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Rigid Rodlike Main Chain Polymers with Conformationally Restricted Nonlinear Optical Chromophores: Synthesis and Properties

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ABSTRACT: The synthesis and characterization of aromatic main chain polyesters with perpendicularly attached nonlinear optical chromophores embedded in long alkoxy side chains are described. The polymers were characterized by differential scanning calorimetry, X-ray diffractometry, and polarized optical microscopy. Nonlinear optical properties of models of the chromophore subunits were investigated separately by electric field induced second harmonic generation (EFISH) and electrooptical absorption measurement (EOAM). Electric poling of the polymers was successfully applied to thin films of the polymer to induce the noncentrosymmetry required for second-order nonlinearity. Characterization of electrooptical properties of the poled polymer films was accomplished by the method of attenuated total reflection. Values for second-order susceptibilities $\chi^{(2)}{}_{zzz}$ ranged from 0.73 to 1.0 pm/V. The long-term stability of the induced polar order of the polymer was investigated by monitoring the intensity of the nonlinear optical response of polymer waveguides as a function of time at a fixed temperature. Excellent stability of the polar order was observed even at 140 °C due to the layered structure of the polymer films. The decay of nonlinearity could be fitted by both biexponential and stretched exponential equations.

Introduction

Organic and polymeric materials containing highly polarizable subunits commonly called chromophores can exhibit a large NLO response[1–4] comparable or even larger than found in inorganic substances, e.g. $LiNbO_3$, KH_2PO_4, ect.[5] The NLO chromophore can be incorporated as a guest into the polymer matrix[6–9] or attached to the polymer backbone in terms of a side chain.[10–14] This approach to the development of NLO materials is interesting because the mechanical and thermal stability as well as processability can be optimized together with the optical performance by suitable chemical synthesis. In general, polymers have a low dielectric constant and with suitably chosen functional, that is chromophoric, groups show large electronic hyperpolarizabilities.

A very attractive approach is the incorporation of the chromophore directly into the polymer backbone. Hall and co-workers[15–17] reported on the synthesis of the first NLO active polymers of this type, and thereafter several researchers[18–22] prepared related NLO main chain polymers. Although the coefficients for second harmonic generation were relatively low for these materials, these investigations were promising since the materials retained the required polar order and therefore NLO activity for long periods of time. However, all of these polymers contain flexible methylene spacer groups in the main or side chains which contribute significantly to the relaxation of the polar order of the chromophores.

The key problem in the design of polymeric NLO materials is to obtain samples with a high degree of polar order and the ability to retain that state of orientation for long periods of time within a given temperature region. This conjecture leads to the attempt to incorporate the chromophores as substituents into rigid rod type polymers such that the main component of the induced dipole moment is either normal or along the trajectory of the polymer backbone. In the following we will only describe polymers belonging to the first case.

It is well-known that rigid rod aromatic main chain polyesters substituted with flexible side chains form two-dimensional layered structures in the bulk.[23] The interlayer distance can be controlled by the length of the side chains. Moreover, thin films can be prepared such that the alkyl chains are oriented perpendicular to the substrate.[45,46] The restriction in motional freedom to be expected for the chromophores in polymers of that design and in the layered structure leads to the prediction that the polar order to be obtained by poling at a given field strength will be enhanced compared to polymers in which the chromophores are free to move in all directions.[22,45]

In this paper we present our results on the synthesis, characterization, and electrooptical properties of new NLO chromophore substituted rigid rod type main chain homopolymers (P-1 to P-3), copolymers (P-4 and P-5), and semiflexible main chain polyesters (P-6). A chromophore was synthesized and incorporated into the polymer main chain which has not been considered for NLO properties so far. Structures of the polymers are shown in Scheme 1.

Experimental Section

Synthesis of Monomers. Bis(sodiothio)dicyanoethene (1, Scheme 2) was prepared by reacting malonitrile with carbon disulfide.[24] 4,7-Dihydroxy-2-(dicyanomethylene)-1,3-benzodithiolane (2) was prepared by the reaction of 1,4-benzoquinone with compound 1 in the presence of acetic acid as a catalyst.[25] The crude product was purified by column chromatography from a mixture of ethyl acetate/*n*-hexene = 1/1 (v/v). The yield was 82%, mp >320 °C (lit. ca. 250 °C).[25] ^{1}H-NMR (DMSO-d_6): δ 10.23 (s, 2H, OH), 6.82 (s. 2H, Ar). IR (KBr): 3195 (O—H str), 3055 (Ar C—H str), 2227 (CN str), 1203 cm^{-1} (C—O str). Anal. Calcd for $C_{10}H_4N_2O_2S_2$: C, 48.38; H, 1.63; N, 11.29; S, 25.83. Found: C, 48.49; H, 1.82; N, 11.30; S, 25.71. 4,7-Diacetoxy-2-

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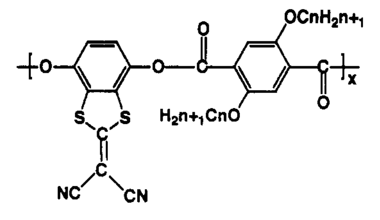
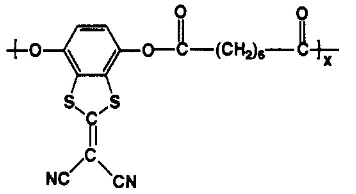
Scheme 1

