Synthesis and Characterization of New Photorefractive Polymers with High Glass Transition Temperatures

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ABSTRACT: Polyamides based on 2′,5′-diamino-4-(dimethylamino)-4′-nitro-stilbene (DDANS) and aliphatic diacids represent a well-established class of polymers for nonlinear optical (NLO) applications, in which the NLO units are fixed in the polymer backbone with their dipole moments oriented transversly to the polymer main chain. The introduction of a hole transport (HT) agent, [4-((diphenylhydrazono)-methyl)phenyl]diethylamine (DEH) or 4-(bis(2-hydroxyethyl)amino)benzaldehyde 1,1-diphenylhydrazone (BBDH), was found to generate or enhance photorefractivity in these materials. Using appropriate chemical pathways, the NLO and HT moieties were connected in various ways, and polymer systems with dramatically different properties were obtained. Thus, (i) polyamides based on DDANS and aliphatic diacids, (ii) polyamide esters based on DDANS, BBDH, and adipic acid, (iii) polymer blends of the DDANS polyamides and a polyester based on BBDH and adipic acid, and (iv) DDANS polyamides doped with DEH have been prepared. All types of polymer systems were processed into transparent thin films by spin coating and could be oriented at elevated temperatures, applying a corona discharge poling technique. Second-order NLO coefficients (d_{33}) of up to 45 pm/V at a fundamental wavelength of 1542 nm have been measured. The poling efficiency was found to depend strongly on the content of the hydrazone moiety and the polymer system, decreasing with increasing content of hydrazone. Preliminary temperature-dependent two-beam coupling experiments demonstrated photorefractivity for DDANS-based systems, even at temperatures below the glass transition.

Introduction

Main-chain NLO polymers have received much attention in the past few years because of an improved orientational stability and a possible high NLO-phore concentration when compared to guest−host or side-chain systems.[1−7] The frequently cited advantages of poled polymers are large nonlinear susceptibilities, fast response times, and easy processability. Moreover, multifunctional polymers can easily be tailored and photorefractive materials can be produced by combining electrooptic and photoconductive properties.[8,9]

In this contribution, we investigate the potential of main-chain NLO polymers based on the NLO-phore DDANS for photorefractive applications. DDANS-based polyamides were found to show large nonlinear optical susceptibilities,[4] high orientational stability,[3,5] and also photoconductive properties.[6] However, to improve the photoconductive properties of these materials, we have incorporated the hole transport agent DEH[10,11] in these polymers. Of course, several possibilities exist to combine the required moieties in a material. We have used the NLO-phore DDANS and the hole transport agents DEH and BBDH[12] and prepared doped NLO polymers, polymer blends, random copolymers, and block copolymers (see Figures 1 and 2). Focusing on the maximal achievable orientational order, as induced by electric-field poling, and the related nonlinear optical response, we compare the properties of the new materials here.

Experimental Section

Methods. All reagents and solvents were purchased from Fluka (Buchs, CH) or Aldrich (Buchs, CH). NMP and pyridine were purified by distillation under reduced pressure from calcium hydride and subsequent drying over molecular sieves. Adipoyl chloride was distilled under reduced pressure. DDANS was prepared according to Weder et al.[4] BBDH was obtained following Yu et al.[12] and recrystallized twice with methanol and toluene. Tetradecanoic diacid dichloride was prepared by reaction of thionyl chloride with tetradecanoic acid according to the standard procedure.[13] Polymerizations were carried out under dry argon atmosphere using standard vacuum-line and glovebox techniques. ^{1}H NMR spectral data are expressed in ppm relative to internal TMS and were obtained on different Bruker NMR spectrometers. Differential scanning calorimetry (DSC) measurements were performed on a Mettler TA-3000 under nitrogen at a heating rate of 20 K/min. Inherent viscosities were measured with a Cannon−Fenske type viscosimeter at a polymer concentration of $c = 0.5$ g/dL at 25 °C in NMP. UV−vis spectra were recorded on a HP8452A diode array spectrophotometer and a Perkin-Elmer Lambda 9. Vapor phase osmometry (VPO) was performed using a "Corona Wescan Molecular Weight Apparatus". Gel-permeation chromatography was carried out on a Knauer GPC using a PLGel mixed C 5 μm column (detectors: differential refractometer Knauer, Viscotek H502 differential-viscosimeter, and light

