# Synthesis and Properties of Aromatic Main-Chain Polyesters Having Disperse Red 1 Nonlinear Optical Chromophores in the Side Chain

C.-S. Kang, H.-J. Winkelhahn, M. Schulze, D. Neher, and G. Wegner*

*Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany*

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Synthesis and characterization of aromatic main-chain polyesters containing nonlinear optical chromophores derived from disperse red 1 (DR1) and long alkoxy residues in the side chain are described. Polymer solutions were spin cast into optical-quality thin films. The electrooptical properties of the polymer films poled by an electric field (20–80 V/$\mu$m) were measured by the ATR (attenuated total reflection) method at 632.8 nm and 685 nm. Second-order susceptibilities $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$ as well as piezoelectric coefficient were linearly proportional to the applied poling voltage at a given temperature. The maximum values of second-order susceptibilities $\chi^{(2)}_{zzz}$ were 140 (632.8 nm) and 91 pm/V (685 nm) when the poling was carried out at a voltage of 79 V/$\mu$m at 60 °C. The thermal relaxation behavior investigated at various temperatures demonstrated an enhanced stability of the presented polymers compared to guest–host or side-chain polymer systems with flexible main chains. The relative stability is ascribed to hindering of the local mobility of the chromophores by the stiff main chains and matrix of long alkoxy side groups in which the chromophores are tightly embedded. Dielectric measurement of P-3 shows only the α-relaxation process in the frequency range $10^{-2}$–$10^{6}$ Hz. This relaxation process is of a WLF (Williams–Landel–Ferry) type behavior. The glass transition temperature ($T_g$) obtained from a WLF fit agrees well with that determined by DSC.

## Introduction

The potential application of second-order nonlinear optical (NLO) processes in photonics has triggered the search for new classes of NLO materials.[1–3] These applications require film-forming materials of high optical quality with low dielectric constant, high optical damage threshold, and sufficiently large and stable NLO susceptibilities. Organic polymers are promising because their molecular structure can be modified to achieve large optical nonlinearities. Their potential for good processability offers advantages over inorganic materials when thin films, optical fibers, or optical waveguides have to be realized.

Electric field poling[4] is the most common process to create a material with second-order NLO response characteristics from a chromophore-containing polymer film to be used as waveguide. A film of polymer-containing chromophores that have large second-order hyperpolarizability $\beta$ is heated and poled near—in most case slightly above—the glass transition temperature ($T_g$) and then cooled below $T_g$ while the electric field is still applied. After the external field has been removed, a net alignment of the dipoles remains essentially locked in the film for a long period of time. Most of the current NLO polymeric materials are based on either side-chain polymers with flexible main chains or on main-chain polymers where the chromophore dipole axis lies parallel to the main-chain direction. In both cases the predominant chromophore—that is dipole—relaxation is always coupled to a motion of the main chain.[5]

Recently, we[6–12] reported on NLO active rigid-rod main-chain polyesters and poly(ester amide)s of layered superstructure in which the chromophores are either directly incorporated into the main chain[6–10] or covalently linked to the polyester backbone by flexible spacers.[6,9–12] They showed promise for further developments in that the materials once poled retained the NLO activity over long periods of time. Moreover their relaxation characteristics were quite different from the usual flexible polymers with the chromophores being attached as side chains. For all systems with rigidly linked chromophores, the temperature dependence of

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* To whom all correspondence should be addressed.

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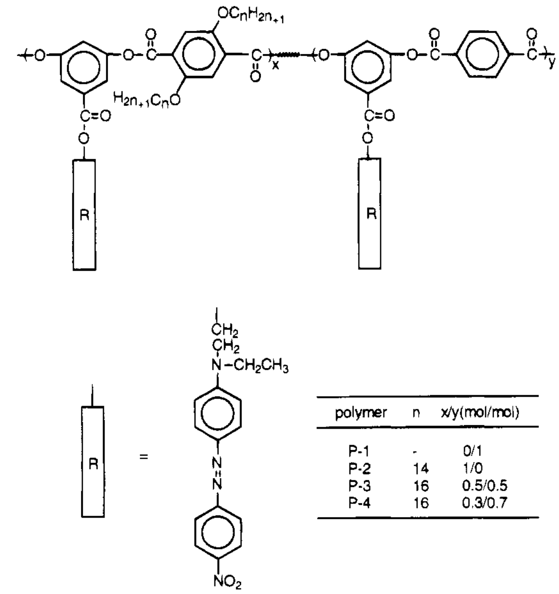

| polymer | n | x/y(mol/mol) |
|---|---|---|
| P-1 | - | 0/1 |
| P-2 | 14 | 1/0 |
| P-3 | 16 | 0.5/0.5 |
| P-4 | 16 | 0.3/0.7 |

**Figure 1.** Structure of the polymers.

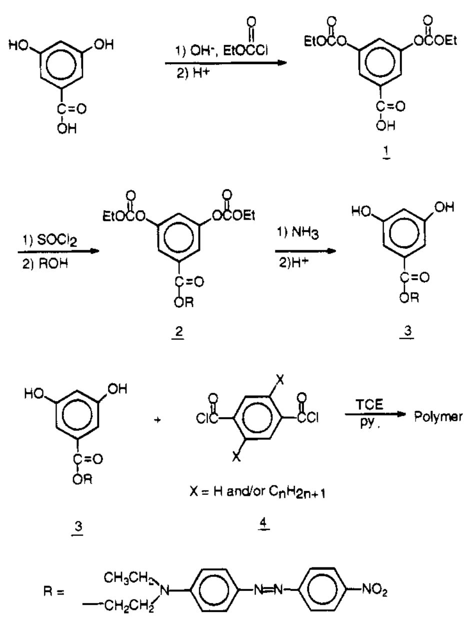

**Figure 2.** Scheme of the polymer synthesis.

relaxation times conformed to an Arrhenius-like rather than to a WLF-like behavior.[9,12] This indicated that the relaxation process is based on a local mechanism, which is not coupled to a collective motion within the main-chain layers. When the chromophores were covalently linked to the rigid-rod main chain by flexible spacers, the relaxation properties changed very much.[12] The relaxation of the polar order was now coupled to a glass transition in the side-chain region. However, in contrast to conventional side-chain NLO polymers[13] and guest–host systems,[14] the relaxation of the polar order in those rigid-rod systems occurred in the range of hours at temperatures even above the glass transition. This unusual relaxation behavior pointed to a restricted mobility of the chromophores in the interlayer matrix.

