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pyrene on the transitional properties can be interpreted in terms of the decrease in the molecular shape anisotropy. In addition to the technological potential these materials may prove also to be of interest for time-resolved fluorescence experiments aimed at studying molecular dynamics in anisotropic phases.

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Registry No. 2 ($n = 3$), 143958-46-7; 2 ($n = 4$), 143958-47-8; 2 ($n = 5$), 143958-48-9; 2 ($n = 6$), 143958-49-0; 2 ($n = 7$), 143958-50-3; 2 ($n = 8$), 143958-51-4; 2 ($n = 9$), 143958-52-5; 2 ($n = 10$), 143958-53-6; 2 ($n = 11$), 143958-54-7; 2 ($n = 12$), 143958-55-8; 1-bromo-7-(4-cyanobiphenyl-4′-oxy)heptane, 143958-44-5; 1-(4-cyanobiphenyl-4′-oxy)-7-(4-formylphenyl-4′-oxy)heptane, 143958-45-6.

Synthesis and Second-Order Nonlinear Optical Properties of Polymethacrylates Containing Organic Salt Dye Chromophore

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New methacrylate polymers containing the *N*-alkylpyridinium salt at the side chain were designed and synthesized in an attempt to enhance both the poling-induced second-order nonlinear optical susceptibility and its temporal stability. The corona poled polymer films showed a large second-order nonlinear optical susceptibility, $\chi^{(2)}(-2\omega;\omega,\omega)$. The larger $\chi^{(2)}$ value of the homopolymer compared to that of the copolymer indicates that the concentration of the nonlinear optical chromophores in the copolymer is lower than the saturation value. The temporal stability of the poled structures seems better than that of some guest–host systems.

Introduction

Side-chain polymers have drawn remarkable interest in recent years as potential candidates for application in electrooptic and photonic devices.[1-6] This interest is partly due to their large optical nonlinearity, relatively high damage threshold, fast response, and high transparency over a wide range of wavelengths. However, one difficulty with second-order organic nonlinear optical (NLO) materials is that most of these compounds crystallize in a centrosymmetric space group and, therefore, even if the microscopic optical nonlinearity, β, may be high, the net bulk susceptibility, $\chi^{(2)}$ vanishes.[1-10] Therefore, the required noncentrosymmetry for a second-order NLO process such as electrooptic effect (EOE) and second harmonic generation (SHG) is usually induced in a polymer by external means of electric field poling. The molecular dipole vector components are aligned by electric poling and subsequent freezing in their new orientation prior to the SHG measurement. Incorporation of NLO molecules to a polymer backbone forming a side-chain NLO polymer backbone forming a side-chain NLO polymer has certain advantages. First, the temporal stability of poled side-chain polymers, in many cases, is better than that of poled guest–host systems.[11-14] Second, a higher concentration of NLO chromophores can be introduced into the polymer matrix to yield a larger second-order optical nonlinearity.

In this paper, we report the synthesis and the second-order NLO behavior of polymers containing a molecular–ionic chromophore, *N*-alkylpyridinium ion, in the side chain. In its powder form, *N*-alkylpyridinium salts have been shown to exhibit significantly high second-order nonlinearities.[15,16] In general, the ionic polymers are difficult to pole because of their intrinsic ionic conductivity. Nevertheless, it has been reported that a significant poling-induced NLO chromophore alignment can be achieved in poled ionic polymers.[17] We show that these molecular

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ionic polymers can be successfully poled to achieve a significant chromophore alignment in them. Moreover, the presence of an ionic salt chromophore in the side chain results in an increase in the glass transition temperature and therefore an improved temporal stability of the poled structure.

Experimental Section

(A) Materials. Polymethacrylates containing *N*-alkylpyridinium salts were synthesized following the published procedure.[18,1]19 4-Picoline, 1-bromohexadecane, 1-bromodocosane, iodomethane, 4-hydroxybenzaldehyde, dodecanethiol, 2-hydroxyethyl methacrylate, triethylamine, methacryloyl chloride, and piperidine were purchased form Aldrich Chemicals and used as received. 6-Chloro-1-hexanol (*Aldrich*) was distilled under vacuum. All solvents used in this study were distilled and stored over molecular sieves (4A). *N,N'*-Dimethylformamide (DMF) and chloroform were distilled under calcium hydride just before polymerization. 2,2′-Azobisisobutyronitrile (Polyscience Inc.) was recrystallized from methanol/water.

