New Amphiphilic Rodlike Polymers with Pendent Hemicyanine Groups. 1. Synthesis and Properties

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ABSTRACT: We have synthesized new wholly aromatic polymers containing hemicyanine dyes in the side chain. The polymers are soluble in both protic solvents (methanol, ethanol, phenol) and aprotic solvents (DMSO, NMP, DMAc). However, they could not be processed into good optical quality films by simple casting or spin-coating. These amphiphilic polymers exhibited a polyelectrolyte effect in deionized water. The excessive positive charges along the hydrophobic rigid backbones, which bear two charged groups per repeat unit at the end of the methylene spacers, dramatically affect their dimension in solution, with intramolecular charge repulsions tending to assume an extended conformation. The bulk susceptibility of these materials was determined by the second harmonic generation technique. Significant SHG activity was observed from the spin-coated films without the aid of electric field induced poling. However, the corona-poled polymer films showed smaller d_{33} values in the range 70−105 pm/V than expected due to the inefficient electric poling, which we discuss in terms of the domains of the chromophores that are not well developed by electric poling.

Introduction

Over the past decades polymeric second-order nonlinear optical (NLO) materials have been attracting the attention of researchers in a number of different fields because of their potential for use in applications including telecommunications, optical computing, optical data storage, and optical information processing.[1,2] Most of such practical applications require a large second-order nonlinearity, low optical loss to be no more than 1 dB/cm, and excellent thermal and chemical stability to withstand processing and device operating temperatures in excess of 100 °C. Although in recent years a variety of thermally stable NLO polymers have been reported,[3−6] the preparation of high efficiency in electrooptic devices remains a technical challenge. In the past several years we have been exploring NLO properties of side-group polymers based on the rigid backbone polymers such as wholly aromatic polyesters and polyamides.[7,8] Interestingly, such materials offered a greater degree of chromophore alignment and higher number densities than any other side-group polymers reported in the literature. In addition, tethering of chromophore molecules to the rigid backbones greatly restricts the formation of aggregates in the solid state and provides a highly ordered domain of the chromophores, an anisotropic chromophore environment induced by backbone rearrangement. Despite relatively low glass transition temperatures due to the pendent side groups, these materials exhibited exceptionally good temporal stability of the chromophore orientation at room temperature due in part to their domain structure.[9]

In this contribution we extend the NLO materials of these rigid backbone polymers to molecular solid assemblies with highly stable properties by introducing ionic pendent groups. An attempt has been made at synthesis of water-soluble polymers with the aim of constructing self-assembled asymmetric structures with NLO properties. The water-soluble polymers studied so far can be classified into two broad groups: the first is hydrophobically modified polymers with the pendent hydrophobic groups distributed along the hydrophilic backbone. Most of the investigations have focused on polyacrylates.[10,11] The second is telechelic polymers with hydrophobes at the ends of a hydrophilic polymer backbone. Thin films based on these hydrophilic backbone systems usually suffer from inhomogeneity and mechanical instability due to microphase separation. Here we describe a new architecture that is a rigid hydrophobic backbone polymer with flexibly attached hydrophilic chromophores. The materials that we focus on in this paper utilize a hemicyanine dye. Among the chromophores developed, hemicyanine dyes or stilbazolium salts present a wide range of chemical and physical properties that make them promising chromophores in second-order optical processes, and several approaches have been explored to artificially achieve noncentrosymmetry. These include stilbazolium salts with various donor groups and counterions, monolayers, and Langmuir−Blodgett films.[12−16] However, there are very few reports in the literature involving the incorporation of an organic salt dye into a polymeric pendent type material.[17−19] This is probably due to the fact that organic salts are difficult to pole because of their high conductivity. The introduction of a hemicyanine unit into rigid backbone polymers might afford a stable multilayer structure through the layer building quarternization reaction without an aggregation problem. The initial results of the synthetic work and general properties of the polymers are described here, and the results on the exceptionally stable monolayers self-assembled from these materials are reported in the accompanying paper.

Experimental Section

Materials. The reagents were purchased from the following sources: 4-picoline (Janssen Chimica), piperidine (Kanto Chemical), thionyl chloride (Merck, >99%). Other reagents were purchased from Aldrich Chemical Co. (99+%). All reagents were used as received unless otherwise noted.