In our efforts to synthesize polymers having large second-order NLO susceptibilities and to investigate the mechanisms contributing to the decay of the NLO activity with time and temperature, we prepared a series of stiff main-chain NLO polyesters based on 3,5-dihydroxy-2-(*N*-ethyl-*N*′-(4-(4′-nitrophenylazo)phenyl)-amino)ethyl benzoate (disperse red 1 modified resorcinol, **3**) and 2,5-dialkoxyterephthalic acid or copolyesters containing the same structural elements in addition to terephthalic acid as the second acid component (cf. Figure 1 for the detailed structure). It is well-known that the DR1 moiety has a large $\beta$ value. Moreover the azo linkage is stable under polymerization conditions and the large dipole moment of DR1 assists the achievement of polar order in the polymer when an electric field is applied. The presence of donor and acceptor groups facilitates resonance enhancement effects.[15,16]

In this paper we present our results on the synthesis, characterization, and electrooptical properties of these polymers. A chromophore subunit with the DR1 moiety in the 5-position of resorcinol was prepared to be incorporated into the stiff main chain via an ester linkage. Since the chromophore was attached in 5-position of the resorcinol moiety, NLO homo- and copolyesters containing a large fraction of chromophore units [43 (P-2) to 88 wt % (P-1)] could be prepared without encountering reactivity problems in the actual synthesis of the polyesters. We expected that this high chromophore concentration would result in high $\chi^{(2)}$ values. Moreover, the stiff main chains and the long alkoxy substituents attached to the stiff main chains were expected to hinder the motion of the chromophores resulting in an enhanced stability of the induced polar order.

## Experimental Section

**Synthesis of Monomers.** 3,5-Diethoxycarbonyloxybenzoic acid (**1**, Figure 2) was prepared by reacting 3,5-dihydroxybenzoic acid with ethyl chloroformate in NaOH solution.[17] 3,5-Dihydroxybenzoic acid (30 g, $1.95 \times 10^{-1}$ mol) was dissolved in the NaOH solution containing 27.3 g of NaOH in 700 mL of distilled water. To this solution, 52.90 g ($4.88 \times 10^{-1}$ mol) of ethyl chloroformate was added in three portions within 3 h at 0–5 °C. The reaction mixture was acidified with 2 N HCl. The oily product was extracted with dichloromethane and washed with distilled water. The solvent was evaporated, and the product solidified on drying in vacuo at room temperature. The yield was 46.5 g (80%), mp 88 °C. $^1$H NMR ($CDCl_3$) $\delta$ 10.30 (s, 1H, OH), 7.82 (s, 2H, Ar), 7.42 (s, 1H, Ar), 4.30 (q, 4H, $OCH_2$), 1.38 (t, 6H, $CH_3$). IR (KBr) 3195, 3055, 1760, 1615, 1203, 1164, 870, 854 cm$^{-1}$. Anal. Calcd for $C_{13}H_{14}O_8$: C, 52.35; H, 4.74. Found: C, 52.32; H, 4.70.

3,5-Diethoxycarbonyloxy-2-(*N*-ethyl-*N*′-(4-(4′-nitrophenylazo)phenyl)amino)ethyl benzoate (**2**) was prepared by the reaction of **1** with DR1. **1** (4 g, $1.34 \times 10^{-2}$ mol) was refluxed with $SOCl_2$ under argon for 4 h. Excess $SOCl_2$ was distilled off. The resulting acid chloride was dissolved in a mixture of 30 mL of THF and 4 mL of dry pyridine. DR1 (4.22 g, $1.34 \times 10^{-2}$ mol) dissolved in 10 mL of THF was added dropwise to this solution kept in an ice bath. The reaction mixture was then stirred at room temperature for 20 h under argon. The reaction mixture was then poured into dilute HCl, and the oily product was extracted with ethyl acetate and washed with water. The organic layer was separated and dried over $MgSO_4$.

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The solvent was evaporated, and the product solidified on drying in vacuo at room temperature. The product yield was 7.21 g (90%) mp 113 °C. $^1$H NMR ($CDCl_3$) $\delta$ 8.25 (d, 2H, Ar), 7.85 (d, 4H, Ar), 7.70 (s, 2H, Ar), 7.30 (s, 1H, Ar), 6.80 (d, 2H, Ar), 4.50 (t, 2H, $OCH_2$), 4.25 (q, 4H, $CH_2$), 3.75 (t, 2H, $NCH_2$), 3.50 (q, 2H, $NCH_2$), 1.35 (t, 6H, $CH_3$), 1.20 (t, 3H, $CH_3$). IR(KBr) 3095, 2980, 1760, 1720, 1608, 1515, 1238, 1100, 1020, 840, 806 cm$^{-1}$. Anal. Calcd for $C_{29}H_{30}O_{10}N_4$: C, 58.56; H, 5.10; N, 9.42. Found: C, 58.75; H, 5.12; N, 9.40.

The dihydroxy compound **3** [3,5-dihydroxy-2-(*N*-ethyl-*N'*-(4-(4'-nitrophenylazo)phenyl)amino)ethyl benzoate] was prepared from **2** as follows: 4 g ($6.73 \times 10^{-3}$ mol) of **2** was dissolved in 40 mL of THF and then 10 mL of concentrated $NH_3$ was added to the solution. The mixture was stirred overnight under nitrogen at room temperature. The reaction mixture was poured into 1 N HCl. The crude solid product was washed with water and dried in vacuo at 70 °C. It was recrystallized from a mixture of $EtOH/H_2O = 3/2$ (v/v). The yield was 2.86 g (94%), mp 220 °C. $^1$H NMR (DMSO-$d_6$) $\delta$ 9.60 (s, 2H, OH), 8.35 (d, 2H, Ar), 7.90 (m, 4H, Ar), 7.00 (d, 2H, Ar), 6.80 (d, 2H, Ar), 6.45 (t, 1H, Ar), 4.44 (t, 2H, $OCH_2$), 3.86 (t, 2H, $NCH_2$), 3.60 (q, 2H, $NCH_2$), 1.20 (t, 6H, $CH_3$). IR (KBr) 3450, 3264, 3085, 2986, 1720, 1608, 1512, 1385, 1330, 1250, 1140, 1020, 1003, 850, 816 cm$^{-1}$. Anal. Calcd for $C_{23}H_{22}O_6N_4$: C, 61.32; H, 4.93; N, 12.43. Found: C, 61.35; H, 4.96; N, 12.52.

