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Rigid-Rod-Like Main Chain Polymers with Rigidly Attached Chromophores. A Novel Structural Concept for Electrooptical Materials. 1. Synthesis and Characterization

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ABSTRACT: A structural concept for nonlinear optical (NLO) polymeric materials optimized for long-term stability of the polar order is presented: rigid-rod-like main chain polymers furnished with long alkyl side chains with a portion of the side chains being replaced by NLO-active chromophores were synthesized. The chromophores are rigidly attached to the main chains, normal to the direction of the polymer backbone. In this particular geometry the motion of the NLO-active chromophores is restricted to a two-dimensional rotation around the stiff main chain. X-ray diffraction experiments on spin-cast films of the polymers show a lamellar structure with a preferential orientation of the layers parallel to the substrate plane. The incompatibility of polar main chains and nonpolar side chains leads to this microphase segregation. This layered structure improves the long term stability of polar order in the poled polymer film. Dielectric spectroscopy revealed only one relaxation process of large dielectric strength. The Arrhenius-type temperature dependence of relaxation times indicates a locally activated motion of the chromophores.

Introduction

Polymer based second order nonlinear optical materials are promising candidates for the construction of integrated electrooptical waveguide modulators.[1] This application requires materials of large electrooptical coefficients which will retain the nonlinear response over a long period of time even at elevated temperature. Several advanced concepts for the development of NLO-active organic materials have been presented in the literature.[2−4] Noncentrosymmetric crystals grown from organic molecules can exhibit giant second order susceptibilities.[5,6] Since it is difficult to process these crystals into integrated waveguide devices, they are generally used in the field of parametric frequency conversion. Langmuir−Blodgett (LB) films have been mostly developed with respect to waveguide frequency doublers of satisfactory conversion efficiency.[7,8] The preparation of these films particularly with a film thickness in the micrometer region and sufficiently small attenuation is, however, difficult. In the widely accepted “poled polymer” concept, molecules with large microscopic hyperpolarizabilities are either dissolved in a polymer matrix or directly linked to a polymer chain.[9] The noncentrosymmetric order essential for a linear electrooptical response is induced by aligning these chromophores in a strong electric poling field at higher temperature. The polar orientation is then frozen in by cooling the sample to the glassy state. Linking the chromophore to a polymer chain offers the advantage that a larger density of chromophores can be achieved while enhanced long term stability can be expected due to their restricted mobility. Systems with chromophores covalently linked to a flexible polymer backbone have been the subject of extensive investigations, comprehensively reviewed by Staring.[10] A further concept has been developed in which chromophores are incorporated into the polymer main chain.[11,12] These systems provide a higher chromophore density than the side chain materials and therefore larger NLO coefficients.

In order to improve the solubility and thus processibility of these materials, flexible units have to be incorporated either into the side chain or directly into the main chain. The dynamics of these flexible groups, however, will significantly contribute to the relaxation of the polar order. Chemical reactions such as thermally induced or photoinduced cross-linking,[13,14] imidization,[15] or elimination[16] as well as the sol−gel technique[17,18] have been applied to densify the polymer matrix during the poling procedure. Unfortunately, the NLO properties often degrade during the curing process due to either a loss of polar alignment or chemical changes of the chromophores, as reported by Nordmann et al.[19]

Rigid-rod-like polymers substituted with flexible side chains represent another approach to processable NLO materials. The flexible side chains can be considered as a solvent permanently attached to the rigid polymer backbone. Thus the melting temperature is decreased relative to the unsubstituted polymer. Previous work by Ballauff and co-workers on rigid-rod-like polymers showed that solution cast films of the polymers exhibit an ordered lamellar structure with layers oriented parallel to the film surface.[20−22] The general architecture of these materials can be described in terms of closely packed rigid rod polymer main chains separated by layers composed of more or less well packed alkyl or alkoxy side chains (Figure 1a). X-ray diffraction and dynamic mechanical measurements clearly demonstrated that the properties of the layers of stiff chains are considerably different from the properties of the side chain layers. Low temperature transitions have frequently been attributed to the onset of disordering processes (“melting”) in the side chain region, while the layered structure and thus the correlation of the main chains are still maintained. Based on the properties of rigid-rod-like polymers substituted with aliphatic side chains we developed a novel concept where NLO-active chromophores are directly linked to the rigid rod main chain (Figure 1b). We expected the motion of the chromophores to be decoupled from the dynamics of the

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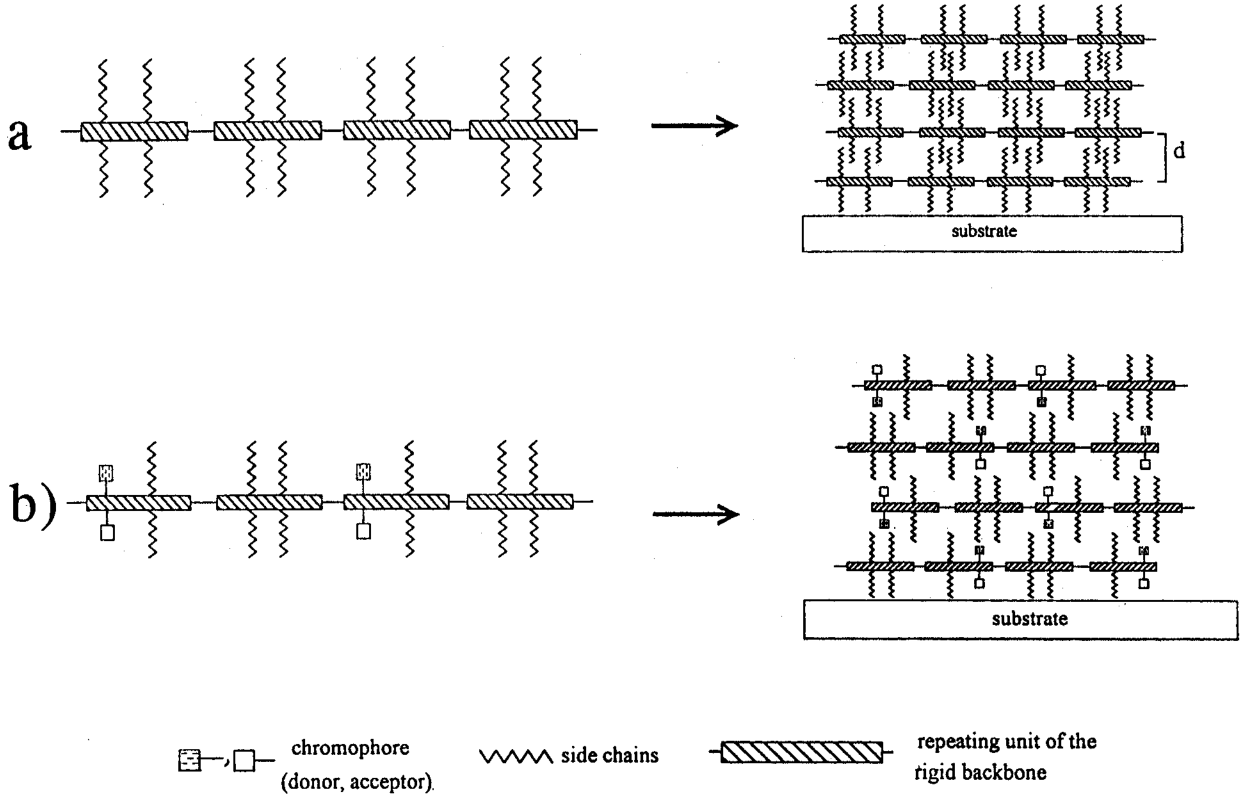


Figure 1. (a) Principal scheme of a rigid rod main chain polymer with flexible side chains (left) and the resulting layered structure (right) in a film cast from solution. *d* is the distance of the main chain layers. (b) Rigid-rod-like main chain polymers with NLO-active chromophores directly linked to the rigid main chain subunits.

solubility-mediating side chains. This should improve the long term stability of the electrooptical response. Previous work on main chain polymers showed that poling is rather difficult with a head-to-tail arrangement of the chromophores in the main chain.[23] Therefore we decided to prepare systems where the dipole axis of the chromophore deviates from the direction of the polymer chain.

In this paper we describe the synthesis and characterization of rigid-rod-like polymers with a typical structure as shown in Figure 1b. The theoretical background of our concept as well as the electrooptical measurements will be presented in a following paper (Heldmann, C., Neher, D., Winkelhahn, H.-J., Wegner, G. *Macromolecules*, in this issue).[24,25]

Experimental Section

Characterization of Compounds. Elemental analyses were carried out at the University of Mainz and at the Analytical Laboratories, Prof. Dr. H. Malissa and G. Reuter GmbH, Gummersbach, respectively. Melting points were determined with a Mettler DSC TC 11. Thin-layer chromatography was performed by using Merck (ATR.-No.: 5594) TLC plates. Column chromatography was performed on silica gel (230−400 mesh, Merck). NMR spectra were recorded on a Bruker AX-300 using $CDCl_3$, CD_2Cl_4, or DMSO-d_6 as solvent and internal standard. Mass spectra were measured on a Trio 2000 Fisions Instruments mass spectrometer. Viscometry measurements were performed in tetrachloroethane at 25 °C by an Ubbelohde Viscosimeter. FTIR spectra were taken on pressed KBr pellets or polymer films cast on a sodium chloride crystal disc by a 60 SX Nicolet FTIR spectrometer. A Mettler DSC TA 3000 system was used for differential scanning calorimetry measurements (at a heating rate of 20 K/min), thermogravimetric analyses were performed using a Mettler Th 50 system with a heating rate of 10 or 20 K/min. X-ray diffraction measurements were carried out on a D 500 Siemens wide angle powder diffractometer with graphite-monochromated CuKα radiation.