Characterization. ^{1}H NMR spectra were recorded on a JEOL Lambda 400. The chemical shifts are reported in ppm (δ) relative to Me_4Si. IR spectra were recorded on a Nicolet 800 Fourier transform infrared spectrometer. UV−vis absorp-

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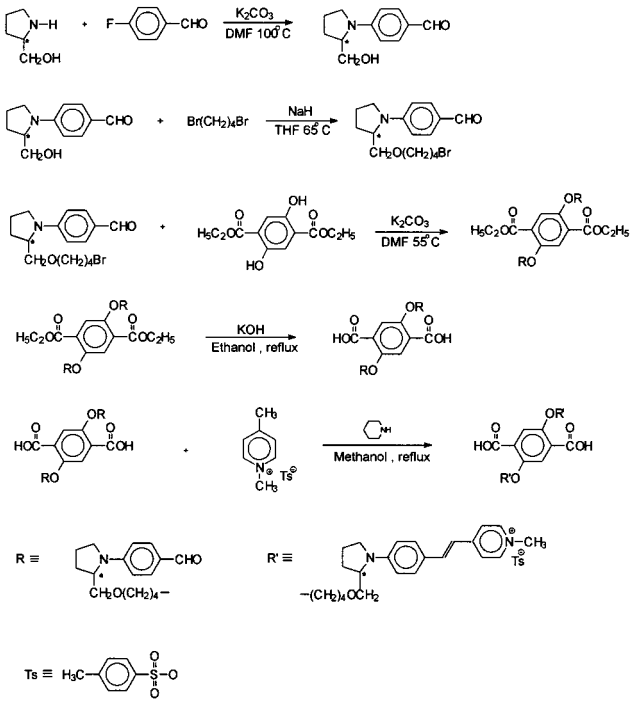
Scheme 1



tion spectra were recorded on a Jasco V-550. The GPC measurements were performed on a Waters RI system equipped with a UV detector and a differential refractometer detector using NMP as an eluent. The molecular weight distribution was determined on the polystyrene standards. Thermal measurements were carried out using a DSC-10 and TGA-50 systems from TA instruments. A scan rate of 10 K/min was used in the differential scanning calorimetry experiments. Wide-angle X-ray diffraction studies were performed using a Rigaku Geiger Flex DMAX IIIa. Melting points were taken on a Fisher-Johns apparatus.

Thin Film Preparation. Polymer films for optical measurement were prepared by dissolution of the polymer powder (ca. 10 mg/mL) in NMP, followed by filtration through a 0.45 μm syringe filter. The solutions were then spin-coated on the glass slide with the spinning rate in the range 2000−4000 rpm. The thickness and refractive indices of the films were determined by spectroscopic ellipsometry using a phase modulation ellipsometer (Jobin-Yvon Elloisel).

Corona Poling and SHG Measurement. A positive charge of 5 kV was applied to a sharp tungsten needle located 10 mm above the grounded electrode. Poling was performed in situ between 80 and 110 °C with the sample oriented at the angle of 45° to the incident beam path. SHG measurements were made using a Q-switched Nd:YAG laser operating at 1064 nm with a pulse repetition rate of 10 Hz. A quartz crystal was used as the reference.