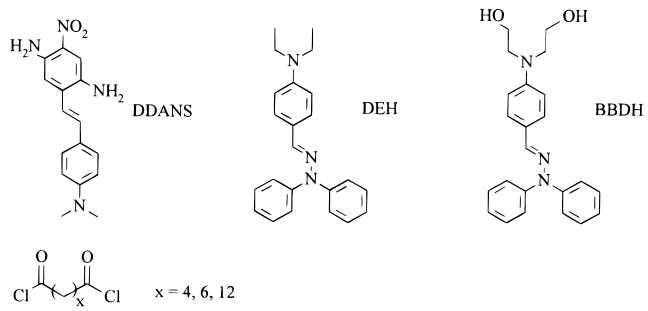

Figure 1. Chemical structure of monomers and dopants used.

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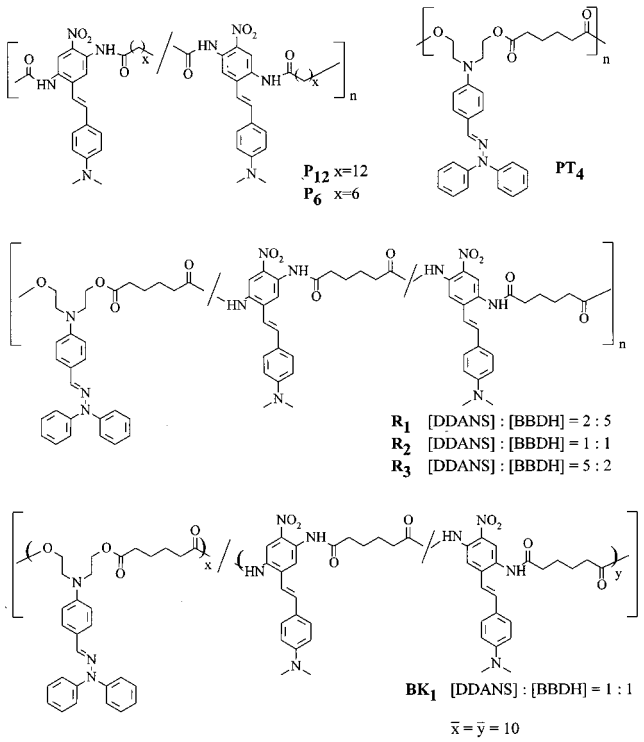

Figure 2. Chemical structures of the polymers under investigation.

scattering detector KMX-6 chromatix; conditions: solvent THF at 45 °C and flow 1.1 mL/min). Wide-angle X-ray scattering (WAXS) measurements were performed as described earlier.[14]

Polyester PT_4. 1.23 g (6.73 mmol) of BBDH was dissolved in 16 mL of NMP. An equimolar amount of adipoyl chloride was added dropwise under stirring at −10 °C through a syringe. After the mixture was stirred at −10 °C for 30 min, 0.57 g (7.40 mmol) of pyridine was added dropwise. The mixture was stirred under further cooling for about 6 h and then at room temperature for another 72 h. Finally the solution was poured into water. The precipitated polymer was washed with water until the water was free of chloride ions and dried in a vacuum to yield 3.01 g (92%) of slightly yellow polymer.

DSC: $T_g = 54$ °C. ^{1}H NMR (300 MHz, 300 K, DMSO): $\delta =$ 1.40 (s, b, 4 H), 2.17 (s, b, 4 H), 3.53 (s, b, 4 H), 4.11 (s, b, 4 H), 6.71 (s, b, 2 H), 7.02 (s, 1 H), 7.09 (m, 6 H), 7.39 (m, 6 H). Anal. Calcd for $(C_{29}H_{31}N_3O_4)_n$, $(485.6)_n$: C, 71.73; H, 6.43; N, 8.65; O, 13.18. Found: C, 71.17; H, 6.48; N, 8.58; O, 13.77. GPC: $M_w = 1 \times 10^4$ in THF.