Synthesis. Acetamidoterephthalic Dimethyl Ester (2). Acetic anhydride (76.5 g, 0.75 mol) was added to a suspension of 106 g (0.5 mol) of aminoterephthalic dimethyl ester in 400 mL of dry toluene at room temperature. The mixture was stirred for 2 h at 80 °C. The reaction product precipitated from the solution either during heating or after cooling to room temperature. The solid was filtered off, washed with cold toluene, and recrystallized from toluene (1.5 L). Yield: 116.3 g (93%). Mp: 160−161 °C.

2. ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 3 H, $NHCOCH_3$), 4.05, 4.07 (s, 6 H, $COOCH_3$), 7.82 (dd, 1 H, 5-H), 8.18 (d, 1 H, 6-H), 9.40 (d, 1 H, 3-H), 11.05 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ 25.39 (s, $NHCOCH_3$), 52.48, 52.65 (s, OCH_3), 118.08 (s, C-1), 121.39 (s, C-3), 123.11 (s, C-5), 130.81 (s, C-6), 135.41 (s, C-4), 141.54 (s, C-2), 166.12, 168.11, 167.00 (s, $NHCOCH_3$, 2 $COOCH_3$). FT-IR (KBr, cm^{-1}): 3400−2800 (broad), 3305 (w), 3136 (w), 2968 (w), 1724 (m), 1695 (s), 1585 (m), 1537 (m), 1448, 1418 (w), 1303 (m), 1279 (m), 1254 (vs), 1214 (m), 1110 (m), 753 (m). MS: $m/z = 251.1$ (M^+), 209.1, 177.0.

2-Acetamido-5-nitroterephthalic Dimethyl Ester (3) and 2-Acetamido-3-nitroterephthalic Dimethyl Ester (4). A mixture of 307.5 g of concentrated sulfuric acid and 307.5 g of 100% nitric acid (mechanical stirrer and inner thermometer) was added dropwise to an ice/salt bath cooled mixture of 83.0 g (0.34 mol) of **2** in 255 g of concentrated sulfuric acid. The temperature was always kept around 0 °C. When the addition was complete, the ice/salt bath was replaced by an ice bath. The mixture was continuously stirred for 30 min at 0−2 °C and for 30 min at 10 °C and finally poured onto ice (1.9 kg). After 2 h the oily product had solidified to a yellow/brown product which was filtered off and washed several times with dilute sodium bicarbonate solution and finally with water. The crude product was several times recrystallized from methanol. Yield: 51.2 g (53%) of **3**.

3. Mp: 136−137 °C. ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 3 H, $NHCOCH_3$), 3.90 (s, 3 H, $COOCH_3$), 3.98 (s, 3 H, $COOCH_3'$), 8.71 (s, 1 H, 3-H), 9.01 (s, 1 H, 5-H), 11.41 (s, 1 H, NH). ^{13}C

NMR (CDCl$_3$): δ 25.42 (s, NHCOCH$_3$), 53.25, 53.40 (s, COOCH$_3$, COOCH$_3$′), 115.24 (s, C-1), 119.76 (s, C-3), 127.52 (s, C-6), 134.29 (s, C-4), 139.67 (s, C-5), 145.65 (s, C-2), 165.51, 166.53, 169.34 (s, NHCOCH$_3$, COOCH$_3$, COOCH$_3$′). FT-IR (KBr, cm^{-1}): 3400−2800 (broad), 3244 (w), 3111 (w), 2963 (w), 1744 (s), 1706 (m), 1574 (m), 1508 (m), 1440 (m), 1341 (s), 1263 (vs), 1245 (m), 1222 (m), 1114 (m), 1034 (w). MS: m/z = 296.1 (M$^+$), 254.1 (−COCH$_3$).

The filtrate contained a mixture of **3** and **4**. The pH of the combined water fractions was adjusted to between 1.5 and 2 by addition of sodium hydroxide, whereup **4** separated as a yellow precipitate. The water was extracted several times with ethyl acetate. After evaporation of the solvent, the remaining solid was combined with the precipitate. The product was further purified by column chromatography over silica. Elution with hexane/ethyl acetate (60/40) gave 5 g (10%) of **4**.

4. ^{1}H NMR, (CDCl$_3$) δ 2.23 (s, 3 H, NHCOCH$_3$), 3.90 (s, 3 H, COOCH$_3$), 3.98 (s, 3 H, COOCH$_3$′), 7.61 (d, 1 H, 5-H), 8.11 (d, 1 H, 6-H), 9.12 (s, 1 H, NH).

2-Amino-5-nitroterephthalic Dimethyl Ester (5) and 2-Amino-3-nitroterephthalic Dimethyl Ester (6). A solution of 50.0 g (0.17 mol) of **3** or **4** in 630 mL of methanol and 250 g of concentrated sulfuric acid was heated to 90 °C and stirred for 4 h under N$_2$. After a short time, the product started to precipitate. The reaction mixture was cooled to room temperature and stored overnight in a refrigerator. The pale yellow crystals were filtered off and recrystallized from ethanol (2 L). Yield: 42.2 g (98%).

5. Mp: 182−183 °C. ^{1}H NMR (DMSO-d_6): δ 3.92 (s, 3 H, COOCH$_3$), 3.94 (s, 3 H, COOCH$_3$′), 6.98 (s, 1 H, 3-H), 8.04 (s broad, 2 H, NH$_2$), 8.58 (s, 1 H, 6-H). ^{13}C NMR, (DMSO-d_6): δ 53.74 (s, COOCH$_3$), 54.78 (s, COOCH$_3$′), 109.84 (s, C-1), 117.54 (s, C-3), 131.18 (s, C-6), 133.91 (s, C-4), 135.53 (s, C-5), 156.35 (s, C-2), 167.24, 167.72 (s, COOCH$_3$, COOCH$_3$′). FT-IR (KBr, cm^{-1}): 3448 (m), 3339 (m), 2957 (w), 1727, 1713 (m), 1620, 1603 (m), 1450 (m), 1320 (vs), 1252 (m), 1106 (m), 589 (m). MS: m/z = 254.0 (M$^+$).

6. Mp: 76−77 °C. ^{1}H NMR (CDCl$_3$): δ 3.88 (s, 3 H, COOCH$_3$), 3.92 (s, 3 H, COOCH$_3$′), 6.78 (d, 1 H, 5-H), 7.98 (s broad, 2 H, NH$_2$), 8.18 (d, 1 H, 6-H). ^{13}C NMR **8**, (CDCl$_3$): δ 52.50, 53.23 (s, 2 OCH$_3$), 114.60 (s, C-5), 115.87 (s, C-1), 132.66 (s, C-4), 135.69 (s, C-3), 137.12 (s, C-6), 145.75 (s, C-2), 166.42, 166.75 (s, 2 CO). FT-IR (KBr, cm^{-1}): 3490 (m), 3350 (m), 3012, 2959, 2848 (w), 1739 (s), 1707 (s), 1613 (s), 1579 (m), 1516 (m), 1463 (m), 1302 (m), 1274 (vs), 1206 (m), 1135 (m). MS: m/z = 254.0 (M$^+$).

2-(*N,N*-Dimethylamino)-5-nitroterephthalic Dimethyl Ester (7). A mixture of 20.0 g (0.078 mol) of **5**, 138.0 g (1.0 mol) of potassium carbonate and 453.0 g (340 mL, 3.6 mol) of dimethyl sulfate was stirred at 80 °C for 5 days in a 2-L three neck flask equipped with mechanical stirrer, dropping funnel, and inert gas inlet. After 1 day, the pale yellow color of the slurry had changed to an intense yellow/orange and 133.0 g (100 mL, ca. 1.0 mol) of dimethyl sulfate and 138.0 g (1.0 mol) of potassium carbonate were added. An additional amount of 133.0 g of dimethyl sulfate and 40.0 g (0.29 mol) of potassium carbonate was added after 4 days [the progress of the reaction could be followed by TLC with hexane/ethyl acetate (50/50) as eluents]. In order to destroy the excess of dimethyl sulfate, the mixture was cooled in an ice bath and concentrated ammonia solution was added slowly. After continuous stirring for 2 h, water was added to dissolve all of the inorganic salt. The solution was several times extracted with ethyl acetate. After evaporation of the solvent, the crude product was recrystallized from cyclohexane/tetrachloromethane to yield 15.0 g (70%) of compound **7**. Mp: 111−113 °C.

7. ^{1}-H NMR (CDCl$_3$): δ 3.05 (s, 6 H, N(CH$_3$)$_2$, 3.93, (s, 3 H, COOCH$_3$), 3.95 (s, 3 H, COOCH$_3$′), 6.87 (s, 1 H, 3-H), 8.47 (s, 1 H, 5-H). ^{13}C NMR (CDCl$_3$): δ 42.82 (s, N−C), 52.57, 53.22 (s, 2 O−CH$_3$), 114.26 (s, C-3), 117.01 (s, C-1), 129.82 (s, C6), 133.02 (s, C-4), 134.35 (s, C-5), 153.91 (s, C-2), 166.31, 167.05 (s, 2 CO). FT-IR (KBr, cm^{-1}): 3100−2800 (broad), 2958 (w), 1745 (m), 1720 (m), 1610 (m), 1562 (m), 1521, 1503, 1486 (w), 1433 (w), 1326 (vs), 1254 (s), 1206 (m), 1097 (m), 1032 (w). MS: m/z = 283.0 (M$^+$), 282.0 (M$^+$ − H), 267.0 (M$^+$ − (CH$_3$ + H)).