Synthesis of Monomers. 2,5-Di-1-[(*E*)-*N*-methyl-4-[2-[4-[(L)-prolinoxy]phenyl]ethenyl]pyridinium *p*-toluenesulfonate]−tetramethyleneoxyterephthalic acid ($POST_4$-acid, Scheme 1). (i) 1,4-Dimethylpyridinium *p*-toluenesulfonate (DMP-Ts) was prepared according to the literature procedure.[20] (ii) 4-[(L)-Prolinol]benzaldehyde (PBA). L-Prolinol (0.242 mol, 23.9 mL) and K_2CO_3 (0.28 mol, 38.65 g) were dissolved in 100 mL of DMF at room temperature. To a three-necked 500 mL flask was added dropwise 4-fluorobenzaldehyde (0.186 mol, 20 mL) via dropping funnel, and the mixture was stirred at 100 °C for 24 h until all the 4-florobenzaldehyde disappeared. The resulting solution was then cooled and extracted with methylene chloride (3 × 300 mL). The extracts were combined and dried over sodium sulfate. The resulting solution was eluted through a column using EtOAc/*n*-hexane (1/1). Removal of the solvent left PBA (72%) as a pale brown solid. Mp: 53 °C. ^{1}H NMR ($CDCl_3$): δ_H 2.0−2.2 (m, 4H, $-CH_2-$), 3.3−3.4 (t, 1H, −OH), 3.5−3.8 (m, 4H, $O-CH_2$, $N-CH_2$), 4.1 (m, 1H, chiral-H), 6.7 (d, 2H, meta from CHO), 7.7 (d, 2H, ortho from CHO), 9.7 (s, 1H, −CH O). IR (KBr), cm^{-1}: 3500 (O−H), 3050−3000 (aromatic C−H), 2960−2900 (aliphatic C−H), 2890−2650 (−CHO), 1700−1350 (aromatic C═C, C═N, C═O), 1300−1250 (C−O), 1040−1000 ($S(=O)_2$). (iii) 1-[[(L)-Prolinoxy]benzaldehyde]-4-bromobutane (PBA_4). PBA (0.073 mol, 15 g) and 1,4-dibromobutane (0.22 mol, 23.19 mL) were dissolved in THF (200 mL). To this mixture was added sodium hydride (0.1 mol, 2.4 g) over a 3 h period under a nitrogen atmosphere. The resulting mixture was stirred for 24 h at 60−65 °C and filtered. The filtrate was concentrated in a vacuum and then separated by column chromatography (EtOAc/*n*-hexane = 1/2). PBA_4 (17.4 g) was obtained as brown viscous liquid in 70% yield. ^{1}H NMR ($CDCl_3$): δ_H 1.6−2.2 (m, 8H, $-CH_2-$), 3.2−3.3 (m, 2H, $N-CH_2$), 3.4 (t, 2H, $Br-CH_2$), 3.6 (m, 4H, $O-CH_2$), 4.1 (m, 1H, chiral-H), 6.7 (d, 2H, meta from CHO), 7.7 (d, 2H, ortho from CHO), 9.7 (s, 1H, −CHO). IR (KBr), cm^{-1}: 3050−3000 (aromatic C−H), 2960−2900 (aliphatic C−H), 2890−2650 (−CHO), 1670−1500 (aromatic C═C, C═O), 1300−1250 (C−O), 1165 (−O−). (iv) Diethyl 2,5-di-1-[[(L)-prolinoxy]benzaldehyde]tetramethyleneoxyterephthalate (PBA_4-ester). Diethyl 2,5-dihydroxyterephthalate (13.0 mmol, 3.4 g) and K_2CO_3 (40.0 mmol, 5.5 g) were dissolved in dry DMF (100 mL) under a nitrogen atmosphere. To this solution was added PBA_4 (29 mmol, 10.0 g) in DMF, and the mixture was stirred at 60−65 °C for 48 h. The resulting mixture was filtered, concentrated, and separated by column chromatography (EtOAc/*n*-hexane = 1/2) to give a brown solid (8.8 g, 85%). Mp: 78 °C. ^{1}H NMR ($CDCl_3$): δ_H 1.3−1.4 (t, 6H, $-CH_3$), 1.7−2.2 (m, 16H, $-CH_2-$), 3.2−3.3 (m, 4H, $N-CH_2$), 3.5 (m, 8H, $O-CH_2$), 4.1 (t, 6H, chiral-H, $Ar-OCH_2$), 4.4 (q, 4H, $COO-CH_2$), 6.7 (d, 4H, metha from CHO), 7.3 (s, 2H, Ar−H from terephthalate), 7.7 (d, 4H, ortho from CHO), 9.7 (s, 2H, −CHO). IR (KBr), cm^{-1}: 3050−3000 (aromatic C−H), 2960−2840 (aliphatic C−H), 2810−2650 (−CHO), 1730−1500 (aromatic C═C, C═O), 1300−1250 (C−O), 1165 (−O−). (v) 2,5-Di-1-[[(L)-prolinoxy]benzaldehyde]-tetramethyleneoxyterephthalic acid (PBA_4-acid). To a solution of PBA_4-ester (6.5 mmol, 5.0 g) in methylene chloride was added ethanol (200 mL) under reflux to give a brownish solution. To this solution was added KOH (0.0019 mol, 1.09 g) in ethanol (30 mL) for 5 min, and the solution was stirred under reflux for 6 h. After the reaction was terminated, the reaction mixture was concentrated in vacuo to give a brown viscous liquid. Water was added to this liquid, and this diluted solution was extracted with methylene chloride and then treated with 2 N HCl (9.7 mL). This mixture was extracted with methylene chloride (3 × 300 mL). The organic phases were then washed with saturated aqueous NaCl solution, dried over sodium sulfate, and evaporated in vacuo to give a brown solid. This was purified by recrystallization in ethanol to give the product (4.3 g, 93%). Mp: 58 °C. ^{1}H NMR ($CDCl_3$): δ_H 1.7−2.2 (m, 16H, $-CH_2-$), 3.3−3.4 (m, 4H, $N-CH_2$), 3.5 (m, 8H, $O-CH_2$), 4.1 (m, 2H, chiral-H) 4.3 (t, 4H, $Ar-OCH_2$), 6.7 (d, 4H, meta from CHO), 7.7 (d, 4H, ortho from CHO), 9.7 (s, 2H, −CHO). IR (KBr), cm^{-1}:3600−2400 (−OH), 3070−3000 (aromatic C−H), 2960−2840 (aliphatic C−H), 2800−2750 (−CHO), 1740−1500 (aromatic C═C, C═O), 1300−1250 (C−O), 1167 (−O−). (vi) 2,5-Di-1-[(*E*)-*N*-methyl-4-[(L)-prolinoxy]phenylethenyl] *p*-toluenesulfonate]−tetramethyleneoxyterephthalic acid ($POST_4$-acid). To a solution of DMP-Ts (16.74 mmol, 4.7 g) in methanol (100 mL) was added PBA_4-acid (5.58 mmol, 4.0 g) in methylene chloride under a nitrogen atmosphere. To this solution was added piperidine (16.74 mmol, 1.7 mL), and the mixture was stirred at 50 °C for 72 h. The resulting mixture was cooled, concentrated, dissolved in methanol (15 mL), and poured into ethyl acetate (500 mL). The precipitate was filtered and dried to give a red solid (4.9 g, 77%). Mp: 102 °C. ^{1}H NMR (CD_3OD): δ_H 1.7−2.1 (m, 16H, $-CH_2-$), 2.3 (s, 6H, Ts-CH_3), 3.1−3.5 (m, 12H, $O-CH_2$,$N-CH_2$), 3.9 (m, 6H, $Ar-O-CH_2$), 4.2 (s, 6H, N^+-CH_3), 6.7 (d, 4H, meta from vinyl), 6.9 (d, 2H, vinyl from PBA), 7.15 (s, 2H, Ar−H from terephthalate), 7.2 (d, 4H, metha from SO_3), 7.5 (d, 4H, ortho from vinyl), 7.7 (t, 6H, vinyl from DMP, ortho from SO_3), 7.8 (d, 4H, meta from N^+), 8.4 (d, 4H, ortho from N^+). IR (KBr), cm^{-1}: 3600−2400 (−OH), 3070−3000 (aromatic C−H), 2960−2840 (aliphatic