The 2,5-dialkoxyterephthalic acid chlorides used as comonomers were prepared according to literature.[19]

**Synthesis of Polymers.** All of the polymers were prepared by the same method. The preparation of P-3 is given as a representative example; a Schlenk flask was charged with 2 g ($4.44 \times 10^{-3}$ mol) of **3**, 20 mL of 1,1,2,2-tetrachloroethane (TCE), and 4 mL of dry pyridine. The contents were allowed to cool to 0 °C in an ice bath with stirring. To this solution, 1.52 g ($2.22 \times 10^{-3}$ mol) of 2,5-dihexadecyloxyterephthaloyl chloride and 0.45 g ($2.22 \times 10^{-3}$ mol) of terephthaloyl chloride separately prepared and dissolved in 20 mL of TCE were added dropwise. After removing the ice bath, the solution was vigorously stirred at 30 °C for 25 h under argon. The reaction mixture was poured into excess methanol. The precipitate was washed with boiling methanol and dried in a vacuum oven at 50 °C for 2 days. The yield was 3.3 g (91%) of a polymer of an intrinsic viscosity [$\eta$] (in TCE at 25 °C) of 0.47 dL/g. $^1$H NMR ($CHCl_3$) $\delta$ 8.30 (m, 8H, Ar), 7.90 (m, 12H, Ar), 7.51 (m, 4H, Ar), 6.91 (d, 4H, Ar), 4.44 (t, 2H, $OCH_2$), 3.86 (t, 2H, $NCH_2$), 3.60 (q, 2H, $NCH_2$), 1.80 (q, 4H, $CH_2$), 1.25 (m, 56H, $CH_2$), 0.85 (t, 6H, $CH_3$). IR (KBr); 3120, 2943, 1741, 1738, 1680, 1600, 1510, 1500, 1453, 1388, 1341, 1220, 1142, 1100, 1065, 863, 842 cm$^{-1}$. Anal. Calcd for $C_{94}H_{112}O_{18}N_8$: C, 67.72; H, 6.27; N, 7.46. Found: C, 67.53; H, 6.31; N, 7.45.

The homopolymer P-1 was prepared by the reaction of the dihydroxy compound **3** with terephthaloyl chloride. This polymer precipitated in the course of the polymerization reaction. The precipitate was filtered from the reaction mixture and then purified using the same procedure as described above. The yield of P-1 was 93%: it showed an inherent viscosity, $\eta_{inh}$ (in TCE at 40 °C) of 0.22 dL/g. IR (KBr) 3060, 2952, 1742, 1720, 1600, 1513, 1453, 1430, 1380, 1340, 1245, 1146, 1108, 1060, cm$^{-1}$. Anal. Calcd for $C_{31}H_{24}O_8N_4$: C, 64.15; H, 4.17; N, 9.64. Found: C, 64.19; H, 4.15; N, 9.65.

P-2 as obtained from the reaction of **3** with 2,5-ditetradecyloxyterephthaloyl chloride had an intrinsic viscosity [$\eta$] (in TCE at 25 °C) of 0.38 dL/g. $^1$H NMR ($CHCl_3$) $\delta$ 6.80 to 8.41 (m, 13H, Ar), 4.44 (t, 2H, $OCH_2$), 3.86 (t, 2H, $NCH_2$), 3.60 (q, 2H, $NCH_2$), 1.80 (q, 4H, $CH_2$), 1.25 (m, 48H, $CH_2$), 0.85 (t, 6H, $CH_3$). IR (KBr) 3060, 2923, 1741, 1680, 1600, 1510, 1500, 1453, 1388, 1341, 1220, 1142, 1100, 1065 cm$^{-1}$. Anal. Calcd for $C_{59}H_{80}O_{10}N_4$: C, 70.48; H, 8.04; N, 5.57. Found: C, 70.51; H, 8.07; N, 5.54.

Copolymer P-4 had an intrinsic viscosity [$\eta$] (in TCE at 25 °C) of 0.52 dL/g. $^1$H NMR ($CHCl_3$) $\delta$ 8.30 (m, 8H, Ar), 7.90 (m, 12H, Ar), 7.51 (m, 4H, Ar), 6.91 (d, 4H, Ar), 4.44 (t, 2H, $OCH_2$), 3.86 (t, 2H, $NCH_2$), 3.60 (q, 2H, $NCH_2$), 1.80 (q, 4H, $CH_2$), 1.25 (m, 56H, $CH_2$), 0.85 (t, 6H, $CH_3$). IR (KBr) 3116, 2963, 1748, 1736, 1687, 1600, 1510, 1508, 1453, 1378, 1339, 1220, 1142, 1113, 1065, 853, 832 cm$^{-1}$. Anal. Calcd for $C_{94}H_{112}O_{18}N_8$: C, 66.29; H, 5.43; N, 8.33. Found: C, 65.82; H, 5.42; N, 8.31.

**Characterization.** The structures of compounds and polymers were confirmed by elemental analysis (Analytical Department of the University of Mainz, Mainz, Germany) and by IR (Perkin-Elmer 1430) and $^1$H and $^{13}$C NMR (Bruker AC 300 FT). Solution viscosities were measured at 25 or 40 °C using a Canon Ubbelohde type viscometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed under $N_2$ atmosphere on a Mettler DSC 30 at a heating rate of 10 °C/min. Wide-angle X-ray diffractograms were recorded on a Siemens D 500 instrument using Ni-filtered Cu K$\alpha$ radiation. UV–vis spectra of monomers and polymers were recorded using a Perkin-Elmer Lambda 9 spectrophotometer. Dielectric relaxation properties were measured in the frequency range of $10^{-2}$–$10^6$ Hz using a frequency response analyzer (Sol-Schlumberger SI 1260).