Random Copolymers. x mol of DDANS and y mole of BBDH were dissolved in NMP. $(x + y)$ mol of adipoyl chloride was added dropwise under stirring at −10 °C through a syringe. After the mixture was stirred at −10 °C for 30 min, $2(x + y)$ mol of pyridine was added dropwise. The mixture was stirred under further cooling for about 6 h and then at room temperature for another 72 h. If necessary, the solution was diluted with NMP to reduce viscosity. Finally the solution was poured into water. The precipitated polymer was washed with water until the water was free of chloride ions and dried in a vacuum at 80 °C to yield dark random copolymers. Detailed reaction conditions for the preparation of copolymers **R_1**, **R_2**, and **R_3** are given in Table 1.

Copolymer R_1. DSC: $T_g = 80$ °C. η_{inh}: 0.40 dL/g (NMP, 25 °C, $c = 0.54$ g/dL). ^{1}H NMR (300 MHz, 300 K, DMSO): δ = 1.39, 1.56, 1.75 (s, br, 4 "amide-H", 4 "ester-H"), 2.16, 2.27, 2.78 (s, br, 4 "amide-H", 4 "ester-H"), 2.89 (s, 6 "amide-H"), 3.53 (s, br, 4 "ester-H"), 4.09 (s, br, 4 "ester-H"), 6.68 (m, 2 "amide-H", 2 "ester-H"), 7.09 (m, 2 "amide-H", 7 "ester-H"), 7.36 (m, 2 "amide-H", 6 "ester-H"), 8.01, 8.17 (s, 2 "amide-H"), 9.75, 10.13 (2 × s, 2 "amide-H") (note: protons from the BBDH acid segment and the DDANS acid segment are referred to as "ester-H" and "amide-H", respectively). Molar ratio DDANS/BBDH: calc. 28:72; determined by ^{1}H NMR, 26:74. Anal. Calc: C, 70.00; H, 6.31; N, 9.90; O, 13.79. Found: C, 70.07; H, 6.31; N, 9.86; O, 13.76.

Table 1. Conditions for Random Copolymerizations

	DDANS (mmol)	BBDH (mmol)	adipoyl chloride (mmol)	pyridine (mmol)	tot. NMP (mL)	yield (%)
R_1	4.996	12.90	17.90	18	14	92
R_2	6.852	5.448	12.30	12	10	92
R_3	6.041	2.325	8.366	16	11	98

Copolymer R_2. DSC: $T_g = 111$ °C. η_{inh}: 0.40 dL/g. (NMP, 25 °C, $c = 0.55$ g/dL). ^{1}H NMR:(300 MHz, 300 K, DMSO): δ = 1.40, 1.56, 1.74 (s, br, 4 "amide-H", 4 "ester-H"), 2.18, 2.31, 2.42, 2.78 (s, br, 4 "amide-H", 4 "ester-H"), 2.89 (s, 6 "amide-H"), 3.57 (s, br, 4 "ester-H"), 4.13 (s, br, 4 "ester-H"), 6.68 (m, 2 "amide-H", 2 "ester-H"), 7.10 (m, 2 "amide-H", 7 "ester-H"), 7.39 (m, 2 "amide-H", 6 "ester-H"), 8.00, 8.17 (s, 2 "amide-H"), 9.75, 10.13 (2 × s, 2 "amide-H"). Molar ratio DDANS/BBDH: calc, 56:44; determined by ^{1}H NMR, 51:49. Anal. Calc: C, 67.81; H, 6.15; N, 11.47; O, 14.57. Found: C, 67.77; H, 6.20; N, 11.11; O, 14.92. VPO: $M_n = 2 \times 10^4$ in DMF.