C−H), 1740−1500 (aromatic C═C, C═O), 1300−1250 (C−O), 1167 (−O−).

Polymerization. $POST_4$-ester: $POST_4$-acid (0.904 mmol, 1 g) was dissolved in thionyl chloride (5 mL) at 0 °C under nitrogen atmosphere. The ice bath was removed, and the mixture was stirred for 30 min at room temperature. After the excess thionyl chloride was removed by distillation under vacuum, the diacid dichloride formed was dissolved in DMSO (20 mL) and pyridine (2.26 mmol, 0.18 mL). To this solution was added hydroquinone (0.904 mmol, 0.0995 g), and the mixture was stirred for 5 h under a nitrogen atmosphere and poured into ethyl acetate. The precipitate was dissolved in methanol and reprecipitated in ethyl acetate/methanol (v/v 5/1) and ethyl acetate. The polymer thus obtained was dried in a vacuum oven at 50 °C. ^{1}H NMR (CD_3OD): δ_H 2.0 (Ts-CH_3), 4.2 (N^+−CH_3), 6.6−9.0 (aromatic C−H, C═H). IR (KBr), cm^{-1}: 3600−3100 (H_2O contained in salt), 3100−3000 (aromatic C−H), 2960−2840 (aliphatic C−H), 1740−1500 (aromatic C═C, C═O). $POST_4$-amide: $Post_4$-acid (1.808 mmol, 2 g) was dissolved in thionyl chloride (10 mL) at 0°C under a nitrogen atmosphere. The ice bath was removed, and the mixture was stirred for 30 min at room temperature. After the excess thionyl chloride was removed by distillation under vacuum, the diacid dichloride formed was dissolved in DMSO (20 mL). To this solution was added *p*-phenylenediamine (1.808 mmol, 0.215 g) in NMP (40 mL) that contained dissolved $CaCl_2$ (2.4 g). The mixture was stirred for 1 h under a nitrogen atmosphere and poured into ethyl acetate. The precipitate was dissolved in methanol and reprecipitated in ethyl acetate/methanol (v/v 6/1) and ethyl acetate. The polymer thus obtained was dried in a vacuum oven at 50 °C. ^{1}H NMR (CD_3OD): δ_H 2.0 (Ts-CH_3), 4.2 (N^+−CH_3), 6.6−9.0 (aromatic C−H, C═H), 7.7 (s, 4H, Ar−H from phenylenediamine). IR (KBr), cm^{-1}: 3600−3100 (NH from amide, H_2O contained in salt), 3100−3000 (aromatic C−H), 2960−2840 (aliphatic C−H), 1740−1700 (carbonyl from amide).