**Sample Preparation for ATR Experiments.** All films for measurements concerning the NLO properties were prepared by spin-coating from TCE solution. Samples for ATR measurement were prepared in the following way. A 2–3 nm thick layer of chromium was evaporated on a cleaned glass substrate followed by 30–50 nm thick layer of gold as a lower electrode. A polymer film (2–5 $\mu$m) was spin-coated onto the gold layer. These films were dried at 60 °C for 30–50 h in a vacuum oven to remove the last traces of solvents. Finally, a 100 nm thick upper gold electrode was evaporated onto the film. The electrodes were contacted with silver paste and the film was poled by applying electric field at a desired temperature. To investigate the dependence of the linear and nonlinear optical parameters on the poling voltage different voltages (20–80V/$\mu$m) were applied at 60 °C.

**Dielectric and ATR Experiments.** For dielectric relaxation spectroscopy, polymer samples were pressed on a hot stage under vacuum at 80 °C between two nickel-plated brass electrodes. The film thickness was controlled by 50 $\mu$m glass fibers inserted as spacers. The measurements were performed in a vacuum-isolated cryostat. The sample temperature was controlled by a heated nitrogen gas jet.

For the electrooptic measurements, the polymer films were spin coated from TCE solution onto glass slides. The slide was then put into optical contact with a prism through which a HeNe (632.8 nm) or near IR (NIR, 685 nm) laser beam was directed onto the sample. The prism was placed on a $\theta$–$2\theta$ goniometer and the reflectivity of the HeNe probe beam with transverse electric (TE) and transverse magnetic (TM) polarization was recorded for incidence angles ranging from 30° to 65°. When the waveguiding resonance condition is fulfilled at given angles, dips occur in the reflectivity corresponding to TM- and TE-guided modes in the polymer film. The experimental reflectivity curves were fitted by a computer program which calculates the reflectivity of a multilayer system using the Fresnel equations. The fitting parameters are the film thickness and the indexes of refraction $n_x = n_y$ and $n_z$. Here $x$ and $y$ correspond to the principal directions in the plane of the film and $z$ is normal to the sample plane. Applying an electric ac field to the poled sample causes a change of the reflectivity of the multilayer system due to the Pockels effect. That was measured by a lock-in amplifier. From the fit of the modulated waveguide spectra, the nonzero components of the second-order nonlinear susceptibility ($\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx} = \chi^{(2)}_{zyy}$) as well as the piezoelectric coefficient were determined.[35]

Relaxation properties of the polymers were investigated by monitoring the modulated reflectivity as a function of time at a certain temperature after the poling voltage had been removed. The temperature was controlled within ±0.1 °C for each measurement.

## Results and Discussion

**Synthesis of Polymers.** All of the polymers were prepared by solution polycondensation of aromatic dicarboxylic acid chlorides and a chromophore-containing

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**Table 1. General Properties of Polymers**[a]

| polymer | $d^b$, Å | $T_S$, °C | $T_g$, °C | $T_m$, °C | $T^D_i$, °C |
|---|---|---|---|---|---|
| P-1 | | | 130 | >240 | 267 |
| P-2 | 24.0 | 45 | | 103 | 243 |
| P-3 | 27.30 | | 42 | 71 | 269 |
| P-4 | 27.21 | | 38 | 82 | 230 |

[a] $T_g$, $T_s$, $T_m$, and $T^D_i$ represents glass transition, side-chain, main-chain melting, and initial decomposition temperatures, respectively. [b] Interlayer spacing in angstroms.

aromatic diol. The problem of attaching a NLO-active chromophore to an aromatic diol with reliable reactivity for polycondensation via a not too flexible spacer was solved as shown by Figure 2. The synthesis starts from 2,5-dihydroxybenzoic acid which is first protected at the diol functions by reaction with ethyl chloroformate. The chromophore DR1 could now be attached via formation of an ester bond, and after removal of the protecting groups the monomer **3** was obtained in very good yields. Polycondensation of this aromatic diol with the desired dichlorides (terephthaloyl chloride, 2,5-dialkoxyterephthaloyl chloride or mixtures of them) could then be carried out under normal Schotten–Baumann conditions.

Polymers P-1 and P-2 are homopolymers consisting of a single structural repeating unit, while P-3 and P-4 are copolymers consisting of two different structural repeating units. The spectroscopic and elemental analyses demonstrated that the actual compositions of the polymers were practically the same as those expected from the feed.

**General Properties of Polymers.** Since all of the polymers except P-1 were soluble in common organic solvents at room temperature, films of good optical quality could be easily prepared. Polymer P-1 was slightly soluble in organic solvents such as *o*-dichlorobenzene, TCE, THF, etc., but the solubility was not high enough to produce films of sufficient quality. It is worth pointing out that linking of the terephthaloyl residues via aromatic units in the 2,5 position ("resorcinol pattern") improves the solubility considerably over similar polymers in which the links had been produced via the 1,4 position ("hydroquinone pattern"). This may be related to geometrical effects which reside in the kinks produced in the backbone with the resorcinol bonding pattern in comparison to the more straight-chain arrangement when the hydroquinone-like bonding pattern is chosen.[22,23] Copolymers P-3 and P-4 were highly soluble even in acetone and slightly soluble even in ethanol.

The data of the various polymers for glass transition ($T_g$), side-chain melting ($T_s$), and main-chain melting ($T_m$) obtained from DSC are summarized in Table 1. The polymer P-1, which does not contain long alkoxy side chains as substituents, shows a glass transition only around 130 °C. Successive heating and cooling cycles up to 240 °C did not reveal any further transition by DSC. Since X-ray investigations on the same polymer—as prepared—revealed weak diffraction peaks in the wide-angle range, we are led to assume that melting of this polymer does not occur below the onset of thermal decomposition found to occur around 270 °C.

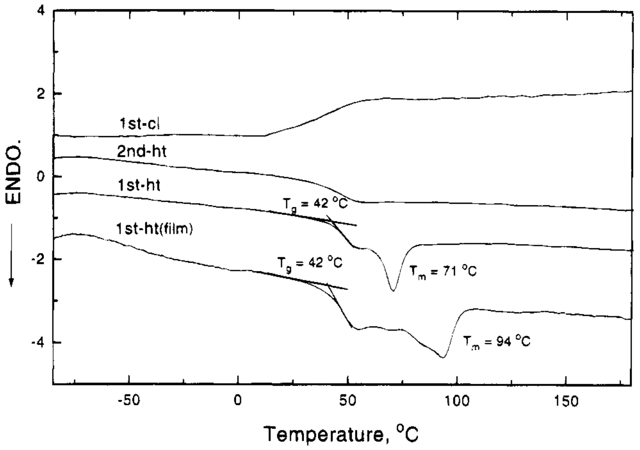

**Figure 3.** DSC thermograms of P-3 (heating rate of 10 °C/min). DSC curves for the first and second heating are indicated by 1st-ht and 2nd-ht, respectively, and the first cooling is represented by 1st-cl.