Copolymer R_3. DSC: $T_g = 131$ °C. η_{inh}: 0.41 dL/g (NMP, 25 °C, $c = 0.54$ g/dL). ^{1}H NMR (300 MHz, 300 K, DMSO): δ = 1.41, 1.57, 1.72, 1.87 (s, br, 4 "amide-H", 4 "ester-H"), 2.18, 2.32, 2.42, 2.69 (s, br, 4 "amide-H", 4 "ester-H"), 2.89 (s, 6 "amide-H"), 3.59 (s, br, 4 "ester-H"), 4.15 (s, br, 4 "ester-H"), 6.68 (m, 2 "amide-H", 2 "ester-H"), 7.11 (m, 2 "amide-H", 7 "ester-H"), 7.40 (m, 2 "amide-H", 6 "ester-H"), 8.01, 8.17 (s, 2 "amide-H"), 9.76, 10.14 (2 × s, 2 "amide-H"). Molar ratio DDANS/BBDH: calc, 72:28; determined by ^{1}H NMR, 68:32. Anal. Calc: C, 66.92; H, 6.08; N, 12.11; O, 14.88. Found: C, 66.00; H, 6.39; N, 11.96; O, 15.65.

Block Copolymer BK_1. 3.877 mmol of DDANS was dissolved in 5 mL of NMP. The solution was cooled to −10 °C, and 3.490 mmol of adipoyl chloride was added dropwise under stirring at −10 °C through a syringe. The reaction mixture was stirred under further cooling for about 5 h. Then 3.599 mmol of adipoyl chloride was added under stirring at −10 °C. After 1 h, 3.209 mmol of BBDH dissolved in NMP was added. After further stirring for 30 min, 6.27 mmol of pyridine was added. The mixture was stirred under further cooling for about 6 h and then at room temperature for another 72 h. Finally, the solution was poured into water. The precipitated polymer was washed with water until the water was free of chloride ions and dried in a vacuum at 80 °C to yield 3.0 g (95%) of the dark blockcopolymer.

DSC: $T_g = 80$ and 160 °C. η_{inh}: 0.21 dL/g (NMP, 25 °C, c = 0.52 g/dL). ^{1}H NMR (300 MHz, 300 K, DMSO): $\delta = 1.39$, 1.56, 1.72 (s, br, 4 "amide-H", 4 "ester-H"), 2.17, 2.27, 2.42 (s, br, 4 "amide-H", 4 "ester-H"), 2.89 (s, 6 "amide-H"), 3.54 (s, br, 4 "ester-H"), 4.11 (s, br, 4 "ester-H"), 6.68 (m, 2 "amide-H", 2 "ester-H"), 7.10 (m, 2 "amide-H", 7 "ester-H"), 7.38 (m, 2 "amide-H", 6 "ester-H"), 7.99, 8.17 (s, 2 "amide-H"), 9.82, 10.20 (2 × s, 2 "amide-H"). Molar ratio DDANS/BBDH: calc, 55: 45; determined by ^{1}H NMR, 48:52. Anal. Calc: C, 68.20; H, 6.13; N, 11.22; O, 14.45. Found: C, 68.11; H, 6.31; N, 11.10; O, 14.48. VPO: $M_n = 1.2 \times 10^4$ in DMF.

Film Preparation. The polymers were dissolved in NMP at concentrations of 5 wt % polymer. The solutions were filtered through a 0.45 μm Teflon filter and were spin-cast under heating on various substrates. The polymer films were dried overnight at 80 °C in a vacuum. The thickness of the films ranged from 0.4 to 0.8 μm as measured with a Tencor Instruments Alpha-Step 200 profilometer.

Samples for two-beam coupling experiments were prepared by solution casting from NMP using a hot stage. The polymer films were dried at 80 °C in a vacuum for about 1 month. The thickness ranged from 50 to 80 μm. For every sample, two of these solution cast films on ITO coated glass slides were pressed together at elevated temperatures under vacuum to result in homogeneous films of a thickness of 100−160 μm.

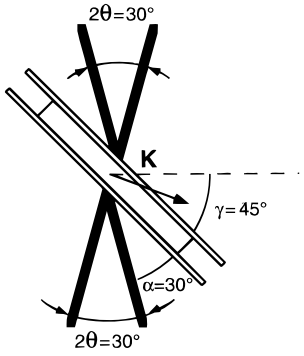

Figure 3. Tilted geometry used in two-beam coupling experiments. Two equally intense coherent laser beams of an argon-pumped Ti:sapphire laser (λ = 820 nm) are incident onto the sample, and their intensities are recorded as the grating is written. (The laser beams used for the stabilization of the phase between the two writing beams are not shown in this representation.)