(B) Synthetic Procedures. *1-Hexadecyl-4-methylpyridinium bromide* (*1*): A mixture of 4-picoline (18.2 mL, 0.018 mol) and 1-bromohexadecane (65 mL, 0.21 mol) in benzene (15 mL) was refluxed to half the volume at 100 °C. The concentrated mixture was then added dropwise into vigorously stirring ether. The yellowish precipitate was filtered out and recrystallized twice from ether, yield 80%, mp 78–80 °C. ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 3 H), 1.18 (m, 26 H), 1.96 (t, 2 H), 4.80 (t, 2 H), 7.80 (d, 2 H).

1-Docosyl-4-methylpyridinium bromide (*2*): By using the same procedure as indicated above, but chloroform as the solvent, a white solid was obtained. The product was recrystallized from acetone, yiled 75% mp 80–82 °C. ^{1}H NMR ($CDCl_3$) δ 0.822 (t, 3 H), 1.2 (m, 40 H), 1.96 (t, 2 H), 4.87 (t, 3 H), 7.83 (d, 2 H), 9.26 (d, 2 H).

1-Hexadecyl-4-[2-(4-hydroxyphenyl)vinyl]pyridinium bromide (*3*): A mixture of 4-hydroxybenzaldehyde (0.183 g, 1.5 mmol), 1-hexadecylpicolinium bromide (0.39 g, 1 mmol), and small amount of piperidine (0.05 mL) in methanol (10 mL) was refluxed for 10 h, cooled to room temperature, and stored overnight in cold room. The solid was filtered out, washed with acetone, and recrystallized from ethanol, yield 75%, mp 140–145 °C. ^{1}H NMR ($CDCl_3$) δ 0.79 (t, 3 H), 1.17 (m, 26 H), 1.82 (t, 2 H), 4.42 (t, 2 H), 6.84 (d, 2 H), 7.24 (d, 1 H), 7.57 (d, 2 H), 7.93 (d, 1 H), 8.12 (d, 2 H), 8.85 (d, 2 H), 10.14 (s, 1 H).

1-Docosyl-4-[2-(4-hydroxyphenyl)vinyl]pyridinium bromide (*4*): The synthetic procedure is the same as that for monomer (3), yield 80%, mp 84–89 °C. ^{1}H NMR ($CDCl_3$) δ 0.81 (t, 3 H), 1.15 (m, 38 H), 1.79 (s, 2 H), 3.40 (s, 1 H), 4.38 (s, 2 H), 6.65 (d, 1 H), 6.75 (d, 2 H), 7.23 (d, 2 H), 7.35 (d, 1 H), 7.65 (d, 2 H), 8.43 (d, 2 H).

1-Hexadecyl-4-[2-(4-methacryloxyphenyl)vinyl]pyridinium bromide (*5*): Freshly dried methacryloyl chloride (4 mL) was added dropwise into an ice–acetone cooled mixture of monomer 4 (18 g), a trace of 2,6-di-*tert*-butyl-4-methylphenol, and triethylamine (7.76 mL) in chloroform (250 mL). The reaction mixture was stored at room temperature for 24 h and then concentrated to half the volume. The solution was washed with a saturated aqueous solution of sodium bicarbonate. The organic layer was separated, dried with sodium sulfate, concentrated to a minimum volume, and then added dropwise into vigorously stirring cold ether. Brown solid was filtered out, recrystallized from butanol and dried in vacuum, yield 70%, mp 140–147 °C. ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 3 H), 1.19 (m, 28 H), 1.90 (s, 3 H), 3.65 (t, 2 H), 5.77 (s, 1 H), 6.34 (s, 1 H), 7.12 (d, 2 H), 7.20 (d, 1 H), 7.63 (d, 2 H), 7.64 (d, 1 H), 8.06 (d, 2 H), 8.98 (d, 2 H). Anal. Calcd for $C_{33}H_{48}NO_2Br$ (570.66): C, 69.46; H, 8.48; N, 2.45. Found: C, 69.30; H, 8.42; N, 2.41.