On the other hand, P-2 shows two clear endothermic transitions which are denoted as side-chain ($T_s$) and main-chain melting ($T_m$), respectively. The first thermal transition at the lower temperature, $T_s$, is caused by loss of order in the side-chain region of the bulk polymer. At this temperature conformational and positional order of the side chains decreases.[19–21] In agreement with observations made in the case of other but similar polymers[11–21] a glass transition could not be found by DSC for this polymer. A cooling run started at a temperature of 200 °C does not show crystallization peaks. However, a second heating cycle shows two endothermic peak, which are weaker than those obtained from the first heating cycle. This implies that some part of the melt supercooled to room temperature crystallized in the course of the second heating cycle.

Copolymers P-3 and P-4 show marked signs of a glass transition ($T_g$) and weak endothermic peaks related to a melting process. DSC thermograms of the polymer P-3 are shown in Figure 3 as a representative example. Comparison of $T_g$ of P-1 (130 °C) and of the copolymers (42 °C for P-3 and 38 °C for P-4) demonstrates that a higher alkoxy side chain content and copolymerization reduces the $T_g$. Both of the copolymers show melting endotherms in the course of the first heating cycle. After melting, recrystallization is not observed during the first cooling followed by the second heating runs. The optical measurements to be discussed later were performed on films the characteristic DSC-trace of which is shown in Figure 3 marked 1st-ht(film). The appearance of a melting endotherm is related to the fact that the poling procedure has to be carried out under conditions of annealing induced crystallization.

All of the as-prepared polymers having long alkoxy side chains (P-2 to P-4) show at least one weak diffraction peak in the small-angle region and a rather featureless broad halo in the wide-angle region of the diffractograms. In accordance with previous results on the structure of aromatic polyesters with long alkyl or alkoxy side chains the small angle reflection may be interpreted as the signature of a layered structure where the space between the layers formed by the main chains is filled by the interdigitated side chains.[19,20] The

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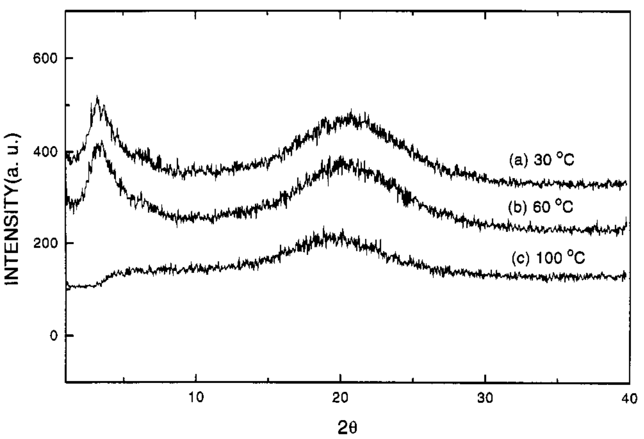

**Figure 4.** Wide-angle X-ray diffractograms of P-3 at (a) 30 °C, (b) 60 °C, and (c) 100 °C.

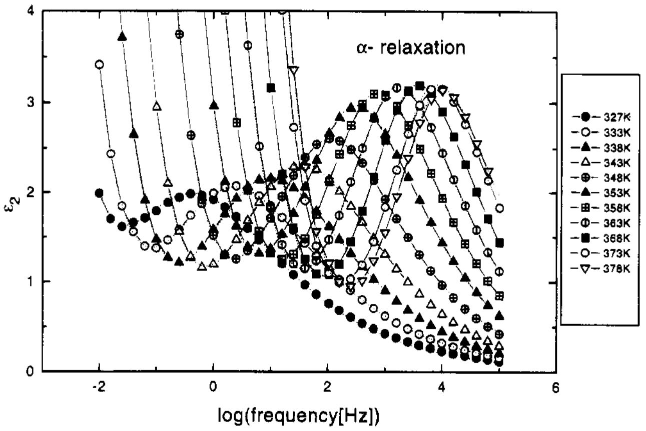

**Figure 5.** Dielectric relaxation spectra of P-3 obtained at various temperatures.

absence of distinct Bragg reflections in the wide angle regions points to a high degree of disorder within the layer planes which is not surprising in the light of the fact that the polymer P-3 and P-4 are random copolymers. Figure 4 shows wide-angle X-ray diffractograms of P-3 obtained at different temperatures as an example. The layered morphology remains stable above the glass transition temperature but disappears completely at the melting transition. After cooling back to room temperature, the diffraction in the small-angle region does not reappear, indicating that the polymer is quenched to an amorphous, glass state. These results coincide with a previous investigation[19] on poly($p$-phenyleneterephthalate)s containing long alkoxy side chains attached to the terephthaloyl units with the exception that somewhat different layer spacings and less intense diffraction peaks were observed in the present case. The reduced diffraction intensity can be traced to either a lower degree of order and/or to a smaller electron density modulation due to the presence of electron-rich chromophores in the side-chain interlayer regions.

The homopolyester P-1 exhibits a different behavior. The X-ray diffractograms showed a number of weak diffraction peaks in the wide-angle region, but a small-angle peak was completely lacking. The intensities and positions of the Bragg peaks did not change up to 240 °C, which—as was already mentioned—indicates that there are no structural changes to be observed below the onset of thermal decomposition.