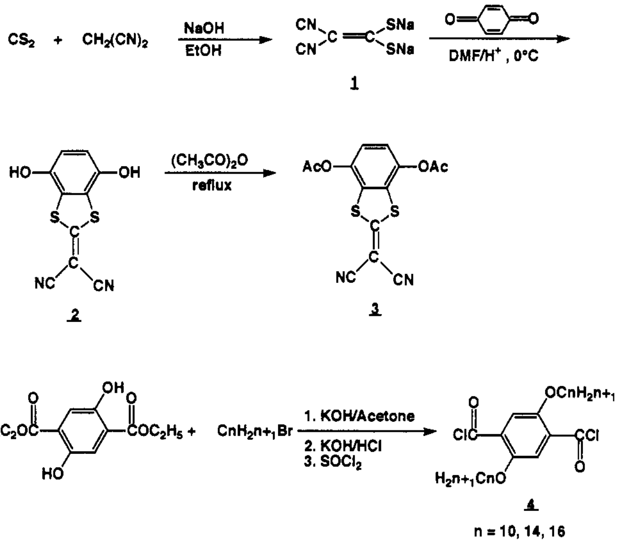


n	polymer
10	P-1
14	P-2
16	P-3
10/14	P-4
10/14/16	P-5



(P-6)

Scheme 2



(dicyanomethylene)-1,3-benzodithiolane (**3**) was prepared by the reaction of **2** with acetic anhydride in the presence of catalytic amounts of concentrated sulfuric acid. A 7 g (2.82 × 10^{-2} mol) amount of **2** was dissolved in acetic anhydride, and 3 drops of concentrated sulfuric acid were added. The solution was refluxed under argon for 10 h. The reaction mixture was poured into 0.1 M Na_2CO_3 and stirred for 1 h. The precipitate was recovered and washed with distilled water. The crude product was recrystallized from acetone/H_2O = 1/1 (v/v). The yield was 8.2 g (87%), mp 207 °C. ^{1}H-NMR (DMSO-d_6): δ 7.56 (s, 2H, Ar), 2,43 (s, 6H, CH_3). IR (KBr): 3085 (Ar C—H str), 2212 (CN str), 1777 (C=O str), 1185 cm^{-1} (C—O str). Anal. Calcd for $C_{14}H_8N_2O_4S_2$: C, 50.59; H, 2.43; N, 8.43; S, 19.29. Found: C, 50.59; H, 2.49; N, 8.34; S, 19.14.

2,5-Dialkoxyterephthalic acid chlorides used as comonomer (**4**, Scheme 2) were prepared according to the literature.[23]

Synthesis of Polymers. All of the polymers were prepared by the same procedure. The preparation of P-2 is given as a representative example. A Schlenk flask was charged with **2** (0.6 g, 2.42 × 10^{-3} mol) dissolved in 10 mL of tetrahydrofuran (THF) and 1 mL of pyridine and then allowed to cool to 0 °C in an ice bath with stirring. 2,5-Bis(tetradecyloxy)terephthaloyl chloride, **4** (*n* = 14), 1.52 g (2.42 × 10^{-3} mol) dissolved in 30 mL of THF was added. After the ice bath was removed, the solution was vigorously stirred at 60 °C for 30 h under argon. The reaction mixture was poured into 500 mL of ethanol. The precipitate was washed with boiling ethanol. The remaining polymer, after being dried, was extracted by ethanol for 3 days using a Soxhlet extractor. The yield of the polymer was 1.63 g (84%). ^{1}H-NMR ($CHCl_3$): δ 7.6 (m, 4H, Ar), 4.15 (t, 4H, OCH_2), 1.9 (m, 4H, CH_2), 1.0–1.6 (m, 44H, CH_2), 0.9 (t, 6H, CH_3). IR (KBr): 3060 (Ar C—H str), 2923 (aliphatic C—H str), 2216 (CN str), 1764 (C=O str), 1180 cm^{-1} (C—O str). P-1 and P-6 formed precipitates in the reaction mixture in the course of the polymerization reaction. The precipitates were filtered from the reaction mixture and then purified by the same procedure as described above. The yield of P-6 was 85%. ^{1}H-NMR ($CHCl_3$): δ 7.32 (s, 2H, Ar), 2.65 (t, 4H, $COCH_2$), 1.8 (m, 4H, CH_2), 1.5 (m, 4H, CH_2). IR (KBr): 3060 (Ar C—H str), 2952 (aliphatic C—H str), 2218 (CN str), 1772 (C=O str), 1175 cm^{-1} (C—O str).

Table 1. Yields, Solution Viscosities, and Elemental Analyses of Polymers

polymer	elemental content[a] (wt %) C	H	N	S	yield (wt %)	η_{inh} (dL/g)
P-1	66.02	6.51	4.06	9.27	74	0.28
	(66.05)	(6.72)	(4.05)	(9.28)		
P-2	68.82	7.64	3.16	7.98	84	0.22
	(68.78)	(7.79)	(3.49)	(8.01)		
P-3	69.89	8.12	3.06	7.43	88	0.20
	(69.93)	(8.16)	(3.26)	(7.47)		
P-4	67.87	7.04	3.88	8.89	85	0.34
	(67.82)	(7.08)	(3.91)	(8.89)		
P-5	67.65	7.34	3.73	8.59	76	0.18
	(67.65)	(7.33)	(3.72)	(8.54)		
P-6	55.49	3.70	7.19	16.51	85	0.26
	(55.94)	(3.66)	(7.25)	(16.59)		

[a] The values in parentheses are those calculated for the chemical formulas.

The yields, after ethanol extraction, and the results of elemental analyses were summarized in Table 1. Polymer yields were 74–88%. The results of the elemental analyses indicated that actual compositions were practically the same as expected from the feed.