Results and Discussion

Synthesis and Characterization. The reaction of PBA with dibromobutane was carried out easily, but the product was separated using a silica gel column. Note that the alkyl spacer of four methylene units was chosen here for the reason that it would exhibit better NLO properties. According to the results from the previous studies, only small changes in side chain length resulted in large changes in the NLO response, and the polymers with the shorter spacers exhibited generally better properties.[8] However, the monomers containing a spacer length less than four methylene units did not polymerize. The synthesis of the monomer $POST_4$-acid was synthesized by reaction of DMP-Ts and a donor-substituted aldehyde, PBA_4-acid in methylene chloride, catalyzed by piperidine or other bases such as dibutylamine (Scheme 1). The red precipitate was filtered and washed at least five times with methanol in order to remove unconverted salt, DMP-Ts. The product was then purified by precipitation from ethyl acetate. All of the intermediate compounds gave satisfactory NMR results. The monomer was polymerized by solution condensation polymerization, and a detailed description of the polymerization of wholly aromatic polyesters and polyamides has been reported elsewhere.[21,22] The polymers are soluble in both protic solvents (methanol, ethanol, phenol) and aprotic solvents (DMSO, NMP, DMAc). The molecular weights of both polymers were on the order of 10^4. The UV−vis spectra of these polymers showed an absorption maximum around 490 nm and the absorption cutoffs at 650 nm due to the chromophore (Figures 1 and 2). After poling the absorbance decreased whereas the absorbance maxima remained virtually unchanged. The order parameter

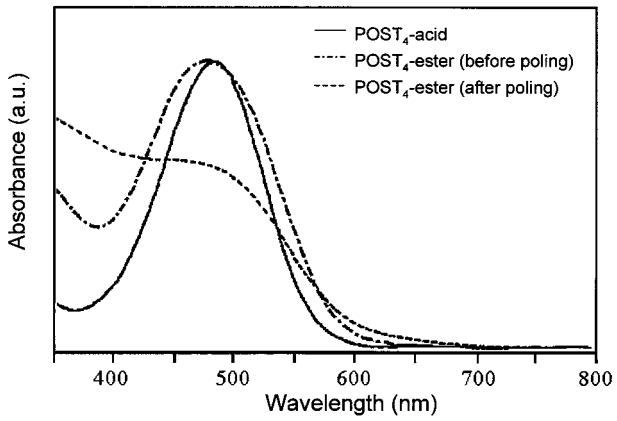


Figure 1. UV−vis absorption spectra of monomer ($POST_4$-acid) and polymer ($POST_4$-ester) film on glass substrates before and after electric poling.

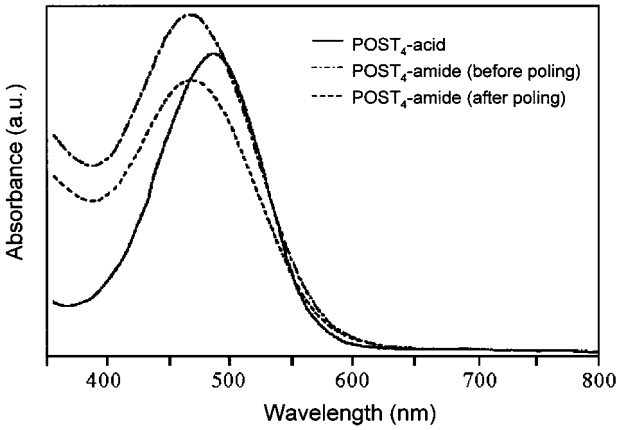


Figure 2. UV−vis absorption spectra of monomer ($POST_4$-acid) and polymer ($POST_4$-amide) film on glass substrates before and after electric poling.

evaluated for $POST_4$-ester and $POST_4$-amide from these absorbance ratios before and after poling was 0.37 and 0.19, respectively. It is interesting to note also that the UV−vis spectrum exhibits the high-energy shift of the charge-transfer band in the polyamide sample compared to the corresponding monomer, indicating through-space coupling of the adjacent transition dipoles due to the stiff backbone.