The thermal stability of the polymers was checked by thermogravimetry, and the results are summarized in Table 1. All polymers show good thermal stability up to 230 °C. The somewhat reduced thermal stability these polymers when compared with simple polyester as, e.g., poly(ethyleneterephthalate) relates to the presence of azo- and nitro groups which are notoriously known to suffer from degredation at temperatures above 200 °C.[24]

**Dielectric Spectroscopy.** Dielectric experiments were carried out with polymer P-3 to confirm the transition temperatures and to compare the thermal relaxation behavior with the results obtained from the relaxation of the polar order to be discussed later. Samples were scanned in the frequency range $10^{-2}$–$10^6$ Hz. The temperature was changed from −170 to 120 °C. Figure 5 shows the results. Only one relaxation process—the α relaxation—is observed in the frequency–temperature regime discussed here besides the onset of a strong but featureless relaxation process due to spurious ionic conductivity in the sample at frequencies below $10^2$ Hz at 105 °C and even lower frequencies at lower temperatures. The α-relaxation peak is first observed at 50 °C. It grew quickly in intensity and reached a maximum value of the dielectric loss $\epsilon_2 = 3.2$ at 95 °C. This value is higher than the one obtained from a MONS ($p$-methoxynitrostilbene) substituted NLO main-chain polyester ($\epsilon_2 = 0.72$).[11] This can be explained by the larger ground-state dipole moment of our DR1 chromophore (9.42 D)[25] compared to the MONS chromophore (4.5 D).[26] Accordingly, the major relaxation process in the present polymer P-3 can be attributed to the motion of the chromophores with large dipole moment. This is corroborated by the finding that the polyester substituted only with alkoxy side chains exhibits three relaxation processes with dielectric losses of at most $\epsilon_2 = 0.04$,[27] which is about 2 orders of magnitude weaker than observed in P-3. The data contained in Figure 5 could be fitted by the Havriliak–Negami equation after contributions from the ac conductivity had been properly subtracted.[28–31] The solid lines in Figure 5 are the results of a fit using a nonlinear fitting routine.[32] The frequency of maximum loss obtained from this fit is plotted in Figure 9 vs the reciprocal temperature. A good fit according to a WLF-type equation with $T_g = 42$ °C, $C_1 = 12.6$, and $C_2 = 52.8$ is obtained. These data were retrieved again from application of the nonlinear fitting routine as stated above. The glass transition obtained from this fit is thus exactly the same as the one determined by DSC. A WLF behavior is characteristic for an α-process related to a glass transition. Thus, the chromophores gain mobility in coupling their motion to the glass transition process. The dielectric relaxation results will be discussed again together with the results of the relaxation of polar order.

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**Linear and Nonlinear Optical Properties.** As classified by Rau,[33] the DR1 moiety is of pseudo-stilbene type, which means that the high-energy $\pi-\pi^*$ transition is overlapping the low-energy $n-\pi^*$ transition. This leads to a large structureless band in the spectra of the trans isomer with an absorption maximum strongly depending on the polarity of the host material which may be either a polymer or a solvent. Figure 6 shows UV-Visible spectra of (a) DR1 and (b) P-3, respectively. The polymers show their absorption maxima at wavelengths slightly lower (475 nm for P-2 and 480 nm for P-3) compared to DR1 (486 nm).

The electrooptical properties of films of P-3 were investigated by the ATR method. The power of the laser probing beam was reduced to a few tens of a microwatt in order to avoid local heating by light absorption inside the sample. Even though the absorption of the DR1 moiety is almost negligible at 632.8 nm as shown by the UV–vis absorption spectra in Figure 6 the waveguiding resonance condition may enhance the energy dissipation inside the polymer film.[34] Thus every care was taken to prevent erroneous results due to local heating, isomerization, or laser damage.

The optimum poling condition was determined by varying the poling temperature at a fixed poling field of 44 V/μm. Obviously, the polymer films can be poled successfully at and above the glass transition temperature within 10 min. All further results reported hereafter were obtained on films that had been poled at 60 °C for 10 min.

To investigate the dependence of the nonlinear optical parameters on the poling voltage, it was changed from 20 to 80 V/μm. From eqs 1 and 2, where $N$ is the

$$\chi^{(2)}_{zzz} = N\beta F\langle\cos 3\theta\rangle \qquad (1)$$

$$\langle\cos 3\theta\rangle = (\mu_0 E/ckT)$$

$$\chi^{(2)}_{zxx} = 0.5N\beta F\langle\cos\theta\sin 2\theta\rangle \qquad (2)$$

number density of the chromophore, $\beta(-2\omega;\omega,\omega)$ (212.9 × $10^{-30}$ cm$^5$/esu for DR1)[25] is the first-order molecular hyperpolarizability, $F$ is the local field correction, $\mu_0$ is the ground-state dipole moment of the NLO moiety, $E$ is the local electric field experienced by the dipole, $k$ is Boltzmann constant, and $T$ is the absolute poling temperature. The factor $c$ is equal to 5 for nonliquid crystalline systems and equal to 1 for liquid-crystalline systems.

The experimentally obtained data on $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$ are plotted versus the poling voltage in Figure 7. A linear relationship is indeed found within the limits of scatter of the experimental data. Small variations of the poling conditions may in fact occur and may be due to change in the ion content of the polymers, which is difficult to control and may slightly vary from poling cycle to poling cycle and thus lead to a scatter in the data.[36] The data are summarized in Table 2.