Characterization. The structures of the compounds and polymers were confirmed by elemental analysis (Analytical Department of the Mainz University in Mainz, Germany) and by IR (Perkin-Elmer 1430 spectrophotometer) and ^{1}H- and ^{13}C-NMR (Bruker AC 300 FT spectrometer) spectroscopy. Solution viscosities of the polymers were measured at 25 °C using a Canon Ubbelohde type viscometer as 0.5 g/dL solutions in 1,1,2,2-tetrachloroethane (TCE). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed under a N_2 atmosphere on a Mettler DSC 30 at a heating rate of 20 °C/min. Wide angle X-ray diffractograms were recorded on a Siemens D 500 instrument using Ni-filtered Cu Kα radiation. The optical textures of the melts and thermal behavior of the monomers and polymers were investigated on a hot-stage equipped Zeiss Axiophot polarizing microscope. Polymer films for the electrooptical experiments were prepared by the spin-coating technique. The film thickness was measured by a Tencor alpha-step 200. UV–vis spectra of monomers and polymers were recorded using a Perkin-Elmer Lambda 9 spectrophotometer. The second-order polarizability of the model chromophore was determined by electric field induced second harmonic generation (EFISH). The ground and excited state dipole moments and first-order polarizabilities as well as the direction of the transition dipole in the molecule-fixed frame were obtained from electrooptical absorption measurement (EOAM) in dioxane solution at 298 K. The measurements were carried out for two polarization conditions with the electric field vector of the linearly polarized incident light either parallel or perpendicular to the static electric field direction.

Sample Preparation for ATR (Attenuated Total Reflection) Measurement. All of the polymer films for optical measurements were prepared by spin-coating from TCE solution. Before spin-coating, the solutions of P-2 and P-3 were heated to 60 °C (P-2) and 65 °C (P-3) because they form gels at room temperature. 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 a 30–50 nm thick layer of gold to serve as the lower electrode. A polymer film (1–3 μm) was spin-coated onto the gold layer. These films were dried at 80 °C for 10–20 h using a vacuum oven to remove the last traces of solvent from the films. Finally, an upper gold layer of 100 nm thickness was evaporated onto the polymer film. The electrodes were contacted with silver paste and the film was poled applying 40 V/μm at the desired temperature.

Results and Discussion

Synthesis of Polymers. All of the polymers were prepared by Schotten–Baumann type solution polymerization of the dicarboxylic acid chlorides and the diol **2** at 60 °C under argon.

Scheme 2 represents the reactions used in the present study for the preparation of the polymers containing long alkoxy side chains and the chromophore unit with its main dipole axis normal to the chain direction.

Polymers P-1 to P-3 are homopolymers consisting of a single structural repeating unit; however P-4 and P-5 are copolymers consisting of two different structural repeating units (P-4; n = 10/4 = 7/3 in molar ratio) or three different structural units (P-5; n = 10/14/16 = 5/3/2 in molar ratio) in one polymer chain. Polymer P-6 is a semiflexible main chain polyester that contains an aliphatic dicarboxylic acid unit in the polymer chain instead of a rigid aromatic dicarboxylic acid unit.

Optical Properties of the Chromophore. Compound **2** constitutes a new nonlinear optical chromophore which combines several important features. It has highly polarizable sulfur atoms acting as π-electron donors and a strong electronegative dicyano group as a π-electron acceptor. The chromophore can be directly used as a comonomer to prepare rigid rod polyesters via polycondensation with the terephthalic acid derivatives **4**. In addition to the studies on the polymers, the nonlinear optical properties of this chromophore were investigated by electric field induced second harmonic generation (EFISH) and electrooptical absorption measurement (EOAM). Because the solubility of compound **2** is very low in dioxane, used as a solvent for the measurement of the electrooptical properties of the chromophore, the better soluble diacetate **3** (Scheme 2) was prepared. Details of the EOAM and EFISH measurements have been described elsewhere.[26–29,37,39,42]

Optical Properties of the Polymers. Since all of the polymers were soluble in common organic solvents, optical quality films could be easily prepared with the exception of P-1. Even though polymer P-1 was soluble in common organic solvents such as chloroform, *o*-dichlorobenzene, TCE, etc., the solubility was not high enough to produce films of sufficient optical quality. Characterization of the optical properties of the polymer films was accomplished by the ATR method. The linear optical properties of the polymer films were measured by recording the reflectivity of the multilayer structure as a function of the incident angle in the total reflection geometry. The electrooptical properties were characterized by the modulation in the reflectivity as a function of the incidence angle when an ac field was applied.[41]

Thermal Properties and Structural Features of the Polymers. The data for the glass transition (T_g), side chain (T_s), and main chain melting transition temperatures (T_m) are summarized in Table 2. The most distinctive feature in the thermal properties of the polymers is their melting transition behavior. All of the rigid rod type polymers show two weak endotherms during the first heating run, which are denoted as T_s and T_m (see Table 2). The first-order transition at the lower temperature T_s is caused by loss of order in the side chain region of the bulk polymers. At this temperature conformational and positional order of the highly ordered side chain segments decreases.[23,30–32] A transition from this disordered crystalline state to a liquid crystalline melt was observed at T_m. In agreement with observations made by other groups[23,30–32] the presence of a glass transition could not be determined unambiguously by the DSC technique for the rigid rod type main chain polymers P-1 to P-5. Moreover, liquid crystalline to isotropic phase transitions could not be observed below the decomposition temperature. Cooling runs started at a temperature of 300 °C showed only the side chains to crystallize again, and the crystalline domains thus formed melted again during a following heating cycle. This means that only the side chain melting transition is reversible under conditions of quenching the liquid crystalline melt down to room temperature. An appreciable supercooling of this transition was always seen between heating and cooling cycles.

Table 2. General Properties of the Polymers[a]

polymer	d,[b] Å	T_s, °C	T_m, °C	T^D_i, °C	LC[c]
P-1	21.22	60	226	360	LC
P-2	24.50	9	216	337	LC
P-3	27.30	41	214	340	LC
P-4	22.30	−20	239	378	LC
P-5	23.30	−29	207	347	LC
P-6		53[d]	186	358	no

[a] T_s, T_m, and T^D_i represent side chain, main chain melting, and initial decomposition temperatures, respectively. [b] Interlayer spacing in Å. [c] Liquid crystallinity. [d] Glass transition temperature (T_g).