2-(*N,N*-Dimethylamino)-5-nitroterephthalic Acid (8). A solution of 10 g (0.035 mol) of **7** in 60 mL of water, 39 mL of ethanol, and 5.0 g (0.88 mol) of potassium hydroxide was stirred at 70 °C for 3 h under N$_2$. The starting material dissolved completely in the course of the reaction. The solution was cooled to ca. 50 °C and acidified with concentrated hydrochloric acid to a pH of ≈1.5, while the product precipitated from the solution. The fine yellow crystals were filtered off and washed with water. The residue was dissolved in 1 M sodium hydroxide solution, filtered, and reprecipitated by concentrated hydrochloric acid. The water phases were extracted with ethyl acetate to increase the yield. Yield: 8.4 g (95%) of **8**. Mp: 215−231 °C, under decomposition and gas evolution.

8. ^{1}H NMR (DMSO-d_6): δ 3.05 (s, 6 H, N(CH$_3$)$_2$, 7.01 (s, 1H, 3-H), 8.25 (s, 1 H, 6-H). ^{13}C NMR (DMSO-d_6): δ 45.35 (s, N(CH$_3$)$_2$, 115.11 (s, C-3), 119.50 (s, C-1), 130.21 (s, C-6), 134.63 (s, C-4), 135.52 (s, C-5), 155.21 (s, C-2), 168.96 (s, sometimes two signals, COOH). FT-IR (KBr, cm^{-1}): 3670−3100 (broad), 3060 (w), 2800−2200 (broad), 2200−1700 (broad), 1725 (w), 1588 (w), 1539 (vs), 1492 (w), 1464 (m), 1450 (w), 1377 (m), 1257 (s), 1173, 1128 (s), 1085 (m), 837 (w), 818 (m). MS: m/z = 254.0 (M$^+$), 239.0 (−CH$_3$).

2-(*N,N*-Dimethylamino)-5-nitroterephthalic Acid Dichloride (9). A suspension of 2.5 g (9.84 mmol) of **8** in 50 mL of dry dichloromethylene was treated with 10.8 g (7.5 mL, 85.1 mmol) of oxalyl chloride and heated to 45−50 °C under N$_2$. The temperature was kept below 50 °C because of the temperature sensitivity of the final product. The progress of the reaction could be followed by the gas produced and by the dissolution of the starting material. After stirring overnight, 3 g (2 mL, 23 mmol) of oxalyl chloride were added. The solution was stirred for an additional 2 h. The excess of oxalyl chloride was removed by successive evacuation and aeration of the flask with nitrogen. The purity of the remaining solid was sufficient for the next step. If higher purity is required, the solid is dissolved in a small amount of dichloromethane at 50 °C and reprecipitated by dry hexane. Yield: quantitative.

9. ^{1}H NMR (CDCl$_3$): δ 3.09 (s, 6 H, N(CH$_3$)$_2$, 6.82 (s, 1 H, 3-H), 8.75 (s, 1 H, 6-H). ^{13}C NMR [(CDCl$_2$)$_2$]: δ d 42.74 (s, N(CH$_3$)$_2$), 114.01 (s, C-3), 117.92 (s, C-1), 128.78 (s, C-6), 133.21 (s, C-5), 133.96 (s, C-4), 153.58 (s, C-2), 167.20 (s, CO). MS: 289.98 M$^+$ (Cl^{35}, Cl^{35}), 291.97 M$^+$(Cl^{35}, Cl^{37}), 293.97 (Cl^{37}, Cl^{37}). Rel intensity. Calcd: 100 64 10. Found: 100 64 12. Anal. Calcd for $C_{10}H_8O_4Cl_2N_2$: C, 41.26; H, 2.77; N, 9.62; O, 21.99; Cl, 24.36. Found: C, 41.39; H, 2.90; N, 9.54; O, 21.82; Cl, 24.32.

3-Hydroxy-4-nitrobenzoic Acid Methyl Ester (11). **10** (150 g, 0.82 mol), 300 mL of methanol, 480 mL of dichloroethane, and 10 mL of concentrated sulfuric acid were refluxed for 24 h under N$_2$. The starting material dissolved slowly as the reaction proceeded. After 1 day, sodium sulfate was added as a drying agent. The drying agent was filtered off, the solvent was evaporated, and the residue was purified by column filtration with silica gel and dichloromethane. The crude product was recrystallized from a small amount of ethanol. Yield: 123 g (76%) of **11**. Mp: 87−89 °C.

11. ^{1}H NMR (CDCl$_3$): δ 3.85 (s, 3 H, OCH$_3$), 7.49 (dd, 1 H, 6-H), 7.60 (d, 1 H, 2-H), 8.05 (d, 1 H, 5-H), 10.39 (s, 1 H, OH). ^{13}C NMR (CDCl$_3$): δ 52.74 (s, OCH$_3$), 120.46 (s, C-2), 121.53 (s, C-6), 125.12 (s, C-5), 135.72 (s, C-1), 137.90 (s, C-4), 154.54 (s, C-3), 164.68 (s, CO). FT-IR (KBr, cm^{-1}): 3400−3100 (broad), 3313 (w), 2960 (w), 1724 (s), 1625 (w), 1589 (m), 1524 (w), 1479 (m), 1437 (m), 1329 (vs), 1286 (m), 1229 (s), 1150 (m). MS: m/z = 197.0 (M$^+$), 166.0 (−OH, −CH$_3$).

3-Alkoxy-4-nitrobenzoic Acid Methyl Ester (12). A suspension of 20.0 g (0.10 mol) of **11**, 28.0 g (0.20 mol) of potassium carbonate, and 0.50 mol of the alkyl bromide in 650 mL of acetone was refluxed for 2 days. The inorganic salts produced were filtered off and washed with acetone. After evaporation of the solvent, the crude product was purified by column filtration with dichloromethane. The solvent was removed and the pure compound was dried at 50 °C at 10^{-2} mbar to eliminate traces of the alkyl bromide. Example, 3-hexyl-4-nitrobenzoic acid methyl ester, mp 38−42 °C.

^1H NMR ($CDCl_3$): δ 0.70 (t, 3 H, CH_3), 1.16 (m, 4 H, $(CH_2)^{4,5}$), 1.30 (quint, 2 H, $(CH_2)^3$), 1.66 (quint, 2 H, $(CH_2)^2$), 3.75 (s, 3 H, OCH_3), 3.98 (t, 2 H, $(OCH_2)^1$), 7.48 (dd, 1 H, 6-H), 7.54 (d, 1 H, 2-H), 7.61 (d, 1 H, 5-H). ^{13}C NMR ($CDCl_3$): δ 13.90 (s, CH_3), 21.21 (s, $(CH_2)^5$), 25.41 (s, $(CH_2)^3$), 28.82 (s, $(CH_2)^4$), 31.17 (s, $(CH_2)^2$), 52.84 (s, $COO\mathit{C}H_3$), 70.03 (s, $(CH_2)^1$), 115.54 (s, C-2), 121.11 (s, C-6), 125.24 (s, C-5), 134.90, 142.93 (s, C-1, C-4), 152.25 (s, C-3), 165.62 (s, CO). FT-IR (KBr, cm^{-1}): 4000−3200 (broad), 3100−2800 (broad), 2956, 2934 (m), 2861 (w), 1728 (s), 1611 (m), 1529 (s), 1438 (m), 1298 (vs), 1240 (s), 746 (m). MS: $m/z = 281.0$ (M^+).

3-Alkoxy-4-aminobenzoic Acid Methyl Ester (13). **12** (35.5 g, 0.125 mol) was dissolved in 200 mL of ethanol and transferred into the glass tube of a stainless steel autoclave. The yellow solution was purged for half an hour with N_2 before adding one spatula of fresh Raney nickel. Hydrogeneration proceeded at 60 °C at a pressure of 60 bar. It was important to care for sufficient stirring of the suspension. After 5 h, no further hydrogen gas was absorbed. The solution was filtered though a membrane filter to remove the catalyst. The solution should be colorless otherwise the reduction of the nitro group was not complete. The solvent was evaporated and the product was recrystallized from a small amount of hexane or ethanol. Yield: 25.0 g (79%). Example, 3-hexyloxy-4-aminobenzoic acid methyl ester, mp 74−75 °C.

^1H NMR ($CDCl_3$): δ 0.74 (t, 3 H, CH_3), 1.19 (m, 4 H, $(CH_2)^{4,5}$), 1.29 (quint, 2 H, $(CH_2)^3$), 1.63 (quint, 2 H, $(CH_2)^2$), 3.68 (s, 3 H, OCH_3), 3.85 (t, 2 H, $(OCH_2)^1$), 4.08 (s broad, NH_2), 6.48 (d, 1 H, 5-H), 7.27 (d, 1 H, 2-H), 7.41 (d, 1 H, 6-H). ^{13}C NMR ($CDCl_3$): δ 14.05 (s, CH_3), 22.66 (s, $(CH_2)^5$), 25.85 (s, $(CH_2)^3$), 29.31 (s, $(CH_2)^4$), 31.65 (s, $(CH_2)^2$), 51.65 (s, $COO\mathit{C}H_3$), 68.56 (s, $(CH_2)^1$), 112.27 (s, C-2), 113.16 (s, C-5), 119.44 (s, C-6), 124.04 (s, C-4), 141.54, (s, C-4), 145.64 (s, C-3), 167.44 (s, CO). FT-IR (KBr, cm^{-1}): 3483 (m), 3366 (vs), 3205 (w), 3100−2800 (broad), 2939 (m), 2855 (w), 1699 (vs), 1621 (s), 1527 (w), 1446 (m), 1312 (s), 1294 (s), 1263 (s), 1216 (w), 1107 (m). MS: $m/z = 251.0$ (M^+), 167.0 ($-C_6H_{12}$).