Corona Poling. Spin-cast films of all copolymers were corona poled with a dc electric field using glass substrates coated with a 20 nm thick ITO conductive layer (Balzers Baltacron 217) as a ground electrode and a tungsten corona needle. The films were heated, in air and in the dark, on a custom-made hot-stage under applied field to the poling temperature. The latter was empirically optimized for each polymer by simultaneously conducting a second harmonic generation (SHG) experiment and was usually about 5−20 °C above T_g. The films were held at this temperature for about 30 min and then cooled to 40−60 °C in 60−80 min in the presence of the electric field. The applied corona voltage was 13 kV. The gap distance between the tip of the needle and the polymer film was 3 cm.

Electrode Poling. Samples for two-beam coupling experiments were oriented by electrode poling prior to the two-beam coupling experiment. The samples were heated to the poling temperature while applying a dc electric field of 15−40 V/μm to the ITO electrodes on the glass substrates. The films were held at this temperature for about 30 min and then cooled to 40−60 °C in 60−80 min in the presence of the electric field.

Linear and Nonlinear Optical Measurements. All linear optical and SHG measurements were performed as described earlier.[4] Two-beam coupling experiments were performed at a wavelength, λ, of 820 nm, an incident beam intensity I_0 of 10 mW/cm^2, and an applied electrical field of up to 20 V/μm. Two s-polarized coherent beams (Ti:sapphire) incident onto the polymer (Figure 3) were recorded, as one of the beams was alternatively blocked; from the ratio of the intensity of the signal with pump beam and its intensity without pump beam, the gain of the polymer was calculated. Since experiments were also performed at temperatures near T_g, to enhance the field-induced orientational contributions to the photorefractive grating, a stabilization of the phase between the two writing beams was necessary. This stabilization was achieved using a piezo-electrical mirror that was driven by a voltage source whose amplitude was inversely proportional to the interference signal of two coherent beams propagating quasi-parallel to the writing beams (wavelength chosen far from the absorption resonance of the polymer to avoid a competing grating). This stabilized setup guarantees a constant phase between the two writing beams over a time period longer than the typical writing times. A detailed description of these experiments will be published elsewhere.[15]

Results and Discussion

Monomer and Polymer Synthesis. DDANS and BBDH have been prepared according to the procedures described elsewhere.[4,12] The preparation of polyamides **P12** and **P6** based on DDANS and tetradecanoic diacid dichloride and suberoyl dichloride, respectively, was also described earlier.[4] All other polymers, compiled in Figure 2, were prepared by low-temperature polycondensation in solution.[16,17] DDANS, BBDH, and different linear aliphatic diacid dichlorides were reacted in NMP as solvent at temperatures of −10 to 0 °C. Using this method, high-molecular-weight polymers could be achieved under relatively mild reaction conditions. To activate the diacid dichloride toward the reaction with hydroxy groups, pyridine was added in the case of polyester and poly(ester amide)s.[18,19]

Table 2. Physical Properties of Polymers

polymer	DDANS (wt %)	T_g[a] (°C)	η_{inh}[b] (dL/g)	molecular weight (g mol^{-1})
P12	67.7	125	0.39	
P6	80.7	180	1.11	$M_w \approx 2.8 \times 10^5$ [c]
PT4	0	54	n.d.	$M_w = 1.0 \times 10^4$ [d]
R1	21.2	73	0.40	
R2	44.4	108	0.40	$M_n = 2.0 \times 10^4$ [e]
R3	59.2	131	0.41	
BK1	43.5	80 and 160	0.21	$M_n = 1.2 \times 10^4$ [e]

[a] Determined by DSC (20 K/min). [b] Inherent viscosity, measured in NMP at 25 °C and a concentration of 0.5 g/L. [c] Estimated from light scattering experiments performed by Weder et al.[4] [d] Measured by gel-permeation chromatography. [e] Measured by vapor phase osmometry in DMF.

Polyester **PT4** is of slightly yellow color with an absorption maximum of 364 nm. It is readily soluble in common solvents such as dioxane, chloroform, or NMP. The new material was characterized by NMR spectroscopy and elemental analysis. The weight-average molecular weight M_w was determined by gel-permeation chromatography (GPC) to be 1×10^4. The glass transition temperature of this fully amorphous polyester is 54 °C as determined by DSC.