On the other hand, the semiflexible polymer P-6 showed a quite different thermal behavior. It has a clearly observable glass transition at 53 °C and a melting transition at 186 °C. The incorporation of polymethylene segments in the main chain causes a decrease in T_m. Cooling runs started at a temperature above T_m showed only the glass transition to be reversible, while the crystallization of the main chain was suppressed.

The thermal stability of the polymers was investigated by thermogravimetric analysis. The results obtained from TG-DTA thermograms are summarized in Table 2. All of the reported polymers show excellent thermal stability up to 330 °C.

Figure 1 shows wide-angle powder X-ray diffractograms of the rigid rod polymers P-1 and P-5. All of the polymers show a very intense diffraction peak in the small angle region related to the formation of a layered structure. At least one higher order of this reflection was observed in each case. The wide angle region shows a broad halo from which a highly disordered structure of the main and side chain segments within the layers is concluded. Thus, the formation of layers is the characteristic type of order in the bulk at ordinary temperature. This observation coincides with previous investigations[23] on poly(*p*-phenylene terephthalate)s containing long alkoxy side chains with the exception that different layer spacings are observed here as a consequence of the presence of the chromophore units. The chromophore attached to the oxy-1,4-phenylene unit induces an increment of about 1–2 Å to the layer spacing as compared to the nonchromophore-containing polyesters. The spacing between the layers, as listed in Table 2, increases from 21.22 Å for P-1 to 27.3 Å for P-3, thus demonstrating that the layers are separated by extended side chains. Copolymers P-4 and P-5 show layer spacings of 22.3 and 23.3 Å, respectively. These values correspond to side chain lengths equivalent to the arithmetic average of the side chain carbon number normalized with regard to the actual composition, which indicates that the larger side chains fill the space provided by the small side chains in their neighborhood. Figure 2 shows the dependence of interlayer distance on the number of methylene groups per side chain. The homopolymers show a linear relationship similar to the results found previously.[30] An increment of 1.01 Å per methylene unit

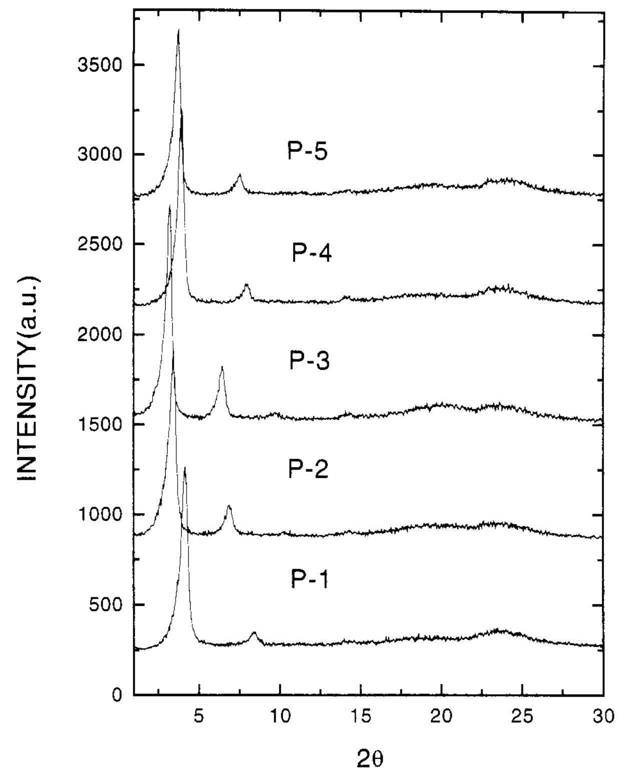


Figure 1. Wide-angle X-ray diffractograms of (a) P-1, (b) P-2, (c) P-3, (d) P-4 and (e) P-5 measured at 30 °C.

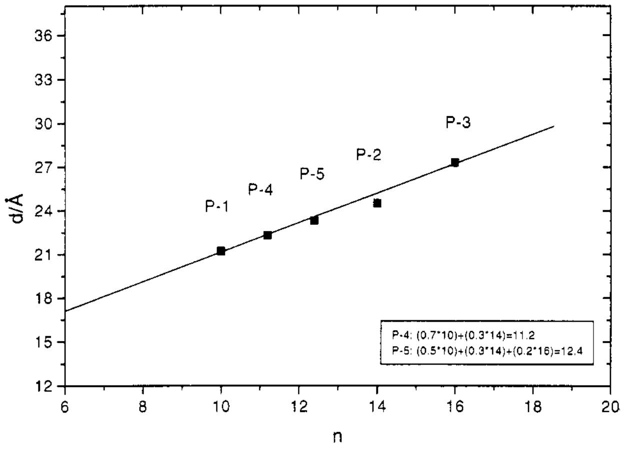


Figure 2. Layer spacing *d* measured at 30 °C as a function of the number of carbon atoms in the side chains.

of the side chain is found from the slope of the line drawn in Figure 2. It deviates from the value expected for a zigzag oligomethylene chain extending normal to the layer plane of 1.25 Å per CH_2 unit. The difference can be explained by assuming an inclination of the chains with regard to the layer normal.

In order to confirm the thermal transition behavior of the polymers seen by DSC, X-ray measurements were conducted at various temperatures. As a representative example, the X-ray diffractograms of P-1 obtained at 30 and 270 °C during heating are shown in Figure 3. The layer spacing increased with increasing temperature. Cooling resulted in recrystallization of the side chains without disturbance of the layered structure. In particular, the X-ray diffraction pattern did not change even above the melting transition temperature T_m, as recorded by DSC. The endothermic peak at T_m can thus be ascribed to the transition from a disordered solid to a layered mesophase, L_m,[31] in which the main chains remain aligned within layers but the correlation between the main chain elements within the layer plane may be of the nematic type. Recently, Damman et al.[33] investigated similar layered mesophases of main chain polymers containing poly(*p*-phenylene terephthalate) backbones decorated with long alkoxy side chains by rheological studies. According to their interpretation, the layered mesophase behaves mechanically more like a solid than a liquid.