1,4-Bis[(2-alkoxy-4-(methoxycarbonyl)phenyl)aminocarbonyl]-2-(*N*,*N*-dimethylamino)-5-nitrobenzene (n = 0, 6, 12) (14). **13** (5.43 g, 21.65 mmol) was added to a solution of 2.86 g (9.84 mmol) of **9** in 40 mL of dimethyl acetamide at 10 °C under N_2. The ice bath was removed after 10 min and the reaction mixture was stirred overnight at room temperature. The temperature was raised to 40 °C, 20 mL of methanol were added, and the solution was stirred for an additional 30 min. For the derivative with $n = 6$, the solution was poured into 300 mL of methanol. The product precipitated from the solution after a short time, while all of the starting materials remained in solution. The product was filtered off, washed with methanol, and recrystallized from a mixture of 150 mL of dichloromethane and 370 mL of methanol. Yield of **14** (n = 6): 5.80 g (82%). For **14** (n = 12), methanol and then a few milliliters of water were added to the reaction mixture whereupon rapid precipitation occurred. The product was filtered off and dissolved in a boiling dimethylacetamide/methanol mixture. Water was added for reprecipitation.

14 (n = 6) (the dashed peak positions refer to the aromatic protons of the amino benzoate unit linked through the 1-carboxylic group, the double dashed positions refer to the aromatic protons of the amino benzoate units linked via the 4-carboxylic group). ^1H NMR ($CDCl_3$): δ 0.78 (t, 3H, $(CH_3)^6$), 0.81 (t, 3 H, $(CH_3')^6$), 1.20−1.40 (m, 12 H, $(CH_2)^{3-5}$, $(CH_2')^{3-5}$), 1.69 (quint, 4 H, $(CH_2)^2$), 1.78 (quint, 4 H, $(CH_2')^2$), 2.98 (s, 6 H, $N(CH_3)_2$), 3.82, 3.85 (2 s, 6 H, 2 $COOCH_3$), 4.00 (t, 2 H, OCH_2), 4.09 (t, 2 H, OCH_2'), 7.06 (s, 1 H, 3-H), 7.46 (d, 1 H, 3′-H), 7.51 (d, 1 H, 3″-H), 7.65 (2 dd overlapped, 2 H, 5′-H, 5″-H), 8.10 (s, 1 H, NH_a), 8.46 (d, 1 H, 6′-H), 8.51 (d, 1 H, 6″-H), 8.53 (s, 1 H, 6-H), 9.50 (s, 1 H, NH_b). ^{13}C NMR ($CDCl_3$): δ 13.85, 13.90 (s, $CH_3)^6$, $(CH_3')^6$), 22.44, 22.49 (s, $(CH_2)^5$, $(CH_2')^5$), 25.52, 25.55 (s, $(CH_2)^3$), 28.83, 29.15 (s, $CH_2)^4$, $(CH_2')^4$), 31.35, 31.42 ($(CH_2)^2$, $(CH_2')^2$), 43.79 $N(CH_3)_2$), 52.09 (s, $COO\mathit{C}H_3$, $COO\mathit{C}H_3'$), 69.14, 69.19 (s, OCH_2, OCH_2'), 111.79, 111.88 (s, C-H_g, C-$H_{g'}$), 116.43 (s, C-3), 119.22, 119.31 (s), 123.16, 123.23 (s), 125.82, 125.95 (s), 128.89 (s), 131.53 (s, C-6), 135.93 (s, C-4), 137.03 (s, C-5), 147.02 (s), 147.27 (s), 154.58 (s, C-2), 163.66, 164.14 (s, $CONH_b$, $CONH_b$), 166.59 (s, $\mathit{C}OOCH_3$).

14 (n = 12) shows the same peak positions but with different intensities.

1,4-Bis(2-alkoxy-4-carboxyphenyl)aminocarbonyl]-2-(*N*,*N*-dimethylamino)-5-nitrobenzene (n = 0, 6, 12) (15). A solution of 4.95 g (7.22 mmol) of **14**, 6.14 g (0.15 mol) of sodium hydroxide in 100 mL of ethanol, 125 mL of water, and 25 mL of dioxane was stirred at 80 °C for 3 h under N_2. The starting material dissolved slowly as the reaction proceeded. The solution was cooled to room temperature and acidified by hydrochloric acid. The precipitate was filtered off and dried i.v. at 80 °C. The product was reprecipitated several times from a mixture of dimethyl formamide/water (pH = 4). The fine crystalline powder was dried i.v. at 120 °C. Yield **15** (n = 6), 4.1 g (83%); **15** (n = 12), 4.5 g (73%).

15 (n = 6). ^1H NMR (DMSO-d_6): δ 0.71 (m, 6 H, $(CH_3)^6$, $(CH_3')^6$), 1.10 (m, 8 H, $(CH_2)^{4.5}$, $(CH_2')^{4.5}$), 1.28 (m (2 quint), 4 H, $(CH_2)^3$, $(CH_2')^3$), 1.68 (m (2 quint), 4 H, $(CH_2)^2$, $(CH_2')^2$), 2.90 (s, 6 H, $N(CH_3)_2$, 3.95 (t, 2 H, OCH_2), 4.02 (t, 2 H, OCH_2'), 6.98 (s, 1 H, 3-H), 7.48 (m, 4 H, 5′-H, 5″-H, 6′-H, 6″-H), 8.02 (2d, 2 H, 3′-H, 3″-H), 8.18 (s, 1 H, 6-H), 9.69 (s, 1 H, NH_a), 10.06 (s, 1 H, NH_b), 13.02 (s broad, 2 H, COOH). FT-IR (KBr, cm^{-1}): 3347 (w), 3352 (w), 2953 (m), 2932 (m), 1678 (s), 1598 (m), 1560 (m), 1555 (vs), 1498 (s), 1437 (m), 1409 (m), 1347 (m), 1320 (m), 1277 (vs), 767.4 (w). Anal. Calcd for $C_{36}H_{44}O_{10}N_4$: C, 62.42; H, 6.40; N, 8.09; O, 23.10. Found: C, 62.38; H, 6.41; N, 8.15. MS: $m/z = 692.3$ (M^+).

15 (n = 12). Anal. Calcd for $C_{48}H_{68}O_{10}N_4$: C, 66.95; H, 7.96; N, 6.51; O, 18.58. Found: C, 66.98; H, 7.85; N, 6.66. MS: $m/z = 860.5$ (M^+).

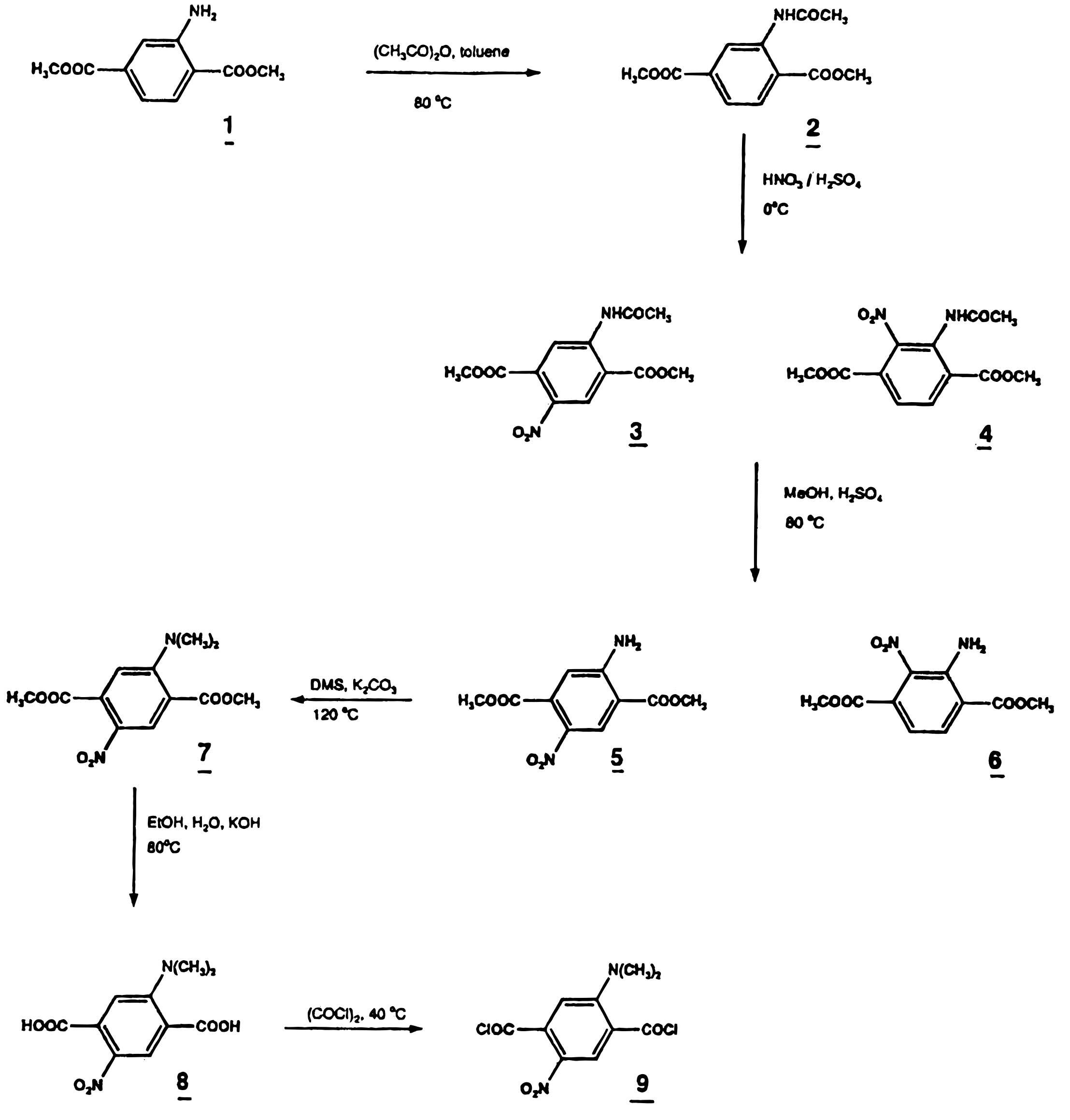
Polycondensation: General Procedure. The quantities of **15** used for the synthesis of various polymers were, for **P1**, 0.8130 g (1.651 mmol), *P2a*, 0.9548 g (1.378 mmol), *P2b*, 1.5514 g (2.224 mmol), and **P3**, 1.7262 g (2.005 mmol). Lithium bromide (0.1734 g, 2 mmol), 0.6985 g (2.6 mmol) of diphenyl chlorophosphate, and 2 mL of oxygen free pyridine (dried over molecular sieve) were stirred at room temperature for 30 min. Lithium bromide was not used in the syntheses of polymers **P2b** and **P3**. A solution of 1.0 mmol of the dicarboxylic acid **15** in 5 mL of pyridine was now added. The yellow, slightly viscous solution was stirred for an additional 35 min at room temperature and then for 10 min at 120 °C. 2,5-Ditetradodecyloxyhydroquinone **16**, 1.0 mmol, in 10 mL of pyridine was added within a few minutes. The amount of pyridine was reduced to approximately 15 mL by evaporation in a strong argon stream. After 2 h, the viscosity of the solution had significantly increased and finally the reaction mixture solidified to a firm gel. To allow stirring of the solution, 10 mL of pyridine were added. After 5 h, the hot solution was poured into 500 mL of methanol. The crude polymer was reprecipitated several times from tetrachloroethane/methanol. Yield: >90%.