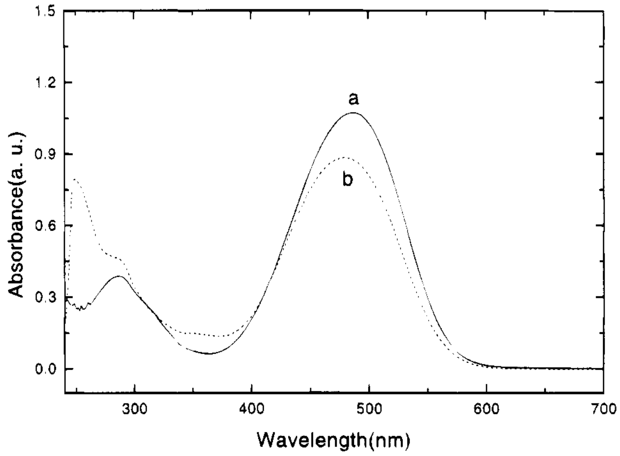

**Figure 6.** UV–visible spectra of (a) DR1 and (b) P-3 dissolved in TCE solution.

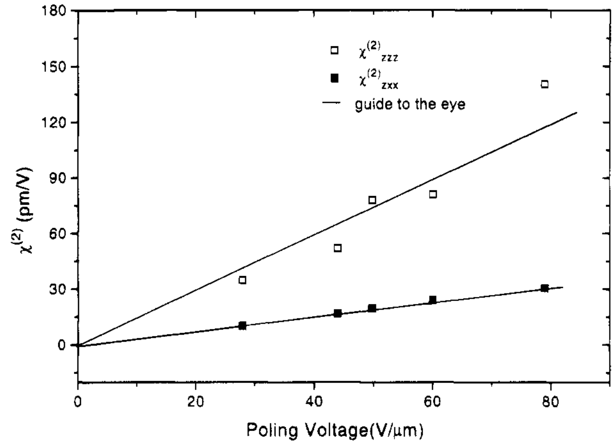

**Figure 7.** Second-order NLO susceptibilities depending on poling voltage.

**Table 2. Poling Voltage ($V_p$) Dependence of Second-Order NLO Susceptibilities of P-3 Poled at 60 °C**[a]

| $V_p$, V/μm | $\chi^{(2)}_{zzz}$, pm/V | $\chi^{(2)}_{zxx}$, pm/V | $\chi^{(2)}_{zzz}/\chi^{(2)}_{zxx}$ |
|---|---|---|---|
| 28 | 35 | 10 | 3.50 |
| 44 | 52(39) | 17(11) | 3.06(3.55) |
| 50 | 78 | 20 | 3.90 |
| 60 | 81(58.7) | 24(18) | 3.38(3.26) |
| 79 | 140(91) | 30(26) | 4.67(3.50) |

[a] The values in parentheses are obtained from the measurements using the NIR (685 nm) laser and the other data are obtained using the HeNe laser (632.8 nm).

The maximum value of $\chi^{(2)}_{zzz}$ = 140 (at 632.8 nm) and 91 pm/V (at 685 nm) was obtained using poling conditions of 79 V/μm at 60 °C. The values of the second-order susceptibilities determined at 632.8 nm were 1.3–1.5 times larger than the ones obtained at 685 nm (see Table 2). This difference is caused by resonance enhancement. It is well-known that polymers containing DR1 type chromophores show resonance enhancement even at wavelengths far from the main absorption peak.[42] Table 2 indicates a ratio of the coefficients $\chi^{(2)}_{zzz}/\chi^{(2)}_{zxx}$ = 3.1–4.7, which is above the value of 3 expected for an initially isotropic sample.[36] Ratios of these tensor elements in the range 3–6 are routinely seen in the literature.[37,38] A restricted motion model has previously

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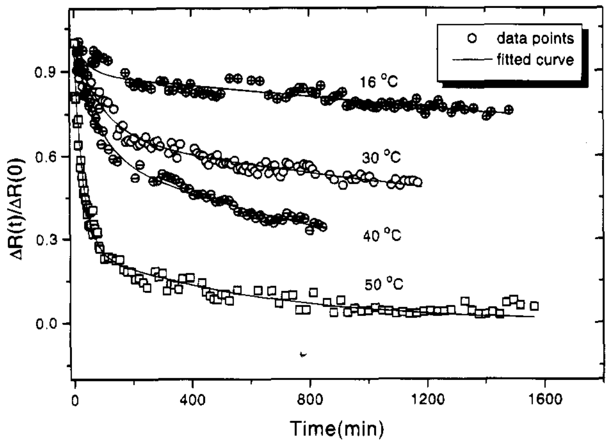

**Figure 8.** Relaxation of the normalized second order susceptibilities of P-3 at various temperatures.

been invoked to account for the fact that the observed tensor ratios can be larger than 3.[8,37]

The piezoelectric coefficients obtained from the fit of the ATR results ranged from 0 to −2 pm/V. This agrees well with the electromechanical properties of the poled films, which were determined separately in an interferometric setup described previously.[41] Since the $\chi^{(2)}$ values obtained from the ATR experiments are 2 orders of magnitude larger than the piezoelectric coefficients, the influence of piezoelectric effect on the determination of $\chi^{(2)}$ values can be neglected.

Next, the question of long-term stability of the polar order at constant temperature or—in other words—the relaxation of polar order was investigated. For all long-term stability measurements, a NIR laser was used at reduced power. When the sample had been irradiated with the full powder of HeNe laser (about 10 mW) for a long time, one could indeed observe a distortion of the modulated signals as well as a faster decay of the $\chi^{(2)}$ values.

The polar order of each sample was initially fixed by poling at 60 °C over 10 min at a dc voltage of 44 V/$\mu$m followed by cooling to 15 °C. The films were then heated to the desired measuring temperature with the field still applied. It is known that the cooling rate has a considerable effect on the relaxation rate at fixed temperature. Thus, the relaxation time at 30 °C was first measured for two different cooling rates, namely, 1 °C/min and 0.1 °C/min. In both cases the decay of the polar order with time was well fitted by a biexponential decay curve. The long-term relaxation time $\tau_2$ increased by a factor of 2 (from 2000 to 4000 min), when the sample was cooled less fast. This can be explained by a free-volume effect. Since the free volume relaxes to the equilibrium distribution faster at higher temperature, annealing just below the glass transition[39] or cooling at a slower rate[12] results in a smaller fraction of free volume remaining. All subsequent relaxation data were obtained at a cooling rate of 0.1 °C/min. The relaxation behavior of the heated films is shown in Figure 8. In all relaxation measurement the decay of the normalized signal intensity can be described by the following biexponential equation:[40]

**Table 3. Parameters Deduced from a Biexponential Fit to the NLO Decay Experiments of P-3 (See Eq 3)**

| temp, °C | $A$ | $B$ | $\tau_1$, min | $\tau_2$, min |
|---|---|---|---|---|
| 16 | 0.11 | 0.89 | 50 | 8473 |
| 30 | 0.33 | 0.67 | 101 | 3832 |
| 40 | 0.39 | 0.61 | 79 | 1438 |
| 50 | 0.73 | 0.27 | 28 | 580 |