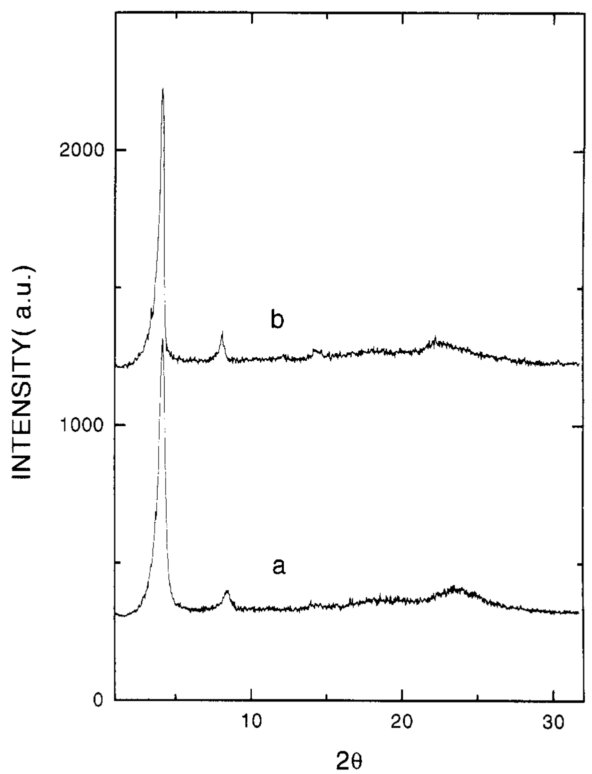


Figure 3. Wide-angle X-ray diffractograms of P-1 at (a) 30 °C and (b) 270 °C.

The X-ray diffractogram of P-6 showed diffraction peaks at 12.7, 6.6, 4.9, 4.4, 4, 3.5, and 3.2 Å. A diffractogram obtained at 200 °C exhibited only liquidlike amorphous halos with maxima at Bragg distances of 10.3 and 4.4 Å. Even after cooling to room temperature, the original crystalline structure was not recovered.

The liquid crystalline properties of the polymers were further investigated by a hot-stage-equipped cross-polarized microscope. All of the polymers except P-6 were thermotropic and formed mesophases on melting which did not disappear up to their decomposition temperature. On the other hand, P-6, containing aromatic moieties separated by nonmesogenic aliphatic segments, formed an isotropic phase upon melting.

Linear and Nonlinear Optical Properties. The second-order polarizability β of the chromophore was investigated by electric field induced second harmonic generation (EFISH). The ground and excited state dipole moments μ_g and μ_a as well as the direction of the transition dipole in the molecule-fixed frame were obtained from electrooptical absorption measurement (EOAM). Both measurements were carried out for two polarization conditions, the electric field vector of the linearly polarized incident light being parallel or perpendicular to the static electric field. Details of the equations and notations used in this study have been described repeatedly.[34-38] Figure 4 shows the optical ($\kappa/\tilde{\nu}$) and electrooptical ($L\kappa/\tilde{\nu}$) absorption spectrum of compound **3** where κ is the molar decadic absorption coefficient, L is the relative change of κ (induced by the applied electric field E_0) divided by E_0^2,[26] and $\tilde{\nu}$ is the wavenumber. The spectra were taken in the region of the first optically allowed singlet excitation from the ground (g) to the first excited singlet state (a).

The electrooptical spectra are governed by a positive electrodichroism; i.e. the absorption coefficient is increased

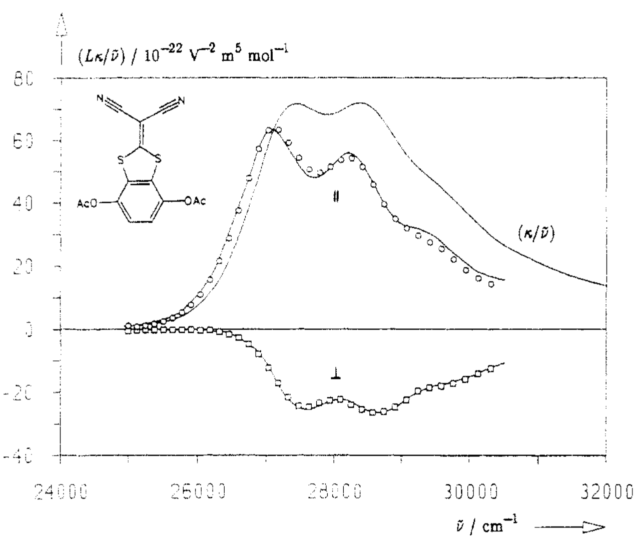


Figure 4. Electrooptical absorption spectra $(L\kappa/\tilde{\nu})$ of **3**. The figure shows experimental data points for parallel (∥) and perpendicular (⊥) polarization of the incident light relative to the applied field and calculated curves obtained by a general linear least squares optimization. The absorption spectrum $(k/\tilde{\nu})$ is displayed in arbitary units.