Anal. Calcd for $C_{70}H_{102}O_{12}N_4$ (**P2a**): C, 70.56; H, 8.63; N, 4.70; O, 16.11. Found: C, 69.41; H, 9.01; N, 5.20. [η] (dL/g): 0.351. Calcd for $C_{70}H_{102}O_{12}N_4$ (**P2b**): C, 70.56; H, 8.63; N, 4.70; O, 16.11. Found: C, 69.93; H, 8.51; N, 5.13. [η] (dL/g): 0.893. Calcd for $C_{82}H_{126}O_{12}N_4$ (**P3**): C, 72.42; H, 9.34; N, 4.12; O, 14.12. Found: C, 71.63; H, 8.01; N, 4.65. [η] (dL/g): 0.654.

Results and Discussions

Synthesis of Monomers. In order to prove the structural concept, polymers were synthesized with a chromophore incorporated in the polymer main chain. The donor−acceptor-substituted terephthalic derivative **9** was regarded as a possible starting compound for preparing chromophore functionalized polyesters. Monomer **9** is prepared by a six-step reaction starting from aminoterephthalic dimethyl ester **1** (Scheme 1). The amino group of aminoterephthalic dimethyl ester **1** is first protected by reacting it with acetic anhydride. Nitration gave then a mixture of two (ortho and para) isomers, which could be easily separated. The protecting group was selectively removed and the methylation of the amino group was achieved by dimethyl sulfate at 120 °C with potassium carbonate as base. These

Scheme 1. Synthesis of the Terephthalic Acid Dichloride 9

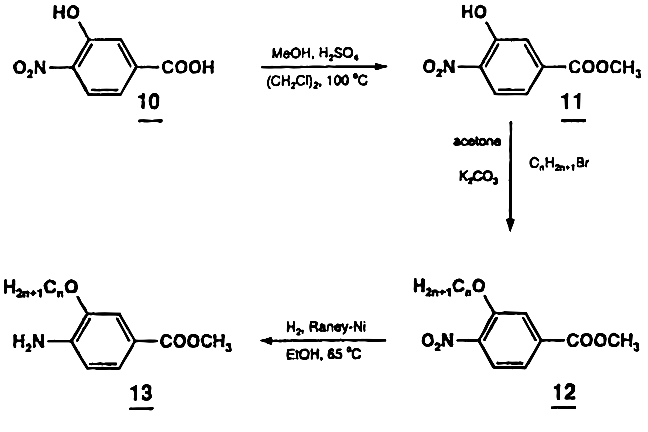


severe reaction conditions are necessary because the amino group is deactivated by the nitro group and the reaction is sterically hindered by the adjacent ester group. The next two steps are the cleavage of the ester groups and the formation of the terephthalic acid dichloride **9** with oxalyl chloride. This step had to be carried out carefully because of the temperature sensitivity of the final product, which starts to decompose at $T > 50$ °C.

Subsequent polycondensation with the hydroquinone **16** (Scheme 4) should give a chromophore containing main chain polyester. Unfortunately, the homopolycondensation could not be accomplished (see later in the text). Therefore, two “spacer units” were introduced into the monomer unit by reacting **9** with 2 equiv of the alkoxy-substituted aminobenzoic ester **13**, which was prepared in a three-step synthesis as described in Scheme 2 starting from 3-hydroxy-4-nitrobenzoic acid (**10**). **10** was first esterified with methanol and then the hydroxyl group was alkylated by using hexyl or dodecyl bromide. The reduction of the nitro group was achieved with Raney nickel as catalyst.

By reacting **9** with **13**, the trimer structure **14** was obtained, in which the neighboring group effects of the nitro and the carboxylic substituents and further possible interactions of this redox system could be successfully suppressed. Cleaving of the two ester groups of **14** gave the final monomer **15** (Scheme 3).

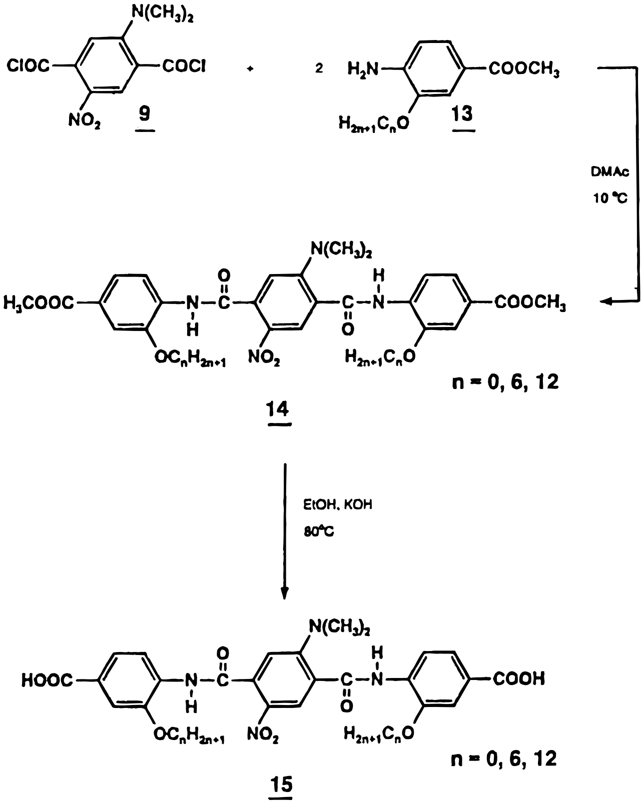
Scheme 2. Synthesis of 13



The 2,5-dialkoxyhydroquinones **16** (Scheme 4) used as comonomers were prepared according to the literature.[25]

Synthesis of Polymers. It was impossible to obtain a homopolymer from 2,5-dialkoxyhydroquinones **16** and

Scheme 3. Synthesis of 15 (n = 0, 6, 12)