Thermal Properties. DSC thermograms showed only glass transition temperatures for the two polymers, $POST_4$-ester and $POST_4$-amide at 80 and 139 °C, respectively. Neither of them showed any other transitions associated with crystalline or liquid crystalline phases in agreement with the measured WAXS results (not shown here). TGA measurements showed that these polymers have a decomposition temperature at ca. 225 °C, which represents 5% weight loss of samples occurred under a nitrogen atmosphere.

Dilute Solution Behavior. During initial solubility experiments, it was discovered that the synthesized polymers were soluble in deionized water, a characteristic not commonly attributed to side group NLO polymers. In this case, the excessive positive charges along the hydrophobic polymer backbone, which bears two charged groups per repeat unit at the end of the methylene spacers, allow the polymer to assume an extended conformation in deionized water. This is illustrated in Figure 3, which shows the reduced viscosity of the polymers in deionized water as a function of polymer concentration. The viscosity data produced a

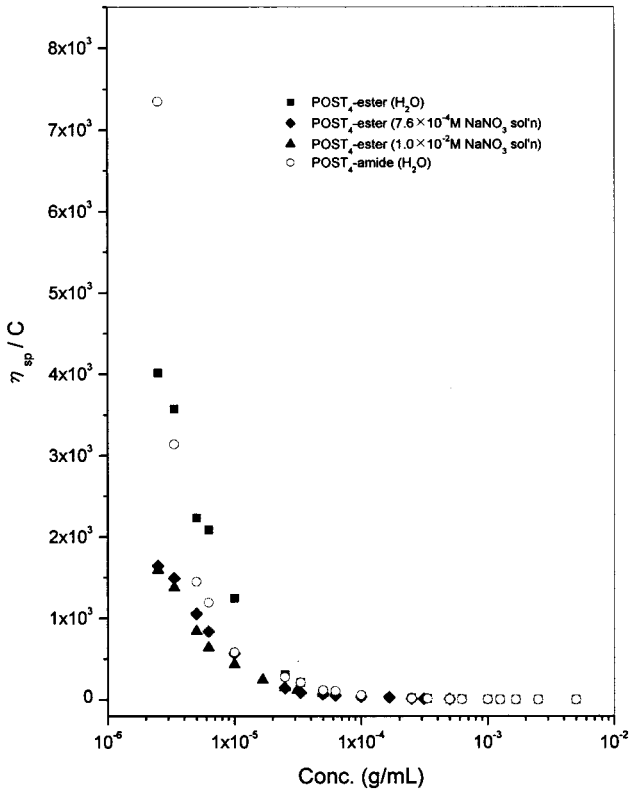


Figure 3. Reduced viscosity plotted vs polymer concentration in deionized water and different salt ($NaNO_3$) concentrations for $POST_4$-ester and $POST_4$-amide.

remarkable upswing at concentrations below $\sim 1 \times 10^{-3}$ g/mL. The behavior immediately suggests a polyelectrolyte effect due to coil expansion at low concentrations. We also observed that the apparent viscosity of each polymer solution decreased as the ionic strength of aqueous medium was increased, typical of polyelectrolyte behavior. However, it is not evident that the changes in viscosity are solely due to the deshielding and shielding of the intramolecular charge−charge repulsions along the polymer backbone. The dependence of the reduced viscosity on concentration of the salt appears to show a slower decline at elevated $NaNO_3$ concentrations. No maximum is found in the Huggins plot (Figure 3) within the limits of the present measurements in contrast to the behaviors reported for flexible polyelectrolytes in litterature.[23,24] There is no direct knowledge of the exact magnitude of the persistent length of these polymers, but we believe that a rigid shape probably persists not only through a single molecular chain but also through longer range interactions of intermolecular dipoles prevalent even at high dilution, thus bringing about the polyelectrolyte behavior. Note that the reduced specific viscosity of $POST_4$-amide is higher than that of $POST_4$-ester at the same concentration, indicating greater contour length.