1-Docosyl-4-[2-(4-methacryloxyphenyl)vinyl]pyridinium bromide (*6*): The synthetic procedure was as same as that of monomer **5**, and recrystallization was done in acetone/ethanol, yield 85%, mp 130–135 °C. ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 3 H), 1.22 (m, 40 H), 1.85 (s, 3 H), 4.63 (t, 2 H), 5.77 (s, 1 H), 6.34 (s, 1 H), 7.15 (d, 2 H), 7.22 (d, 1 H), 7.67 (d, 2 H), 7.74 (d, 1 H), 8.08 (d, 2 H), 8.94 (d, 2 H). Anal. Calcd for $C_{39}H_{60}NO_2Br$ (654.82): C, 71.54; H, 9.24; N, 2.14. Found: C, 71.56; H, 9.19; N, 2.16.

1,4-Dimethylpyridinium iodide (*9*): Iodomethane (3.36 g, 23.7 mmol) and 4-picoline (2 g, 21.5 mmol) were added into dichloromethane (30 mL). The reaction mixture was refluxed for 24 h. After the solvent was evaporated to half the volume, the concentrated solution was added to vigorously stirring hexane. The solid product was isolated and purified in ether/methanol (10:1), yield 80%, mp 150–155 °C (Lit. 153–155 °C).[20] ^{1}H NMR (DMSO-d_6) δ 2.55 (s, 3 H), 4.24 (s, 3 H), 7.93 (d, 2 H), 8.83 (d, 2 H).

4-(6-Hydroxyhexyl)benzaldehyde (*10*): 6-Chloro-1-hexanol (18.2 mL, 0.16 mol) and a trace of potassium iodide were added dropwise into a mixture of 4-hydroxybenzaldehyde (10 g, 0.08 mol) and potassium carbonate (11.0 g, 0.16 mol) in ethanol (150 mL). The contents in the reaction mixture were refluxed for 48 h at 85 °C, washed with water, and extracted from benzene. The yellowish oil obtained was dried under sodium sulfate, yield 65%. ^{1}H NMR ($CDCl_3$) δ 9.71 (s, 1 H), 7.70 (d, 2 H), 6.87 (d, 2 H), 3.91 (t, 2 H), 3.39 (t, 2 H), 1.44 (m, 8 H).

1-Methyl-4-{2-{4-(6-hydroxyhexyloxy)phenyl]vinyl}pyridinium iodide (*11*): Piperidine (0.2 mL) was introduced into a homogeneous mixture of 4-hydroxybenzaldehyde (2 g, 0.01 mol) and 1,4-dimethylpicolinium iodide (2 g, 0.01 mol) in methanol (50 mL). The reaction mixture was refluxed for 20 h at 90 °C and concentrated to half the volume. The mixture was stored in a cold room (0–4 °C) and the solid product was filtered out, yield 80%, mp 210–215 °C. ^{1}H NMR (DMSO-d_6) δ 8.78 (d, 2 H), 8.13 (d, 2 H), 7.95 (d, 1 H), 7.65 (d, 2 H), 7.31 (d, 1 H), 7.01 (d, 2 H), 4.33 (t, 2 H), 4.18 (s, 3 H), 3.98 (t, 3 H), 1.35 (m, 6 H), 1.69 (t, 2 H).

1-Methyl-4-{2-[4-(6-methacryloxy)phenyl]vinyl}pyridinium iodide (*12*): Dried triethylamine (1.2 g, 0.011 mol) was added dropwise into a solution of monomer 11 (5 g, 0.01 mol) in chloroform (130 mL) at 60 °C. Methacryloyl chloride (1.35 g, 0.015 mol) was added dropwise to the above mixture under nitrogen atmosphere. This reaction mixture was kept for 24 h at 60 °C and washed with water. The organic layer was separated out and dried with sodium sulfate. The product, yellow solid, was crystallized from ethanol, yield 65%, mp 220–226 °C. ^{1}H NMR ($CDCl_3$) δ 8.88 (d, 2 H), 7.94 (d, 2 H), 7.66 (d, 1 H), 7.58 (d, 2 H), 7.00 (d, 1 H), 6.91 (d, 2 H), 6.01 (s, 1 H), 5.52 (s, 1 H), 4.46 (s, 3 H), 4.12 (t, 2 H), 3.98 (t, 2 H), 1.90 (s, 3 H), 1.68–1.46 (m, 8 H).

