 2.45 (m, 4 H, 2 × α-CH_2), 2.90 (s, 6 H, $N(CH_3)_2$), 6.70 (m, AA'BB'-system, 2H, aromatic), 7.08 (m, 2 H, vinylene), 7.43 (m, AA'BB'-system, 2 H, Ar), 8.17 (s, 1 H, Ar), 8.20 (s, 1 H, Ar), 9.49 (s, 1 H, NH), 9.92 (s, 1 H, NH). Anal. Calcd for $(C_{22}H_{24}N_4O_4)_n$: C, 64.69; H, 5.92; N, 13.72; O, 15.67. Found: C, 63.33; H, 5.90; N, 13.29; O, 15.85.

Film Preparation. The polymers **P1–P5** were dissolved in dry NMP at concentrations of 3–8% w/w polymer. The solutions were filtered through a 0.45 μm filter and were spin-cast under heating either on substrates of fused silica (for linear optical measurements) or indium tin oxide (ITO) glass (for nonlinear optical measurements). The polymer films were dried at 70 °C in vacuum. The thickness of the films ranged from 0.4 up to 1 μm as measured with a Tencor Instruments Alpha-Step 200 profilometer.

Linear Optical Measurements. Refractive index dispersion formulas of **P1** and **P4** were determined from the interference fringes in the transmission spectra of unpoled polymeric films on fused silica substrates. According to expressions published before,[19] the transmissivity is a function of the wavelength, the film thickness, and all the refractive indices of the substrate, the film, and the covering medium. Knowing the refractive index of the substrate, the real part of the refractive index could be

fitted to a one-oscillator Sellmeier dispersion formula

$$n_f^2(\lambda) - 1 = \frac{q}{1/\lambda_0^2 - 1/\lambda^2} + A$$

where λ_0 is the absorption wavelength of the dominant oscillator, q is a measure for the oscillator strength, and A is a constant containing the sum of all the other oscillators. The thickness of the samples was about 0.65 μm.

For 633 and 1300 nm, the refractive indices for **P1** and **P4** were determined by ellipsometry using a Plasmos SD 2300 ellipsometer. The refractive indices were measured in the substrate mode. Samples of ca. 15 μm thickness on both glass and silicon substrates were used.

Corona Poling. Films of **P1** and **P4** were corona poled with a dc electric field using glass substrates coated with a 20-nm thick ITO conductive layer (Balzers Baltracon 217) as the ground electrode and a tungsten corona needle. The films were heated on a custom made hotstage under applied field to about 15° above T_g. The films were held at this temperature for about 10 min and then cooled to room temperature in 30–120 min in the presence of the field. The applied corona voltage was +(12–15) kV at a poling current of <0.1 mA. The gap distance was ca. 3 cm.

NLO Measurements. Nonlinear optical measurements were performed using a standard Maker-fringe technique.[20] The experimental setup is shown in Figure 5. A continuum Q-switched Nd:YAG laser with a pulse width of 7 ns at a 5 Hz repetition rate and a pulse energy of ca. 250 mJ was used as pump laser at λ = 1064 nm. Stimulated Raman scattering in CH_4 gas at a pressure of around 20 bars provided the fundamental wavelength of λ = 1542 nm. The polymer films were rotated perpendicular to the incoming laser beam. The polarization was chosen to be in the plane of incidence (p polarization). SHG coefficients have always been measured after switching off the poling field.

The nonlinear optical coefficients $d_{33} = 3 \cdot d_{31}$ were evaluated following the formula given in ref 20

$$I^{2\omega}(\theta) = \frac{8}{\epsilon_0 c} d_{33}^2 (t_{af}^{\omega})^4 T^{2\omega}(\theta) (t_{sa}^{2\omega})^2 p^2(\theta) I_{\omega}^2 \left(\frac{1}{n_{\omega}^2 - n_{2\omega}^2}\right)^2 \sin^2\left(\frac{\Delta k L}{2}\right)$$

where I_ω and $I^{2\omega}(\theta)$ are the intensities at the fundamental and second harmonic frequency and θ is the angle of incidence. The t_{af}^{ω}, $T^{2\omega}(\theta)$, and $t_{sa}^{2\omega}$ are transmission coefficients at the interfaces air/film, film/substrate, and substrate/air, $p(\theta)$ is a projection factor, and n_ω and $n_{2\omega}$ are the refractive indices at the fundamental and second harmonic frequency. L is the film thickness and Δk the phase mismatch between the free and the bound wave in the sample.

For film thicknesses much smaller than the coherence length $l_c = \lambda/(4|n_{2\omega} - n_\omega|)$ the term $\sin^2(\Delta k L / 2)$ can be approximated by a power series:[24]

$$\sin^2\left(\frac{\Delta k L}{2}\right) \approx \left(\frac{\pi}{2}\frac{L}{l_c}\frac{(n_\omega + n_{2\omega})/2}{[(n_\omega^2 + n_{2\omega}^2)/2 - \sin^2\theta]^{1/2}}\right)^2$$

We used this approximation since our sample thicknesses of around 800 nm were small enough compared to the coherence length of 6.3 μm for **P1** and 4.9 μm for **P4** at λ = 1.542 μm. The signals from the polymer films were compared to a quartz reference crystal (d_{11} = 0.4 pm/V).