NLO Properties. SHG measurements were taken on spin-coated samples. These film samples were not of good optical quality. Attempts to obtain better films by slowly evaporating the solvents did not succeed. Surface topographies of such films were measured on an atomic force microscopy (AFM; Park Science Instrument Autoprobe LS, operated in a contact mode). As can be seen from the AFM micrographs (Figure 4), the films show protrusions or holes ranging from 50 to 200 nm in depth. These topographic defects were generally larger in either casting or spin-coated films of $POST_4$-amide compared with the corresponding polyester samples. We have examined whether this inhomogeneous organization gives rise to the SHG intensity without the aid of any dc poling field. Figure 5 shows weak SHG signals

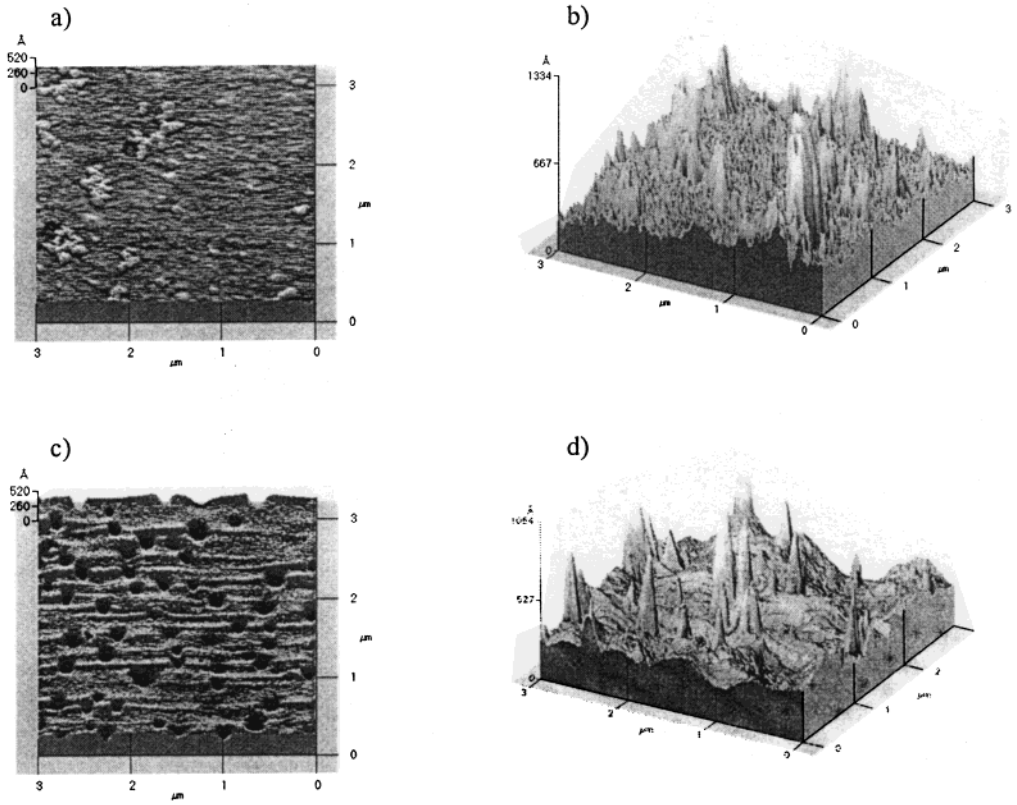


Figure 4. AFM images for spin-coated films of (a) $POST_4$-ester and (c) $POST_4$-amide. AFM scans (b) and (d) were taken for corona-poled films of $POST_4$-ester and $POST_4$-amide.

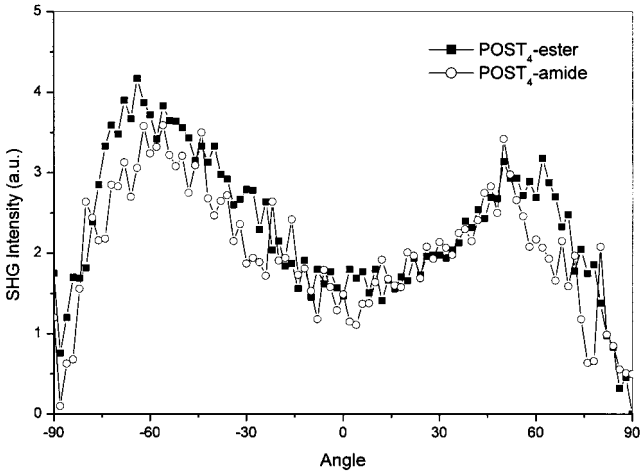


Figure 5. SHG intensities for the films of $POST_4$-ester and $POST_4$-amide as spin-coated without the aid of electric field poling.

