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Communications to the Editor

Main-Chain Accordion Polymers for Nonlinear Optics

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Polymeric materials which display nonlinear optical properties are of great interest for potential applications in high-speed integrated optical signal processing.[1] Initial interest centered on organic dyes (guests) in glassy matrices (hosts) in which the dipoles were aligned at elevated temperature by electric-field poling.[2] Relaxation of the dipole alignment in guest–host systems, even at temperatures well below the glass transition temperature (T_g) of the matrix, has led to new approaches for stabilizing alignment, such as incorporating the dyes (chromophores) into side chains[3] or into the main chain[4] or cross-linking the polymer.[5]

This paper describes a new approach which seeks "geometric" stabilization of polar order. It combines this concept with structural designs aimed at achieving high glass transition temperatures. To implement these concepts, we have carried out the synthesis and characterization of new syndioregic (head-to-head configuration) main-chain chromophoric polymers.[6] These polymers are called "accordion" polymers because the backbone is designed to fold like an accordion. The idea for accordion polymers evolved from investigations on isoregic main-chain chromophoric polymers in which the chromophoric dipole moments point in the same direction along the chain, i.e., in a head-to-tail configuration.[4]

Unlike most main-chain liquid crystal polymers,[7] in which the long axes of the rigid mesogenic units are essentially parallel with the axis of the polymer chain (Figure 1a), in accordion polymers, the long axes of the rigid chromophoric units are essentially perpendicular to the axis of the polymer chain (Figure 1b).

Instead of using the liquid crystal polymer terminology "flexible spacer groups", we prefer to use the term "bridging groups" for the groups between chromophores (or mesogens) in accordion polymers, in order to emphasize that these groups are designed to allow (or force) adjacent chromophores to fold together with their dipole moments essentially parallel. Hence, the bridging groups are generally U-shaped connections. Polarization in syndioregic polymer films, produced by electric-field poling or by Langmuir–Blodgett (LB) processing,[8] can be further enhanced by incorporating groups which facilitate the formation and stability of folds (S groups in Figure 2).

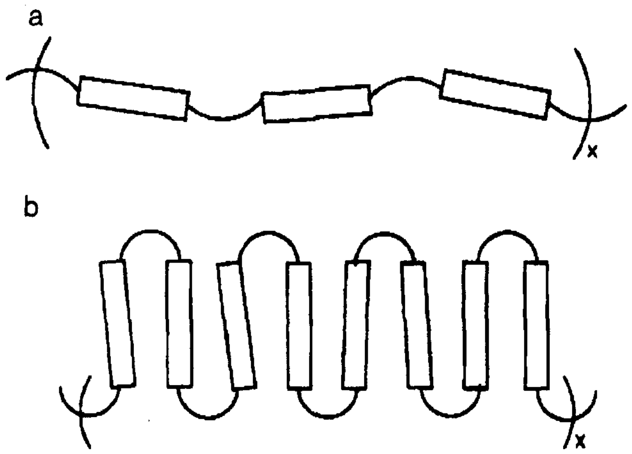


Figure 1. (a) Liquid crystal polymer in the extended conformation. (b) Accordion polymer in the folded conformation.

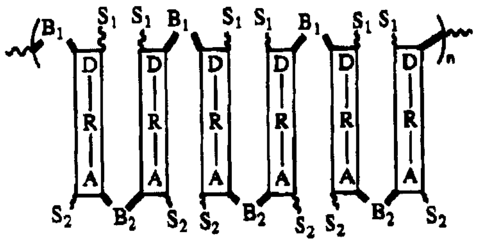


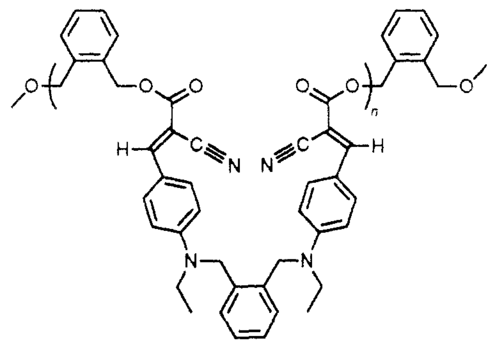
Figure 2. B_1 and B_2 are bridging groups, A–R–D is a chromophore, A is an electron-accepting group, D is an electron-donating group, R is a rigid group providing a π-conjugated electron path coupling the donor and acceptor groups, and S_1 and S_2 are groups which help stabilize the folded conformation.

The hydrophobic/hydrophilic nature of the bridging and stabilizing groups may be designed to facilitate alignment on an LB trough. By appropriate deposition of these monolayers onto solid substrates, the polarized conformation of the accordion polymers can be maintained in multilayer films which will exhibit nonlinear optical properties,[6a] and presumably piezoelectric and pyroelectric properties.