Table 3. Linear and Nonlinear Optical Properties of Compound 3 Determined in Dioxane Solution at T = 298 K

λ_{ag} (nm)	352
κ_{max} (m^2 mol^{-1})	2250
μ_{ag} (10^{-30} C m)	17
μ_g (10^{-30} C m)	20.3 ± 0.1
μ_a (10^{-30} C m)	29.7 ± 0.7
$\Delta\mu$ (10^{-30} C m)	9.4 ± 0.7
$\beta_z CT(-2\omega;\omega,\omega)^{a,b}$ (10^{-50} C m^3 V^{-2})	2.5
${}^1\beta_z(-2\omega;\omega,\omega)^b$ (10^{-50} C m^3 V^{-2})	1.4 ± 0.1
${}^2\beta_z(-2\omega;\omega,\omega)^b$ (10^{-50} C m^3 V^{-2})	1.3 ± 0.2
$\beta_z(0;0,0)^c$ (10^{-50} C m^3 V^{-2})	0.7

[a] Charge transfer contribution of the first excited singlet state to the second-order polarizability estimated applying the two-state approximation (eqs 1 and 2 in ref 38). [b] At λ = 1064 nm. [c] Static second-order polarizability estimated from ${}^1\beta_z$ using the dispersion factor of the two-state approximation. The following conversions between SI and esu units are valid: μ, 10^{-30} C m = 0.2998 Debye; β, 10^{-50} C m^3 V^{-2} = 2.694 × 10^{-30} esu.

for light linearly polarized parallel to the applied field and decreased for perpendicular polarization. This indicates that the transition dipole μ_{ag} and the ground state dipole μ_g in the chromophore are parallel. The agreement of the experimental and the approximated EOA spectra suggests that there is only one intense electronic transition contributing in this spectral region. The usual regression analysis[26] yields the EOA coefficients $D = (50 \pm 15) \times 10^{-20}$ m^2 V^{-2}, $E = (9920 \pm 90) \times 10^{-20}$ m^2 V^{-2}, $F = (980 \pm 50) \times 10^{-40}$ m^2 V^{-1}, and $G = (850 \pm 50) \times 10^{-40}$ m^2 V^{-1}. The contributions of coefficients H and I were found to be insignificant. The close agreement of the coefficients F and G qualitatively shows that the ground and excited state dipoles, μ_g and μ_a, as well as the transition dipole μ_{ag} lie essentially in the same direction. In this case the ground state dipole can be calculated from $E - 6D$ and the excited state dipole from F and G as described for 4-nitroaniline elsewhere.[37] The results are given in Table 3. Lorentz type local field corrections were applied.[38] The magnitude of the transition dipole μ_{ag} was determined from the integral absorption I_A = 280 m^2 mol^{-1} in the wavelength range 315–400 nm.

Compound **3** shows a high ground state dipole moment μ_g of 6.1 Debye (D) which is mainly due to the strongly polar dicyano group. The ground state dipole moment μ_g of **3** may be compared with 4-nitroaniline (pNA, μ_g = 6.2 D)[37] and MONS, *p*-methoxynitrostilbene (4.5 D[40a], 4.1 D[40b]). The magnitude of the transition dipole (μ_{ag} = 5.1 D) is slightly larger compared to pNA (μ_{ag} = 4.4 D).[37] However, the change of the dipole upon electronic excitation in compound **3** ($\Delta\mu$ = 2.8 D) is smaller than for pNA (9.2 D).[37] Consequently, the charge-transfer contribution β_z^{CT} to the second-order polarizability of **3** (Table 3) is rather small. The calculation of β_z^{CT} from μ_{ag} and $\Delta\mu$ was described elsewhere.[37,38]

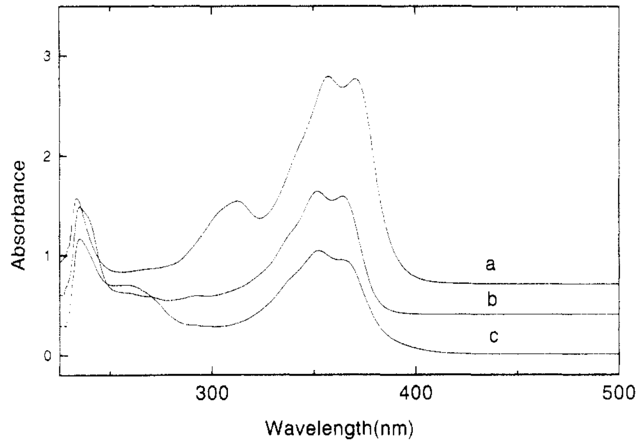


Figure 5. UV–visible spectra of (a) **2**, (b) **3** and (c) P-2 dissolved in THF solution.

The evaluation of the concentration dependent EFISH measurements (mass fractions w_2 in the range 0–0.013) yields the partial molar third-order polarizabilities[38] $Z_2^{\Gamma}(\parallel) = (35 \pm 2) \times 10^{-36}$ C m^4 V^{-3} mol^{-1} and $Z_2^{\Gamma}(\perp) = (13 \pm 1) \times 10^{-36}$ C m^4 V^{-3} mol^{-1} of the solute (index 2). These can be converted to model molar third-order polarizabilities[38] $\zeta_2^{\Gamma}(\parallel) = (27 \pm 2) \times 10^{-36}$ C m^4 V^{-3} mol^{-1} and $\zeta_2^{\Gamma}(\perp) = (10 \pm 1) \times 10^{-36}$ C m^4 V^{-3} mol^{-1} with the partial molar first-order polarizability $Z_2^{\epsilon\omega} = (35 \pm 1) \times 10^{-16}$ C m^2 V^{-1} mol^{-1} (at 589 nm) and the partial molar volume $V_2 = (239 \pm 4) \times 10^{-6}$ m^3 mol^{-1} obtained from refractivity and density measurements, respectively. Then using the ground state dipole from the EOA measurement the vector parts ${}^1\beta_z = \beta_{zzz} + \beta_{zyy}$ and ${}^2\beta_z = \beta_{zzz} + \beta_{yzy}$ of the second-order polarizability in the dipole direction (z axis of the molecule) were calculated (Table 3). An effective C_{2v} symmetry of the chromophore was assumed, and tensor components perpendicular to the π-electron plane (yz plane of the molecule) were neglected.[38] Since ${}^1\beta_z \approx {}^2\beta_z$, the deviation from Kleinman symmetry is not significant in this chromophore and β_{zzz} is the main tensor component of β. The agreement between the experimental vector parts, ${}^1\beta_z$ and ${}^2\beta_z$ and the charge-transfer contribution β_z^{CT} of the lowest excited singlet state is not as good as in the case of pNA. This is possibly due to negative contributions of higher excited states. The value of ${}^1\beta_z(-2\omega;\omega,\omega)$ was used to estimate the static second-order polarizability $\beta_z(0;0,0)$ given in Table 3.