Random copolymers **R1**, **R2**, and **R3** with different contents of DDANS and BBDH were also obtained by low-temperature polycondensation in NMP. These copolymers were of dark color and easily soluble in NMP. The polymers were characterized by NMR spectroscopy and elemental analysis. The inherent viscosities measured at a polymer concentration of c = 0.5 g/dL at 25 °C in NMP were all in the range of 0.4 dL/g and prove the polymeric character of all random copolymers. In addition, the number-average molecular weight M_n of **R2** was determined by vapor phase osmometry and found to be 2×10^4. The glass transition temperatures depend on the composition and range from 80 °C (**R1**, low content of DDANS) to 131 °C (**R3**, high content of DDANS), in good agreement with the Fox−Flory theory.[20]

Block copolymer **BK1** was obtained by a one-pot, stepwise reaction procedure. In a first step, oligomers of DDANS and adipoyl chloride were produced by nonequimolar oligomerization in NMP under low-temperature polycondensation conditions. Subsequently, BBDH, the corresponding amount of adipoyl chloride, and finally pyridine were added. Block copolymer **BK1** has a theoretical average block length of 10 DDANS units. The obtained polymer is readily soluble in NMP and exhibits an inherent viscosity of 0.2 dL/g. The number-average molecular weight M_n of this polymer was 1.2×10^4, as determined by VPO. **BK1** shows two separate glass transitions at 80 and 160 °C, a behavior consistent with the block character of the polymer. The physical properties of all polymers described here are summarized in Table 2.

Preparation of Polymer films. All polymers could be processed into dark red and transparent films of

various thickness by spin coating or solution casting from NMP solutions on heated substrates. All films were amorphous as could be shown by WAXS of solution-cast films.

Preparation of Doped Polyamides and Polymer Blends. In addition to the pure materials, doped polymers and polymers blends were prepared by spin coating or solution casting of solutions of polyamides **P12** or **P6** and DEH or polyester **PT4** in NMP. Doping of polyamides **P12** and **P6** with DEH was found to plasticize the polyamides as discussed in detail in ref 21. Transparent films could be obtained with up to 40 wt % DEH. Films with higher contents of DEH were opaque, consistent with the occurrence of phase segregation in this regime. Blending of **P12** and **P6** on one hand and **PT4** on the other hand yielded transparent films up to a maximum content of 40 wt % **PT4**. All polymer blends exhibited two glass transitions at temperatures very similar to those of the pure components. Hence, these polymer blends are incompatible in a thermodynamic sense but seem to be compatible in the sense of optical homogenity,[22] i.e., featuring domain sizes considerably smaller than the wavelength of light. With respect to blends, only polymers **P6** and **PT4** were investigated in more detail, employing the abbreviation **BD**$_x$ for a polymer blend of **P6** with x wt % of **PT4**.

Linear Optical Properties. All polymers containing DDANS exhibit a charge-transfer band in the visible with a maximum at 472−474 nm but are essentially transparent above about 700 nm. All polymers containing DEH or BBDH show an absorption band at 364 nm, related to the charge-transfer band of the hydrazone moiety. Polymers containing both, DDANS and DEH or BBDH, show a linear superposition of both spectra. Refractive indices were determined from the interference fringes in the UV/vis/NIR transmission spectra of thin polymeric films on fused silica substrates, using a one-oscillator Sellmeier dispersion formula that was fitted to the experimental data for each polymer.[23] Refractive indices of the polymers described here are in the range of 1.6−1.7; values measured at 771 and 1542 nm are listed in Table 3.

Poling Procedure. Films used for SHG experiments were oriented using a corona discharge technique while electrode-poling was applied to samples that were used for two-beam coupling experiments. Poling was performed in air and in the dark, at temperatures empirically found to yield the maximum NLO response (see Experimental Section).