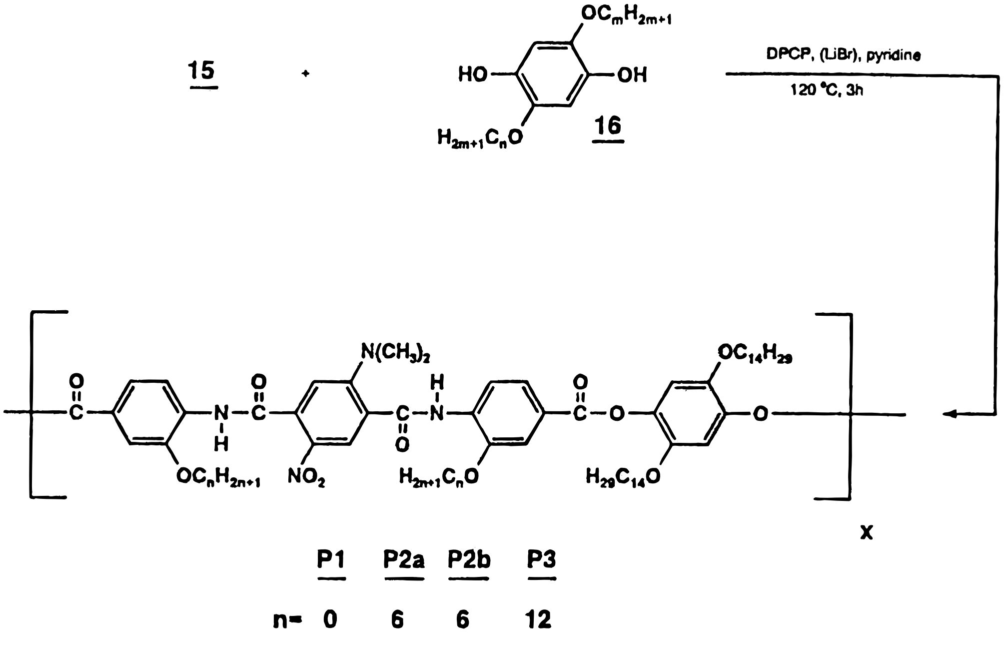
terephthalic acid dichloride **9**. Oxidation of the hydroquinone to the benzoquinone occurred during the reaction, while **9** decomposed to a brown insoluble compound which could not be further analyzed. Compound **9** is quite unstable, decomposing at around 55 °C in solution (dichloromethane, toluene), whereas the free acid **8** shows good thermal stability up to 220 °C, where it decomposes under gas evolution (presumably carbon dioxide). For this reason it was assumed that the specific activation of the carboxylic group to an acid chloride would be the main reason for the failure of the polycondensation process. Therefore several other polycondensation methods were applied: Higashi's method of direct polycondensation with thionyl chloride/pyridine or DPCP/pyridine (see below)[26] as the condensating reagent and melt condensation using the bisacetate or the bis(trimethylsilyl) derivative of **16**.[27-30] In none of these attempts was a homopolymer formed. Another interesting result is that it was possible to condensate (*N*,*N*-dimethylamino)terephthalic acid with **16**, but impossible to get a homopolymer from nitroterephthalic acid. For this reason it was concluded that a strong neighboring group effect between the nitro and the activated carboxylic group prevents the successful formation of a homopolymer. It is important to note that **16** is perfectly stable under the reaction conditions used. Oxidation only occurred in the presence of **8** or **9**. On the other hand, it is possible to isolate at least traces of oligomers of low molecular weight when **9** is reacted with unsubstituted hydroquinone. This means that steric hindrance plays an important role as well.

To circumvent the problems described we synthesized compound **15**. Now the NLO-active groups and the reactive carboxylic groups are well separated so that neighboring group effects can be neglected.

Scheme 4 shows the polycondensation procedure. The polycondensation was carried out according to Higashi's method with diphenyl chlorophosphate (DPCP) as condensation agent and pyridine as colvent. The structure of the polymers was proven by ^{1}H and ^{13}C NMR (Figures 2 and 3), IR, and elemental analysis. Polymers **P2a**, **P2b**, and **P3** are soluble in common organic solvents like tetrachloroethane, tetrahydrofuran, and pyridine and give homogenous transparent films with good mechanical and optical properties when spin-coated or cast from tetrachloroethane solution. Since the solubility of polymer **P1** in organic solvents is not sufficient for the preparation of spin-coated films, it was impossible to measure the nonlinear optical properties of this material. Polymers **P2a** and **P2b** exhibit different degrees of polymerization according to viscosity determination in tetrachloroethane, with **P2b** being the higher molecular weight sample.

To our knowledge, Higashi's method has only been applied to more or less "standard" monomers such as terephthalic acid, isophthalic acid, simple hydroquinone derivatives, or 2,2-bis(4-hydroxyphenyl)propane so far.

Scheme 4. Synthesis of Polymers P1, P2a, P2b, and P3



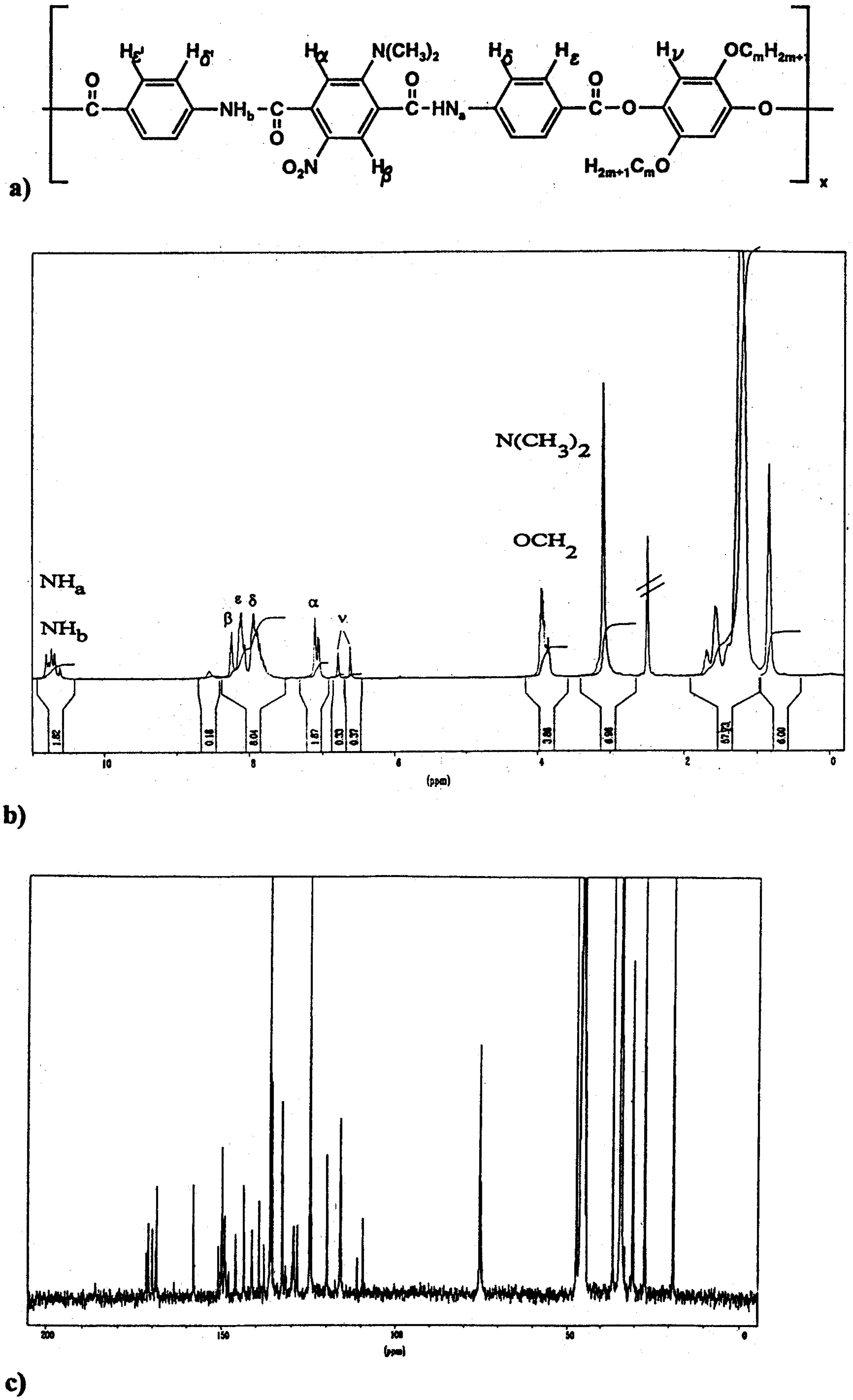


Figure 2. (a) Molecular structure of **P1**. (b) ^{1}H-NMR spectrum of **P1** in DMSO-d_6 at 120 °C. The assignment of the aromatic protons according to the formula given in (a) is shown in the diagram. The following additional assignments can be made (in ppm): 1.82, 1.58 (m, 4 H, $(CH_2)^2$), 1.5−1.0 (m, 46 H, $(CH_2)^{3-13}$), 0.87 (m, 6 H, CH_3). (c) ^{13}C-NMR spectrum of **P1** in DMSO-d_6 at 120 °C.