Experimental Section. Several variations of the α-cyanocinnamoyl chromophore have already been reported in the isoregic main-chain nonlinear optical polymer literature,[4] and we have found this chromophore to be quite amenable to the syndioregic accordion architecture.[6] Reported here are the synthesis and characterization of two cinnamoyl polymers, one with *o*-xylylene bridging groups (polymer VII), which was designed for electric-field poling, and another with fatty stabilizing groups (polymer XIV), which was designed for LB deposition. The optical properties will be reported in a future paper.

Synthesis of *o*-Xylyl-Bridged Polymer for Electric-Field Poling. α,α'-Dibromo-*o*-xylene (I) is allowed to react with *N*-ethylaniline (II) to produce the bisaniline III,[9] which is subsequently converted to the 4,4′-bisaldehyde IV by the Vilsmeier reaction.[10] The synthetic route is shown in Scheme Ia. Then, α,α'-dibromo-*o*-xylene (I) is condensed with sodium cyanoacetate (V) to yield bisester VI[11] as shown in Scheme Ib. Finally, compound IV is condensed with compound VI in a Knoevenagel polymerization to produce polymer VII.[12]

Several other approaches to polymer VII were attempted. A transesterification method[4d] for polymerizing the



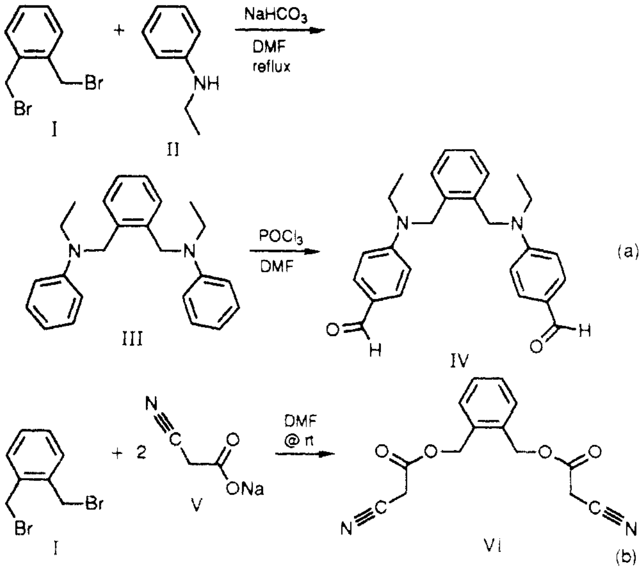
VII

ethyl α-cyanocinnamate derivative of IV with 1,2-benzenedimethanol yielded mostly dimers due to evaporative loss of the benzenedimethanol. Increasing the ratio of alcohol to ester provided only marginally higher molecular weight. Melting IV and VI together in stoichiometric amounts without a catalyst in a differential scanning calorimeter (DSC) pan from 30 to 250 °C (four times) also gave low molecular weights. The Knoevenagel condensation in Scheme I, described by Wright,[13] yielded the high molecular weight polymer VII, which was soluble in chloroform. The infrared spectrum of this polymer[14] gives evidence of the synthesis of high polymer by the absence of CHO absorption (1661 cm^{-1} in IV) and a shift in the CN frequency from that observed in VI (from 2262 cm^{-1}).

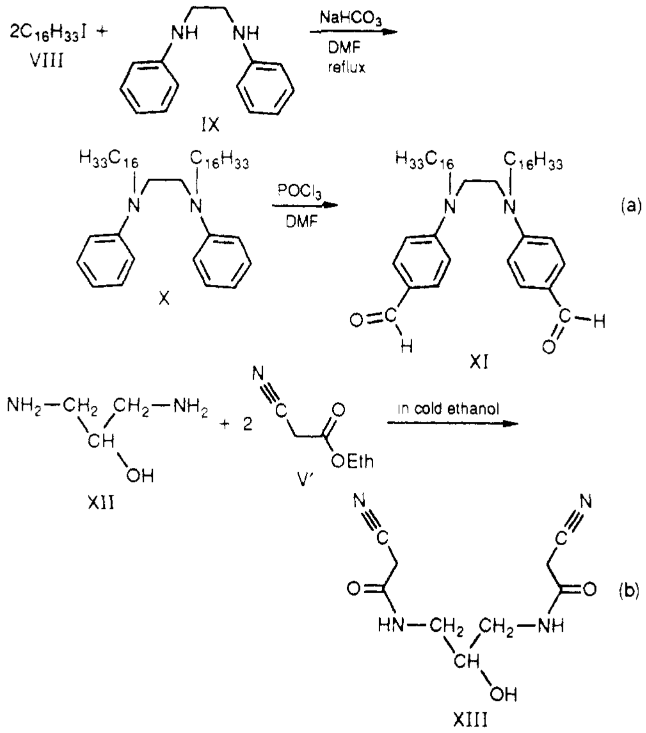
The proton nuclear magnetic resonance (^{1}H NMR) assignments for polymer VII[15] are in excellent agreement with the proposed structure. Using end-group counting of the ^{1}NMR spectrum (the ratio of aldehyde protons to benzyl amine methylene protons), the number-average molecular weight of the polymer was determined to be about 55 000 (n = 85), which is in agreement with the M_n estimated from preparative gel permeation chromatography (GPC) using a polystyrene calibration standard. The T_g of polymer VII was found to be 143 °C by DSC with no evidence of crystallinity. The upper limit of thermal stability of polymer VII is 200 °C, which explains the unfavorable results obtained with the melt condensation approach.