Acknowledgment. Financial support by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* (NF Sektion II) is gratefully acknowledged. We also acknowledge J. Stejskal of the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences for static light scattering measurements.

IUPAC Nomenclature

1	*N*-[4-(Acetylamino)-2-methylphenyl]acetamide
2	*N*-[4-(Acetylamino)-2-methyl-5-nitrophenyl]-acetamide
3	*N*-{4-(Acetylamino)-2-[2-(4-(dimethylamino)-phenyl)vinyl]-5-nitrophenyl}acetamide
4	2-{2-[4-(Dimethylamino)phenyl]vinyl}-5-nitrobenzene-1,4-diamine
P1	Poly{[2-[2-(4-(Dimethylamino)phenyl)vinyl]-5-nitro-1,4-phenylene]iminocarbonyldodecamethylenecarbonylimino}
P2	Poly{[2-[2-(4-(Dimethylamino)phenyl)vinyl]-5-nitro-1,4-phenylene]iminocarbonyldecamethylenecarbonylimino}
P3	Poly{[2-[2-(4-(Dimethylamino)phenyl)vinyl]-5-nitro-1,4-phenylene]iminosebacoylimino}
P4	Poly{[2-[2-(4-(Dimethylamino)phenyl)vinyl]-5-nitro-1,4-phenylene]iminosuberoylimino}
P5	Poly{[2-[2-(4-(Dimethylamino)phenyl)vinyl]-5-nitro-1,4-phenylene]iminoadipoylimino}

References and Notes

(1) See, for example: *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., Ed.; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1983. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic: New York, 1987. *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum Press: New York, 1988. *Nonlinear Optical Effects in Organic Polymers*; Messier, J., Kajzar, F., Prasad, P. N., Ulrich, D. R., Eds.; Kluwer Academic Publishers: Dordrecht, 1989. *Materials for Nonlinear Optics*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991.

(2) Meredith, G. R.; Van Dusen, J. G.; Williams, D. J. *Macromolecules* **1982**, *15*, 1385.

(3) Hampsch, L. H.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1988**, *21*, 526.

(4) Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, *49*, 248.

(5) Eich, M.; Sen, A.; Looser, H.; Bjorklund, G. C.; Swalen, J. D.; Twieg, R.; Yoon, D. J. *J. Appl. Phys.* **1989**, *66*, 2559.

(6) Leslie, T. M.; DeMartino, R. N.; Choe, E. W.; Khanarian, G.; Haas, P.; Nelson, G.; Stamatoff, J. B.; Stuetz, D. G.; Teng, C. C.; Yoon, H. N. *Mol. Cryst. Liq. Cryst.* **1987**, *153*, 451.

(7) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1989**, *1*, 167.

(8) Eich, M.; Reck, B.; Yoon, D. J.; Willson, C. G.; Bjorklund, G. C. *J. Appl. Phys.* **1989**, *66*, 3241.

(9) Green, G. D.; Weinschenk, III, J. I.; Mulvaney, J. E.; Hall, H. K., Jr. *Macromolecules* **1987**, *22*, 722.

(10) Willand, C. S.; Williams, D. J. *Ber. Buns. Ges. Phys. Chem.* **1987**, *91*, 1304.

(11) Roviello, A.; Sirigu, A. *Makromol. Chem.* **1982**, *183*, 895.

(12) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 441.

(13) Levine, B. F.; Bethea, C. G. *J. Chem. Phys.* **1978**, *69*, 5240.

(14) Cheng, L. T.; Tam, W.; Meredith, G. R.; Rikken, G. L. J. A.; Meijer, E. W. In *Nonlinear Optical Properties of Organic Materials II*; Khanarian, G., Ed.; SPIE: 1989; Vol. 1147, p 61.

(15) Morgan, G. T.; Micklethwait, F. M. G. *J. Chem. Soc.* **1913**, *103*, 1398.

(16) Imai, Y.; Oishi, Y. *Prog. Polym. Sci.* **1989**, *14*, 73.

(17) Meyer, W. R.; Gentile, F. T.; Suter, U. W. *Macromolecules* **1991**, *24*, 642.

(18) Gentile, F. T.; Meyer, W. R.; Suter, U. W. *Macromolecules* **1991**, *24*, 633 and references cited therein.

(19) Manifacier, J. C.; Fillard, J. P. *J. Phys.* **1976**, *E9*, 1002.

(20) Jerphagnon, J.; Kurtz, S. K. *J. Appl. Phys.* **1970**, *41*, 1667.

(21) Bosshard, Ch.; Sutter, K.; Günter, P. *J. Opt. Soc. Am.* **1993**, *B10*, 867.

(22) Sigelle, M.; Hierle, R. *J. Appl. Phys.* **1981**, *52*, 4199.

(23) Bosshard, H. H.; Schmid, R. M.; Zollinger, Hch. *Helv. Chim. Acta* **1959**, *42*, 1653.

(24) Kuzyk, M. G.; Singer, K. D.; Zahn, H. E.; King, L. A. *J. Opt. Soc. Am.* **1989**, *B6*, 742.