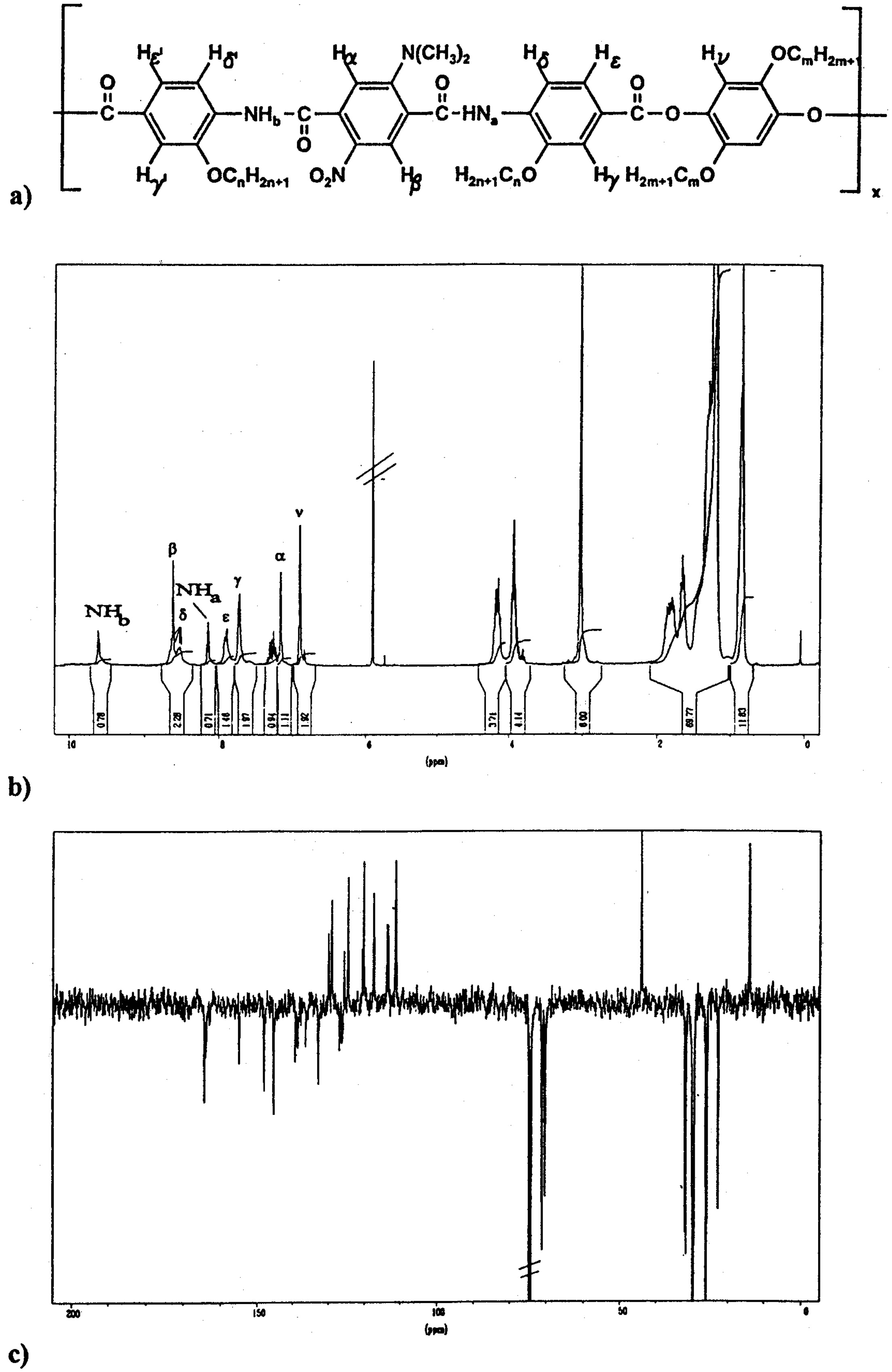


Figure 3. (a) Molecular structure of **P2b**. (b) ^{1}H-NMR spectrum of **P2b** in CD_2Cl_4 at 80 °C. The assignment of the aromatic protons is given in the diagram. The following additional assignments can be made (in ppm): 4.13 (m, 4 H, OCH_2-aminobenzoic acid), 3.92 (m, 4 H, OCH_2-hydroquinone), 3.03 (m, 6 H, $N(CH_3)_2$), ca. 1.82, 1.67 (m, each 4 H, $(CH_2)^2$-hydroquinone, $(CH_2)^2$-aminobenzoic acid), 1.5–1.0 (m, 56 H, $(CH_2)^{3-13}$-hydroquinone, $(CH_2)^{3-5}$-aminobenzoic acid), 0.87 (m, 12 H, CH_3-hydroquinone, CH_3-aminobenzoic acid). (c) ^{13}C-spin echo of **P2b** at 120 °C in CD_2Cl_4 (concentration: 150 mg/mL).

The successful polycondensation of monomers like **15** and **16** with a variety of different functional groups (ether, amide, nitro, dimethylamino groups) represents an important extension of Higashi's method and dem-

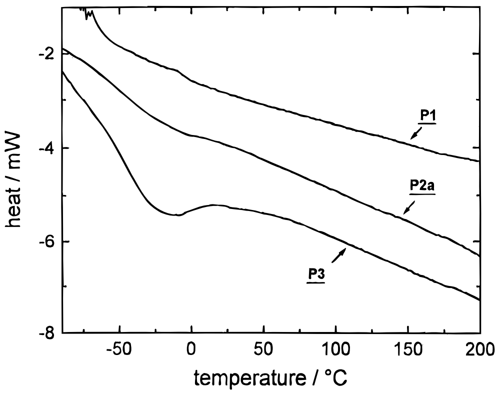


Figure 4. DSC thermograms of polymers **P1**, **P2**, and **P3**.

onstrates the wide applicability of this polycondensation process.

Characterization of the Molecular Weight. It was very difficult to obtain reliable data for the molecular weight of the synthesized poly(ester amide)s. The determination of the molecular weight by gel permeation chromatography (GPC) was strongly hampered by adsorption of the polymer on the column and by aggregation (intercalating side chains) of the polymer main chains leading to extremely broad elution curves. Owing to the tendency to aggregate, it was also impossible to evaluate the molecular weight by light scattering. Therefore, viscosity measurements in tetrachloroethane as solvent were performed. The required concentrations were prepared by subsequent dilution of a starting solution. It was very important to give the system enough time to reach a new equilibrium state after each dilution step. A linear (reproducible) relationship between the viscosity η and the concentration c could only be obtained when a sufficiently long "waiting time" after each dilution step was taken into account. The derived inherent viscosity data are collected in the Experimental Section.

Thermal and Structural Properties. DSC thermograms of the polymers (second heating scan) are shown in Figure 4. Below $T = 0$ °C a broad endothermic peak is observed, becoming more distinct as the number n of the side chain methylene groups increases. We thus attribute this peak to a transition associated to changes in side chain packing ("side chain melting"). The DSC scans show no evidence for a glass transition up to the decomposition temperature. This is in agreement with observations made by other groups and can presumably be explained by the micro-phase-separated structure of the polymers.[22,25,31] Investigations by polarization microscopy indicate that all polymers undergo a transition from a liquid crystalline phase to an isotropic melt at around 240 °C. Noticeable decomposition occurs at this temperature.

Thermogravimetric analysis (TGA) indicated two decomposition processes. The first process, starting at around 230 °C with a weight loss of 6−7%, was attributed to degradation of the chromophoric group and was accompanied by a bleaching of the polymer sample. A second decomposition process, starting at around 330 °C, is caused by the loss of the alkoxy side chains (see Table 1).

Table 1. TGA Data for P1, P2a/b, and P3[a]

peak	T_s, T_p, T_e/°C	weight loss, exptl/%	weight loss, theoretical/%	assignment
		P1		
I	230, 294, 320	−7.8	−8.9	$N(CH_3)_2$, NO_2
II	320, 396, 500	−44.2	−43.0	all OR groups
		P2a/b		
I	250, 316, 339	−6.9	−7.5	$N(CH_3)_2$, NO_2
II	337, 392, 496	−53.2	−52.7	all OR groups
		P3		
I	235, 318, 337	−6.4	−6.6	$N(CH_3)_2$, NO_2
II	340, 391, 500	−58.8	−58.6	all OR groups

[a] T_s, T_p, T_e: start, peak, and end temperature of the peaks in the $\Delta m/t$ curve. The first peak is accompanied by a bleaching of the compound.

Table 2. Main Chain Layer Distance Calculated from the X-ray Powder Diffractograms of Polymer P1, P2a/b, and P3[a]

	layer distance d/Å at 50 °C	
polymer	before heating	after one heating cycle
P1	22.77	
P2a/b	16.99	17.96
P3	19.04	19.55

[a] A layer distance of 40.2 Å can be expected for a system where the side chains are not intercalated, assuming an increment of 1.25 Å for each CH_2 group and 5.2 Å for the aromatic ring system. For this estimation, it was presumed that the layer distance is governed by the longest side chains (hydroquinone unit).

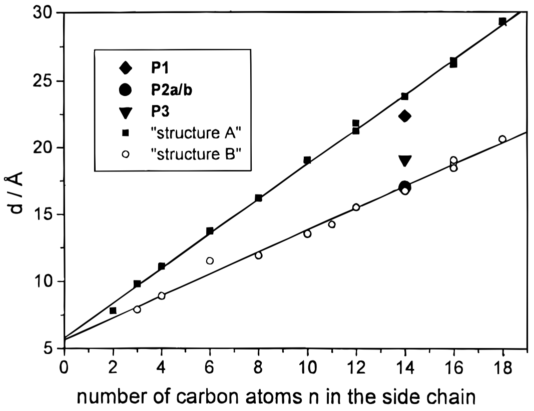


Figure 5. Comparison of the layer spacings of polymers **P1**, **P2**, and **P3** with the data obtained on poly(1,4-phenylene-2,5-dialkoxyterephthalate)s with different numbers of methylene groups in the side chains for the two structural modifications A (with perpendicular exdending interdigitating side chains) and B (with inclined side chains).[21]

Powder X-ray diffractograms of all polymers showed a Bragg peak in the small angle region that can be associated with the distance between main chain layers (Table 2) when all side chains are fully interdigitated. In addition, a diffuse halo is seen in the wide angle region, which indicates a disorder of the side chain packing. The data clearly indicate that positional correlation between the main chains does not exist. Note that all X-ray investigations have been performed at temperatures above the first DSC transitions (Figure 4). Upon heating to 200 °C structural relaxation is observed, accompanied by a sharpening of the small angle Bragg peak and an irreversible increase in layer distance. In agreement with the thermal analysis measurements we found no evidence for structural transitions below the decomposition temperature.