Figure 5 shows UV–visible spectra of (a) 4,7-dihydroxy compound **2**, (b) 4,7-diacetoxy-2-(dicyanomethylene)-1,3-benzodithiolane (compound **3**), and (c) P-2, respectively. Compound **3** shows the same absorption maximum value (352 nm) as for all polymers, while a slightly higher absorption maximum value (358 nm) is obtained in compound **2**. Probably the hydroxy groups contribute to the conjugation between the benzene ring and chromophore in the dihydroxy compound.

The nonzero component of the second-order nonlinear susceptibility ($\chi^{(2)}_{zzz}$, $\chi^{(2)}_{xxz}$, and $\chi^{(2)}_{zyy}$) as well as the piezoelectric coefficient were determined for all polymers using the ATR method. For polymer P-6 with a semiflexible main chain the ratio of $\chi^{(2)}_{zzz}$ (0.73 pm/V) to $\chi^{(2)}_{zxx}$ (0.23 pm/V) was close to the theoretical ratio of 3 for an

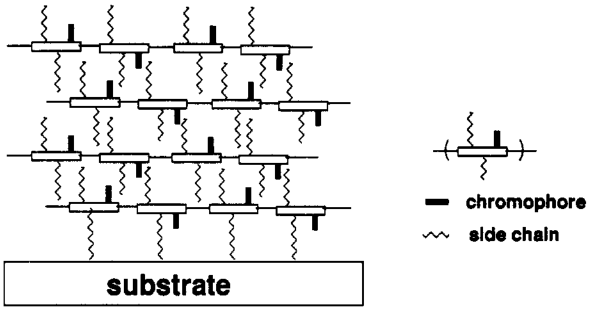


Figure 6. Structural model of rigid rod type polymer films.

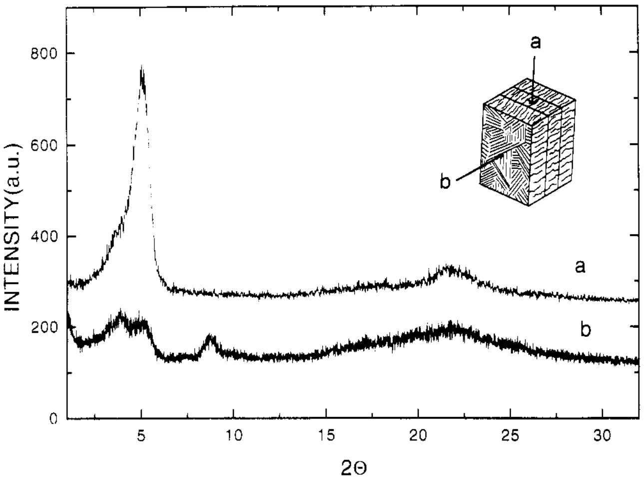


Figure 7. Two-dimensional X-ray diffractograms of the P-2 film obtained from the direction of incidence (a) parallel and (b) perpendicular to the film surface.

isotropic sample. However, the estimation of $\chi^{(2)}_{zzz}$ from the equation $\chi^{(2)}_{zzz} = N\beta F(\mu_g E/5kT)$ with an effective second-order polarizability $\beta(-2\omega;\omega,\omega)$ of 1.4×10^{-50} C m^3 V^{-2} from the EFISH experiment, a chromophore number density $N = 1.04 \times 10^{21}$ cm^{-3} (P-2), a ground state dipole moment $\mu_g = 20 \times 10^{-30}$ C m, and a poling field of 40 V/μm yields a value of 0.22 pm/V, which is definitely below the experimental findings. Different resonant contributions in the ATR and EFISH method as well as errors in the local field factors may explain this discrepancy. For the rigid rod polymers P-1 to P-5 a reliable analysis of the ATR data was not possible due to strong piezoelectric effects. Nevertheless the ratio of $\chi^{(2)}_{zzz}/\chi^{(2)}_{zyy}$ was found to be well below 3 (if an isotropic elastooptical contribution is assumed), which suggests an anisotropic structure of the spin-coated films. The magnitude of $\chi^{(2)}_{zzz}$ close to 1 pm/V is in rough agreement with the results on the semiflexible polymer P-6. Further experiments on the electromechanical properties are necessary to prove the reliability of these data.

Figure 6 shows the two-dimensional geometry of the rigid rod type main chain polymer film geometry obtained from casting the polymer solution. In order to support this structural model we obtained a two-dimensional X-ray diffractogram of a typical representation. Figure 7 shows X-ray diffractograms of P-2 as a cast film. With the incident beam parallel to the film surface (Figure 7a), a very strong diffraction peak corresponding to a Bragg value of $d = 17.4$ Å is seen; it is related to the interlayer spacing. In addition an amorphous halo around $2\theta = 23°$ is observed. The interlayer distance is much shorter than the layer spacing obtained from an unannealed powder sample (24.5 Å). The difference may be explained by the probability of having two different modifications which differ by the angle of inclination and packing density of the side chains, as has been observed for similar polyesters.[30-32] On the other hand, the X-ray diffractogram obtained with the incident beam perpendicular to the film surface (Figure 7b) shows a different diffraction pattern. In addition to weak diffraction peaks in the small angle region, a narrow peak $d = 10.2$ Å was observed. It may be associated to in plane distances between adjacent polymer backbones or repeat unit periodicities.