Nonlinear Optical Susceptibility. The nonlinear optical coefficients d_{31} have been determined using a standard Maker fringe technique,[24] and d_{33} values were calculated by applying the isotropic model.[25,26] Measurements have been performed at 1.5 μm, which results in NLO coefficients that are essentially free from resonance enhancement. As discussed above, poling conditions were optimized for each polymer. In most cases, the optimal poling temperature was found to be slightly higher than T_g. Surprisingly, the best poling temperature for block copolymer **BK1** was determined to be 125 °C, which is similar to that of the corresponding random copolymer **R2**, which is optimally poled at 120 °C. This behavior is consistent with the assumption that the average block length of **BK1** is so short that the polymer behaves at 125 °C similarly to a random copolymer because more polymer segments are moving cooperatively than at T_g of the hydrazone block. The highest d_{33} values that were obtained are given for all materials under investigation in Table 3. These values, up to 45 pm/V, are among the best for polymers with this NLO-phore. For the purpose of comparison, the ratio of d_{33} and the content of NLO-phore in the materials is plotted against the poling temperature in Figure 4 (note that the ratio d_{33}/wt % DDANS is used to compare materials of different NLO-phore content).

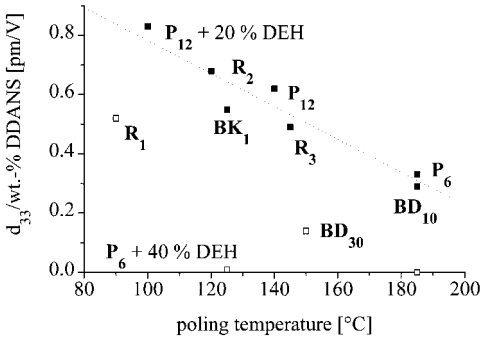

Figure 4. Ratio of optimized nonlinear optical coefficient d_{33} and NLO-phore content (d_{33}/wt % DDANS) plotted against (optimized) poling temperature. Polymers which can efficiently be poled show an apparently linear dependence of optimum poling temperature on d_{33}/wt % DDANS; this might be due to thermal decomposition at elevated temperatures.

As can be seen clearly from Figure 4, the ratio d_{33}/wt % DDANS decreases with increasing poling temperature. This can be understood by thermal decomposition effects, as discussed in detail in refs 3 and 5. However, some materials cannot be poled efficiently (**BD**$_{30}$, **P**$_6$ + 40% DEH, **R**$_1$), even at low poling temperatures. In general, polymers with a high content of hydrazone moieties show a significantly smaller nonlinear optical susceptibility than expected from the concentration of the NLO-phore present in the material and the poling temperature, as discussed above. These results are

Table 3. Linear and Nonlinear Optical Properties of Polymers

polymer	T_g (°C)	poling temp (°C)	refractive index 771 nm	refractive index 1542 nm	d_{33} (pm/V)	d_{33}/wt % DDANS (pm/V)
P12	125	140	1.73	1.64	42	0.62
P6	180	185	1.69	1.62	27	0.33
PT4	54	70	1.59	1.56	<1	
P12 + 20% DEH	95	100	1.68	1.62	45	0.83
P6 + 40% DEH[a]	117	125	1.59	1.56	<1	<0.02
BD10	64 and 176	185	n.d.	n.d.	21	0.29
BD30	52 and 173	140	1.66	1.60	8	0.14
R1	73	90	1.72	1.65	11	0.49
R2	108	120	1.71	1.64	30	0.68
R3	131	145	1.71	1.64	29	0.52
BK1	80 and 160	125	1.70	1.64	24	0.55

[a] **P6** + 40% DEH was used, because **P12** + 40% DEH exhibits a T_g of 60 °C and, thus, is prone to a fast orientational relaxation.

consistent with a high electrical conductivity of the hydrazone moieties. Materials investigated here with high concentrations of hydrazones approach or reach the percolation threshold of this component, which lowers the effective electric field applied to the NLO-phores during poling and consequently results in lower orientation of the NLO-phores and, thus, smaller d_{33} values.