Synthesis of a Polymer Containing Fatty Stabilizing Groups for LB Deposition. Mixing 1-iodohexadecane (VIII) with *N,N'*-diphenylethylenediamine (IX) produces compound X.[16] Compound X is converted to the corresponding bisaldehyde XI by the Vilsmeier reaction.[17] The synthetic route is shown in Scheme IIa. Condensing 1,3-diamino-2-hydroxypropane (XII) with ethyl cyanoacetate produces compound XIII,[18] as shown in Scheme IIb. Finally, compound XI is condensed with compound XIII in a Knoevenagel polymerization to produce polymer XIV.[19]

Scheme I



Scheme II



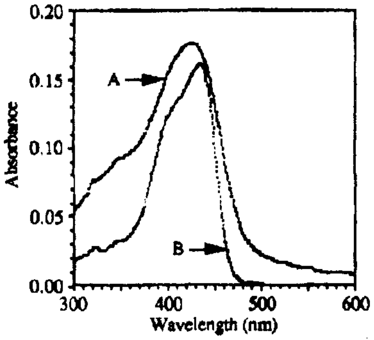
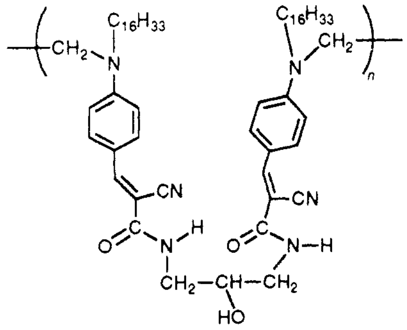


Figure 3. UV–vis absorption of polymer XIV: (A) in the solid state (22 Y-type LB layers on hexamethyldisilazane-treated quartz); (B) in chloroform solution.



XIV

UV–vis absorption spectra of polymer XIV are shown in Figure 3. Spectrum A, transmission through 22 monolayers of polymer XIV on hexamethyldisilizane-treated quartz, is broader than spectrum B, polymer XIV in chloroform solution. It appears that the absorption due to the first excited state of the chromophore in solution,

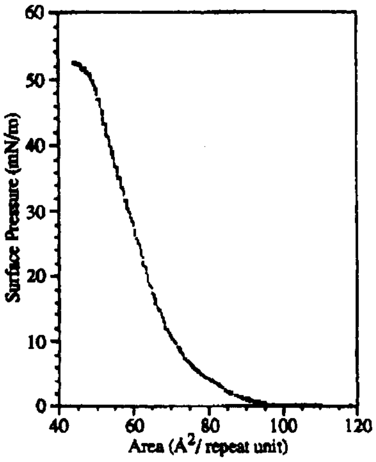


Figure 4. Pressure–area isotherm of polymer XIV, spread from 0.5 mg/mL of a chloroform solution on 18-MΩ water at 23.5 °C and compressed at approximately 0.15 α^2 per repeat unit per s.

at 425 nm (600 nm/min scans), is partly overlapped by another absorption in the solid-state spectrum at about 350 nm (we are checking the disilazane absorption). The ^{1}H NMR assignments for polymer XIV are in good agreement with the proposed structure.[20]

Figure 4 shows the well-behaved pressure–area compression isotherm of a monolayer of polymer XIV, formed by injecting a chloroform solution on an LB trough. The film can be compressed to 50 mN/m of pressure before collapsing. Twenty-two Y-type layers on hexamethyldisilizane-treated quartz were easily deposited at 30 mN/m. The Y-type multilayer film gave no SHG, which is not unexpected (because the dipoles in adjacent layers should be pointing in opposite directions). We are now in the process of making polarized multilayered LB films by depositing alternating layers of polymer XIV with an optically inert polymer.