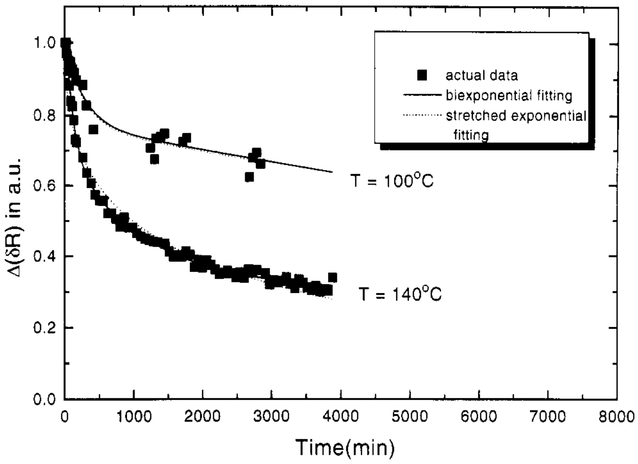


Figure 8. Relaxation of the normalized second-order susceptibilities of P-2 at 100 and 140 °C.

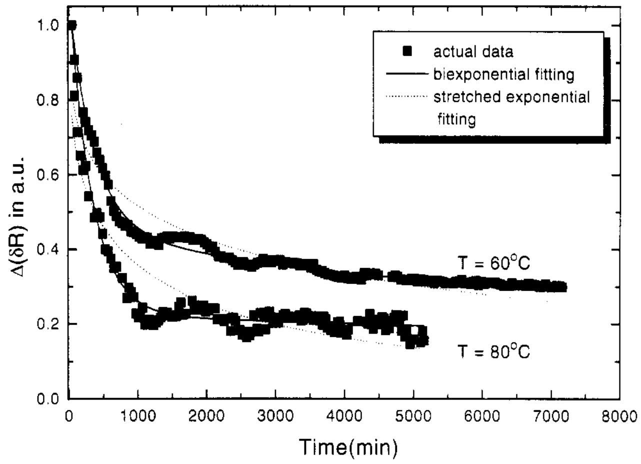


Figure 9. Relaxation of the normalized second-order susceptibilities of P-3 at 60 and 80 °C.

The two X-ray diffractograms clearly demonstrate the uniaxial character of the films oriented parallel to the film surface. Considering the chemical structure of the polymer this leads to the assumption that the chromophores are oriented normal to the film plane. This two-dimensional film geometry is able to enhance the $\chi^{(2)}$ values of the present polymers in comparison to conventional three-dimensional isotropic systems and gives rise to the observed deviation of the ratio of $\chi^{(2)}_{zzz}/\chi^{(2)}_{zxx}$ from the value expected for three-dimensional systems.

The relaxation of polar order in the poled polymers was investigated by monitoring the $\chi^{(2)}$ activity as a function of time at a given temperature. Poled polymer films were heated to 100 and 140 °C for P-2 and 60 and 80 °C for P-3 under the poling field. The temperature was controlled within ±0.1 deg for each measurement. The relaxation behavior after the poling field had been removed is shown in Figure 8 for P-2 and Figure 9 for P-3. In all cases the decay of the normalized signal intensity $\Delta R(t)$ can be described by the following biexponential equation[20]

$$\Delta R(t)/\Delta R(0) = A\exp(-t/\tau_1) + B\exp(-t/\tau_2) \qquad (1)$$

where $\Delta R(t)/\Delta R(0)$ is the ratio of the modulation of signal at the time (t) after the beginning of the measurement ($t = 0$), A is the fraction of chromophores relaxing at a

Table 4. Constants for the Fitting Relaxation Data

	biexponential eq 1			stretched exponential eq 2	
polymer/ °C	A	τ_1, min (h)	τ_2, min (h)	β	τ, min (h)
P-2/100	0.23	274 (4.6)	19 296 (321.6)	0.47	17212 (286.9)
P-2/140	0.48	236 (3.9)	6 631 (110.5)	0.44	2240 (37.3)
P-3/60	0.64	389 (6.5)	18 120 (302)	0.37	3095 (51.6)
P-3/80	0.87	330 (5.5)	19 870 (331)	0.41	932 (15.5)

relatively fast rate with time constant τ_1, and B is the rest of the chromophores relaxing at a relatively slow rate with time constant τ_2. In aged polymer films, the relaxation behavior often conforms rather well to the KWW (Kohlrausch–Williams–Watts)[43] or stretched exponential relaxation equation:[44]

$$\Delta R(t)/\Delta R(0) = \exp[-(t/\tau)^{\beta}] \qquad (2)$$

Curves based on eqs 1 and 2 have been fit to the data points by a least-squares routine. These fitted curves are shown in Figures 8 and 9. The parameters are summarized in Table 4. The relaxation rate constants τ and values of preexponential factors A and B strongly change with temperature between 100 and 140 °C for P-2. P-3 shows a trend similar to that of P-2. The stability of the ordered structure strongly depends on the chemical structure of the polymer. P-2 shows a better stability than P-3, which is probably due to the lower contents of alkyl chain and higher molecular weight. The stability may be due to the intercalation of the chromophores into the matrix of the extended alkyl side chains (cf. Figure 6).

Conclusion

A novel class of NLO polymers based on the (dicyanomethylene)-1,3-benzodithiolane chromophore **2** incorporated in rigid rod type main chains was developed. Five rigid rodlike main chain polymers were prepared together with one semiflexible polymer to compare their thermal and electrooptical properties. These polymers are soluble in common organic solvents and can be spin-coated to provide optical quality thin films. The poled polymer films showed reasonably high second-order susceptibilities and excellent long-term stabilities of the polar order. The built-in tendency of the polymers to form layered structures induces an ordered structure in films cast from solution that enhances the long-term stability of polar order compared to isotropic systems.

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