Differences exist, however, among the various materials investigated here, in the maximum concentration of hydrazone that allows for efficient poling. Random copolymer **R_2** contains 44 mol % BBDH and still can be oriented rather efficiently. In contrast are doped polymers and polymer blends; **P_{12}** + 20% DEH and **BD_{10}** both show high d_{33}/wt % DDANS values relative to their poling temperature, but an increase of the hydrazone content in these materials drastically reduces the achieved d_{33} values. The materials **P_6** + 40% DEH and **BD_{30}** show no detectable SHG signal or strongly decreased d_{33} values. Both material classes, doped NLO polymers and polymer blends, exhibit phase separation, which might be responsible for the lower percolation thresholds. Block copolymer **BK_1** seems to behave somewhere between homogeneous and phase-separated materials. It shows two glass transitions in DSC measurements, but the poling behavior and orientability are similar to those of the corresponding random copolymer **R_1**.

In summary, it is evident that the best way to incorporate high amounts of hydrazone moieties in the DDANS polymer is to prepare random copolymers. This approach yields much better orientability in corona poling than corresponding doped polymers or polymer blends.

Photorefractive Properties. Using the stabilized two-beam coupling setup, preliminary experiments were performed on films of **P_{12}** doped with 20% DEH which show a clear asymmetric energy exchange between the two writing beams. Temperature-dependent experiments revealed that the orientational contribution to the photorefractive effect increases as the temperature aproaches T_g. The response measured at 100 °C (slightly above the T_g of 95 °C) and under an applied electric field of 20 V/μm is shown in Figure 5. The observed gain and loss of the two writing beams is the signature of the photorefractive nature of the observed grating. However, the asymmetry observed in the amplitude of the gain and loss intensities of the two writing beams also indicates that the observed effect is not only of pure photorefractive nature and suggest the presence of a second grating which could be related to an absorption grating. In a grating translation technique,[27] a phase shift of 55° was measured at the same temperature of 100 °C. From the preliminary two-beam coupling experiments, the coupling observed between the two writing beams can be related mainly to a photorefractive or field-induced orientational effect, but the presence of a second grating of absorption nature cannot be neglected. Detailed examinations are in progress and will be published later.[15]

Conclusion

We have presented the synthesis and characterization of new multifunctional NLO main-chain polymers. Random copolymers and block copolymers of DDANS, BBDH, and adipoyl chloride have been prepared and characterized. Further polyamides, based on DDANS and doped with DEH, and finally polymer blends have been prepared.

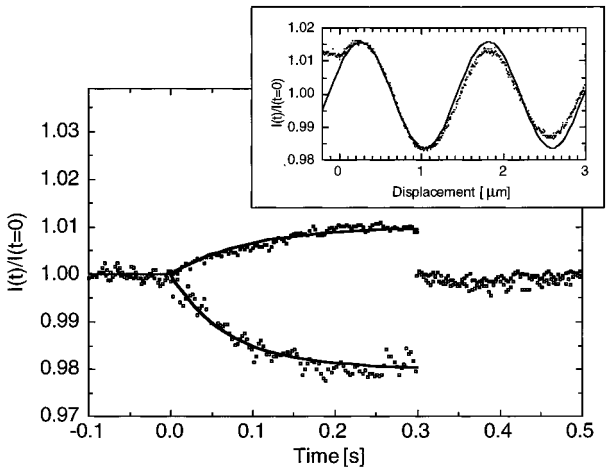

Figure 5. Results of a two-beam coupling experiment obtained on a 150 μm thick film of **P_{12}** containing 20% DEH, measured in the tilted geometry shown in Figure 3. The experiment was conducted at 100 °C (slightly above the material's T_g at 95 °C), where a clear asymmetric energy exchange is observed, as the beam 1 (solid squares) (or beam 2, open squares) is switched on at time $t = 0$. The solid lines display the exponential behavior of the intensity of the beams with a time constant of $t = 0.2$ s. The inset shows the results of the translation grating method which allows a separate determination of the phase of the grating with respect to the light intensity grating. The solid line represents the theoretically expected sinusoidal response. A phase of 55° is calculated from the measured data.

Conditions for the efficient orientation of the new materials in electric fields were developed. The maximum content of the hydrazone moiety in the different polymer classes allowing efficient corona poling depends on the type of polymeric material. Random copolymers represent the polymer class where the highest amounts of hydrazone moiety could be incorporated in the polymeric material while efficient poling in the electric field is still possible.

The multifunctionality of these materials could be demonstrated by two-beam coupling experiments that clearly prove photorefractivity. Detailed investigations of the photorefractive effects are in progress.

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