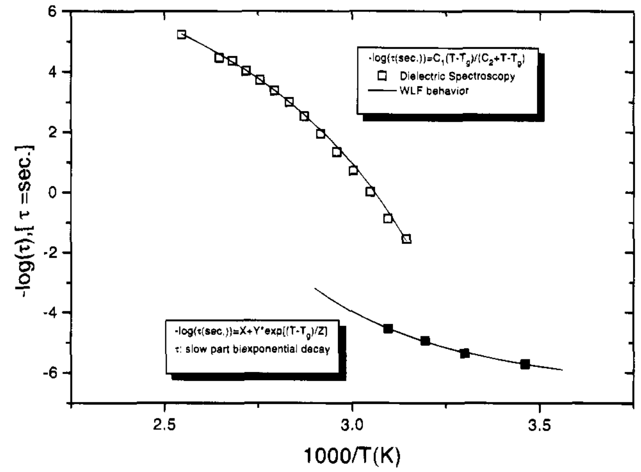

**Figure 9.** Comparison of the temperature dependence of the dielectrically measured α-relaxation process and the decay of polar order as measured by ATR.

$$\Delta R(t)/\Delta R(0) = A\ \exp(-t/\tau_1) + B\ \exp(-t/\tau_2) \quad (3)$$

where $\Delta R(t)/\Delta R(0)$ is the intensity of the modulated signal at any time ($t$) after the beginning of the measurement normalized to the modulated reflectivity at $t = 0$. $A$ is the fraction of chromophores relaxing at a relatively fast rate with time constant $\tau_1$, and $B$ is the fraction relaxing at a relatively slow rate with time constant $\tau_2$. The data points were fitted to eq 3 by a least-squares routine, and the constants retrieved are summarized in Table 3. The relaxation rate constants and values of preexponential factors $A$ and $B$ strongly change with temperature between 16 and 50 °C. Surprisingly, the polymer P-3 shows a relaxation time several tens of hours even above the glass transition. This is quite different from usual guest–host systems[13] or flexible main-chain polymers to which the chromophores are attached.[14] This unusual relaxation behavior has also been observed in para-linked polyesters with NLO-active chromophores in the side chain and seems to be typical for a layered structure of the polymer as reported previously.[6-12] It seems that the relaxation of the chromophores is strongly impeded when they are embedded in the interlayer matrix.

The temperature dependence of the relaxation times was compared to the relaxation data obtained from dielectric spectroscopy as shown in Figure 9. While the temperature dependence of the dielectric data is well fitted by the WLF equation, it was not possible to fit the temperature dependence of the relaxation of the polar order by either the WLF or Arrhenius equation.

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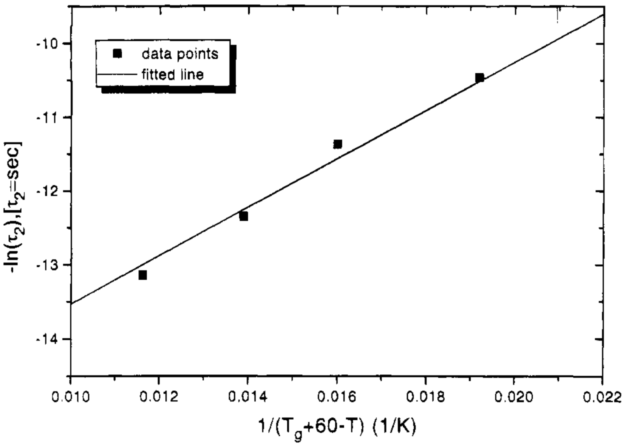

**Figure 10.** Dependence of the relaxation time $\tau_2$ on a temperature function according to eq 4 (see text).

A qualitative description could be obtained using an empirical function (see Figure 9), which has been used previously to explain the relaxation behavior of a NLO polymer based on an aromatic polyester backbone to which MONS chromophores were attached by a hexyl group as discussed before.[12] The disagreement between the activation behavior of the dielectric process and the temperature dependence of the relaxation of polar order can be understood by the following considerations. In both experiments dipole motions are detected. The dielectric spectroscopy measures a small-angle dipole fluctuation of the chromophores that might be mainly governed by the dynamics of the flexible side chains. However, the relaxation of polar-order measures the dipole reorientation of the poled system below as well as above the glass transition. The latter is a process proceeding from nonequilibrium toward equilibrium state, which contains local motions of the chromophores as well as collective motions of the main chains. The orientation and reorientation properties of the NLO-active chromophore dipoles in polymer P-3 are strongly coupled to the motion of the polymer backbone. This coupling together with the local motion of the chromophores might cause the difference between the temperature dependence of the relaxation times obtained from dielectric spectroscopy and poling relaxation.

The temperature dependence of the relaxation times of the induced polar order could also be described by a different emprical, eq 4, introduced by Stählin et al.[13]

$$\tau(T) = A \exp(-[B/(T_0 - T)]) \qquad (4)$$

$$T_0 = T_g + 60$$

This equation has successfully been applied to describe the relaxation behavior of guest–host systems below their glass transition[13,43] and of a number of NLO side-chain methacrylate copolymers over a limited temperature range, that is, from $T_g$ − 50 °C to $T_g$ but deviates sharply upward (larger $\tau$) for temperatures below $T_g$ − 50 °C.[44] Surprisingly, we could apply this equation for the polymer P-3 in the temperature range of $T_g$ − 30 to $T_g$ + 10 °C. The fit to the poling relaxation data of P-3 is shown in Figure 10. Further investigations with high-$T_g$ polymers over a wide temperature range are necessary to confirm the relaxation behavior of the stiff main-chain type NLO polymers. As demonstrated by Figures 9 and 10 the available data do not allow us to differentiate between the two different empirical equations.

## Conclusion

Soluble main-chain NLO polyesters containing DR1 modified resorcinol chromophore, **3**, in the side chain was developed. Two homopolyesters as well as two copolyesters were prepared, and their properties were compared. Relaxation times in the range of tens of hours are obtained even above the glass transition of the polymer. The reduction of mobility of the chromophores by the stiff main chains and the long alkoxy side chains might be a main reason for the enhanced long-term stability of the present polymer compared to usual guest–host or side–chain systems based on flexible main chains. Two empirical functions, which have been previously used to explain the relaxation behavior of a rigid main-chain polyester having MONS chromophores in the side chain and of guest–host and a number of side-chain NLO systems based on the methacrylate backbone were successfully applied to fit the poling relaxation data. The ratio of $\chi^{(2)}_{zzz}/\chi^{(2)}_{zxx}$ repeatedly showed values larger than 3, indicating that some ordering is induced by the interaction with the substrate. Further work will be devoted to the dynamics of the chromophore alignment and the details of the decay of polar order in these materials.

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