Figure 5 compares the main chain layer distance with data obtained on substituted rigid rod poly(1,4-phenylene-2,5-dialkoxyterephthalate)s with different numbers of methylene groups in the side chains for two structural modifications A (with perpendicular extending interpenetrating side chains) and B (with inclined side chains). Figure 5 clearly indicates that the layer

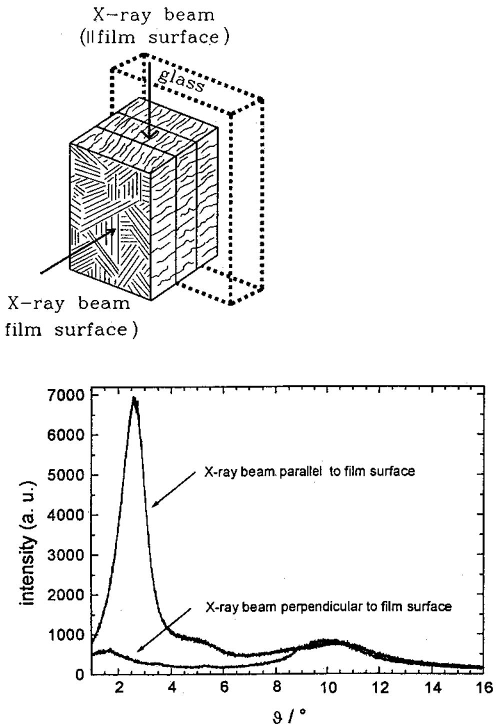


Figure 6. X-ray diffractograms of a solution cast film of polymer **P2b**. The geometry of the X-ray experiment is shown on the left, the resulting X-ray diffractograms on the right (the incident beam was held at a fixed position at 0.1° and only the diffracted beam was recorded as a function of the angle ϑ; the glass substrate was removed before the X-ray diffractograms were measured).

distance in our systems is controlled by the long side chains on the hydroquinone unit. Surprisingly, the largest distance was found for polymer **P1** with n equal to zero. In this system the long side chains must extend almost perpendicular to the main chain layers (modification A). For polymers **P2** and **P3**, smaller values for d are observed, which requires a structural model with the side chains tilted at an angle of around 40° with respect to the backbone (modification B). We presume that this tilted structure is thermodynamically preferred in order to minimize the density of voids in the side chain region. Another explanation could be derived from the observation that in many similar polymers the side chains are tilted with respect to the main chains in order to decrease the distance between neighboring side chains to approximately 4.5 Å. Only at this distance is a sufficient interaction between neighboring alkyl chains possible, which then leads to a side chain crystallization at lower temperature. For the **P1** system this effect should be less pronounced, since the distance between neighboring side chains is extremely large (only every fourth aromatic ring is substituted with side chains) and could only be reduced to 4.5 Å by an extreme tilt angle.

Information about the layer orientation which is essential for the interpretation of the electrooptical properties was gained by performing X-ray experiments on cast films of **P2b** in two geometries (Figure 6). The almost complete disappearance of the Bragg peak, when the incident X-ray beam is perpendicular to the surface, proves a structure with layers extending uniformly parallel to the film plane over the whole sample. This has been already found for alkoxy substituted polyesters.[22]

Dielectric loss spectra recorded at different temperatures are shown in Figure 7. The interpretation of the spectra was complicated by the large conductivity of the sample. Only one process is observed within the investigated temperature region that was fitted well by the Havriliak–Negami equation:[32]

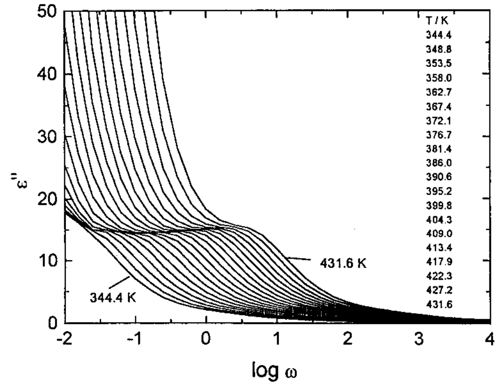


Figure 7. Dielectric loss spectra of polymer **P2a** at different temperatures.

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_{\mathrm{st}} - \epsilon_\infty} = \frac{1}{(1 + (i\omega\tau)^{\alpha})^{\gamma}} \tag{1}$$

yielding the dielectric strength $\Delta\epsilon = \epsilon_{\mathrm{st}} - \epsilon_\infty$, the relaxation time τ, and the line shape parameters α and γ of the dielectric process. For all temperatures a high dielectric strength of about 26 was found that can be only associated with the dipole moment of the chromophore. The analysis following the procedure by Fröhlich[33] gives an effective dipole moment of about 13 D (using $\epsilon_\infty = 2.5$, $\Delta\epsilon = 26$, $N = 5 \times 10^{20}$ cm^{-3}), which is nearly double the ground state dipole moment known for the p-nitroaniline chromophore. A collective coupling between dipoles along the main chain (for example, between the dimethylamino-nitro chromophore and the neighboring C=O bond) can be assumed. This will be further discussed together with the temperature dependence of relaxation times in the subsequent section.

Conclusions

Rigid-rod-like main chain poly(esteramide)s with long flexible alkoxy side chains and rigidly attached NLO-active chromophores were synthesized. It is important to emphasize that the chromophores are rigidly attached to the main chain. The synthesized polymers form a well ordered layered structure with interdigitating side chains in the bulk. The distance between the main chains is controlled by the length of the longest side chain. The main chains self-organize parallel and the side chains perpendicular to the substrate surface when cast from tetrachloroethane solution. The TGA data demonstrated a thermal stability up to 230 °C, sufficient for NLO applications. No indication of a glass transition could be found in either the heating or cooling cycles of the DSC or the dielectric data within the investigated temperature region. The electrooptical results are described in the subsequent paper.[24]

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References and Notes

(1) Möhlmann, G. R. In *Nonlinear Optics: Fundamentals, Materials and Devices*; Miyata, S., Ed.; North Holland: Amsterdam, 1991; p 415.
(2) Hornak, L. A., Ed. *Polymers for Lightwave and Integrated Optics*; Marcel Dekker: New York, 1992.
(3) Hann, R. A., Bloor, D., Eds. *Organic Materials for Nonlinear Optics II*; The Royal Society of Chemistry: Cambridge, 1991.
(4) Messier, J., et al., Eds. *Organic Molecules for Nonlinear Optics and Photonics*; NATO ASI Series E; Kluwer Academic Publishers: Dodrecht, 1991; Vol. 194.
(5) Zyss, J.; Ledoux, I.; Betault, M.; Toupet, E. *Chem. Phys.* **1991**, *150*, 125.
(6) Bosshard, Ch.; Sutter, K.; Schlesser, R.; Günter, P. *J. Opt. Soc. Am. B.* **1993**, *10*, 867.
(7) Küpfer, M.; Flörsheimer, M.; Baumann, W.; Bosshard, Ch.; Günter, P. In *Organic Materials for Nonlinear Optics III*; Ashwell, G. J., Bloor, D., Eds.; The Royal Society of Chemistry: Cambridge, 1993; p 74.
(8) Hickel, W.; Bauer, J.; Lupo, D.; Menzel, B.; Falk, U.; Scheunemann, U. In *Organic Materials for Nonlinear Optics III*; Ashwell, G. J., Bloor, D., Eds.; The Royal Society of Chemistry: Cambridge, 1993; p 80.
(9) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.
(10) Staring, E. G. J. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 492.
(11) Lindsay, G. A. *Trends Polym. Sci.* **1993**, *1*, 138.
(12) Mitchell, M. A. *Trends Polym. Sci.* **1993**, *1*, 144.
(13) Eich, M.; Reck, B.; Yoon, D. Y.; Willson, C. G.; Bjorlund, G. C. *J. Appl. Phys.* **1989**, *66*, 3241.
(14) Yu, L.; Chan, W.; Bao, Z. *Macromolecules* **1992**, *25*, 5609.
(15) Wu, J. W.; Binkley, E. S.; Lytel, R.; Garito, A.-F. *J. Appl. Phys.* **1991**, *69*, 7366.
(16) Jin; J.-I.; Lee, Y. H.; Shim, H. K. *Macromolecules* **1993**, *26*, 1805.
(17) Kador, L.; Fischer, R.; Haarer, D.; Kasemann, R.; Brück, S.; Schmidt, H.; Dürr, H. *Adv. Mat.* **1993**, *5*, 270.
(18) Marturunkakul, S.; Chen, J. I.; Jeng, R. J.; Sengupta, S.; Kumar, J.; Tripathy, S. K. *Chem. Mater.* **1993**, *5*, 743.
(19) Nordmann, J.; Röhl, P. In *Organic Materials for Nonlinear Optics III*, G. J. Ashwell, G. J.; Bloor, D. Eds.; The Royal Society of Chemistry: Cambridge, 1993; p 190.
(20) Ballauff, M. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 407.
(21) Ballauff, M. *Angew. Chem.* **1989**, *101*, 26.
(22) Schrauwen, C.; Pakula, T.; Wegner, G. *Makromol. Chem.* **1992**, *193*, 11.
(23) Wright, E.; Mullik, S.; Lackritz, H. S.; Liu, L.-Y. *Macromolecules* **1994**, *27*, 3009.
(24) Heldmann, C.; Neher, D.; Winkelhahn, H.-J.; Wegner, G. *Macromolecules*, following paper in this issue.
(25) Rodriguez-Parada, J. M.; Duran, R.; Wegner, G. *Macromolecules* **1989**, *22*, 2507.
(26) Higashi, A.; Hoshito, J.; Kiyoshige, J. *Polym. Sci. Polym. Chem. Ed.* **1983**, *21*, 3241.
(27) Kricheldorf, R.; Schwarz, G. *Makromol. Chem.* **1983**, *184*, 475.
(28) Kricheldorf, R.; Schwarz, G. *Polym. Bull.* **1979**, *1*, 383.
(29) Schwarz, G.; Alberts, H.; Kricheldorf, R. *Liebigs Ann. Chem.* **1981**, 1257.
(30) Kricheldorf, R.; Zang, Q.-Z.; Schwarz, G. *Polymer* **1982**, *23*, 1821.
(31) Damman, S. B.; Mercx, F. P. M.; Kootwijk-Damman, C. M. *Polymer* **1993**, *9*, 1891.
(32) Havriliak, S.; Negami, S. *J. Polym. Sci. C* **1966**, *14*, 99.
(33) Fröhlich, H. *Trans. Faraday Soc.* **1948**, *44*, 238.

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