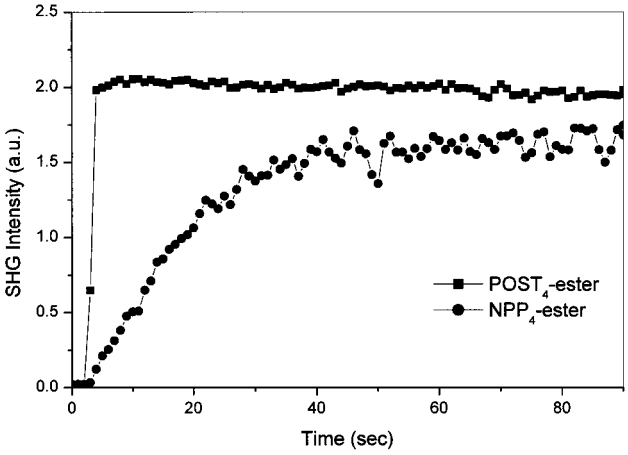


Figure 6. Corona poling field-induced growth of the SHG signal obtained at 90 and 110 °C from the same backbone polymer with different chromophores (a) NPP_4-ester (filled square)[2] and (b) $POST_4$-amide (filled circle).

observed for the film as spin-coated, indicating that some chromophores in the polymer assemble in an accentric polar organization upon spin coating. The reason for this spontaneous organization of the NLO chromophores is unclear thus far. This may be due to a surface-anchoring effect. The amphiphilic structure induced by a hydrophobic polymer backbone including methylene spacers and appended hydrophilic stilbazolium salt groups may lead to dye aggregates during the film preparation. These aggregates in the surface region in turn influence the optical nonlinearity due to the symmetry breaking nature of the surface.

Application of poling field caused additional orientation of chromophores resulting in larger d_{33} values of 58−102 pm/V for the two polymers, but these values were considerably smaller than predicted by a randomly oriented gas model. Rough calculations of the d_{33} value predicted for $POST_4$-amide indicated an expected value of an order of 300 pm/V without taking into account possible resonance enhancement. It is possible that poling is less efficient for this chromophore system. As suggested by Choi et al.,[19] in the case of polymer containing molecular ionic chromophores a counterion can migrate relatively easily in the polymer matrix upon application of the poling field, thereby reducing the poling efficiency. We see this inefficient poling effect on the development of the domain structure during electric poling for this polymer.

Domain Structure. Figure 6 shows the poling transient for $POST_4$-amide obtained at 110 °C. The SHG intensity reached a maximum value within 1−2 min after the electric field was applied. This step rise in SHG is somewhat different from the monoexponential behavior observed for the same rigid polymer but nonionic chromophores (Figure 6). We have observed so far that the poling kinetics for these rigid backbone polymers is described by a single-exponential function in contrast to a biexponential one usually observed in a flexible matrix.[25−27] Furthermore, polar ordering of the chromophores in these polymers occurs only when the rigid backbone segments are able to respond simultaneously by changing their local conformations to adapt to the anisotropic orientation distribution of the poled chromophores resulting in NLO domains.[8,9] In view of these observations, the single rate process was understood on the basis that these rigid backbone polymers had an intrinsic tendency to organize into oriented domains through a completely coupled motion between the backbone and side groups. In contrast to this poling behavior, a possible implication of the step rise in SHG shown in Figure 6 is that domains or their tendency to form would decrease for this polymer system since the time scale is likely to be too short in a context of backbone rearrangement. To confirm this, we attempted to investigate the topographic changes of the film after poling by AFM. A noticeable change in the surface topography was observed, but these topographic changes were highly localized and more nonuniform as shown in Figure 4 compared to the observations for the same backbone polymers with nonionic pendent chromophores. From these observations, we considered that the formation of domains by backbone rearrangement was not as well developed in observations thus far, resulting in low d_{33} value.[8,28] We believe that the ionic interactions of the pendant groups would oppose the cooperative alignment of backbones and their side group dipoles, thereby restricting the formation of domains. Further study of these materials will be necessary to investigate in depth whether the spontaneous accentric orientation behavior of the ionic chromophore is related the development of the domain structure in this polymer by electric poling.

Conclusions

A new type of rigid backbone amphiphilic polymers with pendant hemicyanine units was synthesized. The prepared polymers exhibited polyelectrolyte behaviors in deionized water. DSC thermograms showed glass transition temperatures for the two polymers, $POST_4$-ester and $POST_4$-amide at 80 and 139 °C, respectively. A significant SHG activity was observed from the spin-coated films without the aid of electric field induced poling. However, the NLO properties observed from these materials were found to be smaller than expected due to the inefficient electric poling, which we discussed in terms of the observed topographic structures, indicating that the domain structures were not well developed for these polymers.

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