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(9) A mixture of 26.4 g (0.1 mol) of α,α'-dibromo-*o*-xylene (I), 24.3 g (0.2 mol) of *N*-ethylaniline (II), 18.0 g of $NaHCO_3$, and 150 mL of dimethylformamide (DMF) was stirred and refluxed for 24 h. After cooling, the mixture was poured over K_2CO_3/ice water. The product was extracted into methylene chloride (1 × 200 mL, 1 × 100 mL), filtered, and evaporated. The semisolid mass was slurried with methanol. The first product to recrystallize is *N*-phenylisoindoline, which was discarded. Compound III was recovered from the methanol mother liquors and was recyrstallized from ethanol, yielding 8.3 g, mp 73–74 °C. Anal. Calcd: C, 83.67; H, 8.19; N, 8.13. Found: C, 83.57; H, 8.25; N, 8.18.

(10) Vilsmeier conditions: 6.8 g of $POCl_3$ was added to 14 mL of cold, dry DMF. After stirring 2.5 h at 0 °C, 6.3 g of compound III was added and stirred for 1 h at 25 °C and 2 h at 86–93 °C then poured over ice and 15 g of sodium acetate. After two recrystallizations from ethanol, the yield of compound IV was 4.6 g of green-yellow plates, mp 130.5–131.5 °C. Anal. Calcd: N, 7.00. Found: N, 6.91.

(11) A mixture of 2.64 g (0.02 mol) of compound I and 2.36 g (0.022 mol) of compound V was stirred in 10 mL of DMF at room temperature for 42 h. After heating for 8 h on a steam bath, the mixture was cooled and poured over ice. Recrystallization from benzene yielded 1.1 g of yellow crystals (mp 78–79.5 °C). Compound VI of the same melting point was also made from 1,2-benzenedimethanol, cyanoacetic acid, and dicyclohexylcarbodiimide (dehydrating agent). Anal. Calcd: C, 61.75; H, 4.44; N, 10.29. Found: C, 61.38; H, 4.38; N, 10.15.

(12) A mixture of 0.128 g (0.32 mmol) of compound IV and 0.087 g (0.32 mmol) of compound VI and 0.04 g (0.32 mmol) of 4-(dimethylamino)pyridine was stirred in 7 mL of dry tetrahydrofuran (THF) and refluxed for 24 h. THF was evaporated, and the polymer was rinsed with hexanes and then dissolved in chloroform. The polymer was purified by preparative GPC (only the cut above 25 000 molecular weight was used for analysis).

(13) Wright, M. E.; Sigman, M. S., submitted to *Macromolecules*.

(14) Assignments for the infrared spectrum of a film of polymer VII on a silicon substrate are as follows: 2974 (mw), 2929 (mw), 2214 (mw), 1714 (m), 1611 (m), 1571 (s), 1519 (s), 1175 (s), 757 (w).

(15) Assignments for the 80-MHz ^{1}H spectrum of polymer VII in $CDCl_3$ are as follows: δ 7.9–8.1 (10 H, cinnamoyl), 6.7–7.5 (8 H, xylyl aromatic), 5.5 (s, 4 H, benzyl ester methylene), 4.6 (s, 4 H, benzyl amine methylene), 3.6 (q, 4 H, ethyl aminemethylene), 1.29 (t, 6 H, methyl).

(16) A mixture of 59.2 g (0.168 mol) of compound VIII and 17.0 g (0.08 mol) of compound IX was refluxed with $NaHCO_3$ in DMF for 42 h. After cooling and pouring over an ice water/Na_2CO_3 mixture, the crude product X obtained was recrystallized from 2-propanol, mp 38–46 °C.

(17) Vilsmeier conditions were the same as those in ref 10. After recrystallization from ethanol, felted masses of compound XI were recovered, mp 90–93 °C. Anal. Calcd: C, 80.39; H, 11.24; N, 3.91. Found: C, 80.68; H, 11.19; N, 3.93.

(18) A mixture of 22.99 g (0.204 mol) of ethyl cyanoacetate (V′) and 9.01 g (0.1 mol) of compound XII was added to 40 mL of cold absolute ethanol. After 3 days, the white cake of crystals was boiled with 450 mL of ethanol and filtered hot from 17.6 g of undissolved solid, mp 165–166 °C. Anal. Calcd: C, 48.21; H, 5.40; N, 24.99. Found: C, 48.36; H, 5.48; N, 25.12.

(19) A mixture of 0.1207 g (0.17 mmol) of compound XI and 0.0377 g (0.17 mmol) of compound XIII was reacted under the same conditions as those in ref 12. A chloroform solution of the polymer was purified by preparative GPC (the cut above 25 000 molecular weight was used for analysis).

(20) Preliminary assignments for the 400-MHz ^{1}H spectrum of polymer XIV in $CDCl_3$ are as follows: δ 7.8–8.1 (10 H, cinnamoyl), 6.6 (2 H, amide), 4.0 (1 H, methine), 3.7 (8 H, amine α-methylene), 3.5 (1 H, hydroxyl), 3.3 (4 H, amide methylene), 1.3 (64 H, fatty alkyl methylene); 1.6 (4 H, amine β-methylene + adventitious H_2O), 0.85 (6 H, methyl).