Polymerization Procedure. 2,2′-Azobisisobutyronitrile (7.5×10^{-2} mmol), was added to a mixture of the monomer (1.5 mmol) and a trace of dodecanethiol in chloroform (20 mL). The mixture was subjected to several freeze–thaw cycles and stored in an argon atmosphere at 60 °C for 48–72 h. Thin-layer chromatography was performed in order to check whether the unreacted monomer was present in the mixture. Reaction mixutre was then poured into the vigorously stirring cold ethanol or methanol. The product, polymer, was filtered out and purified by reprecipitating from ethanol. In the case of copolymerization, various molar ratios of the monomer and the initiator were used (2 mol % AIBN was used for this copolymerization).

Melting temperatures of all the monomers were determined by using a Melt-Temp II capillary melting point apparatus and reported here uncorrected. Elemental analyses were done at Atlanta Microlab Inc. Thin-layer chromatography was performed on a precoated hard-layer plate with a fluorescent indicator (J. T. Baker, Phillipsburg, NJ). DSC thermograms of each polymer were taken by using a Shimadzu DSC-50 instrument under nitrogen. Proton NMR spectra were recorded by using Varian Gemini-300 spectrometer. UV-visible spectra were recorded with a Shimadzu uv-3101 PC spectrometer.

(C) Material Processing. Polymer films were spin coated at 800–1500 rpm onto borosilicate microslides using filtered solutions in chloroform or DMF. All films were dried in vacuum at 100–110 °C for more than 96 h. The thicknesses of the polymer films were measured by a Surface Profilometer (Tencor Alpha Step). All films were poled using the corona poling technique in a wire-to-plane geometry.[21,22] The films were palced on a

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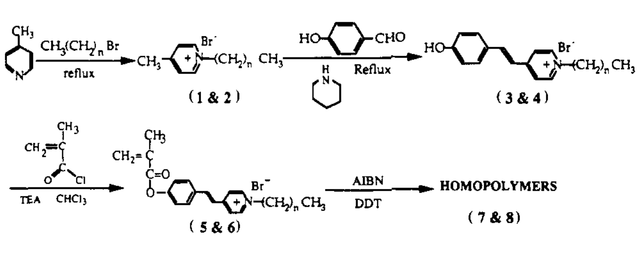

* n = 15: 1, 3, 5, and 7 n = 21: 2, 4, 6, and 8

Figure 1. Synthetic scheme I. AIBN, 2,2′-azobisisobutyronitrile; BHT, 2,6-di-*tert*-butyl-4-methylphenol.

grounded, planar aluminum electrode which was heated by two cartridge heaters. The temperature of the samples was continuously monitored with a thermocouple. When the temepratureure was close to the glass transition temperature (T_g) a large positive (4–5 kV) voltage was applied to the top electrode (diameter ~25 μm) which was suspended 1 cm above the planar electrode. The current from the cathode was monitored by measuring the voltage drop across a 10 MΩ resistor. The typical corona current was 3 mA. The samples were slowly cooled to room temperature in the presence of the applied electric field.

All films were examined by optical microscopy and spectroscopy to check whether the films were damaged in the process of poling. It was evident that if the poling was performed 5–10 °C above the T_g, irreversible changes and visible damages (whitening of the films) occurred in the films even at a poling current of 1 mA. On the other hand, if the poling was done in the vicinity of the T_g (~5 °C bellow the T_g) films could be poled at a current of 3 mA without damage. We used a larger (6 × 8 cm^2) bottom electrode to minimize higher current densities, which cause breakdown in the polymer. To estimate the approximate strength of the poling field, the surface potential of the poled films was measured with a high-voltage electrostat voltmeter. For example, initial voltage across a ~1-μm thick polymer, HP6I (see Figure 2) film deposited on a 1-mm-thick substrate was about ~78 V, which corresponds to a field of ~7.8 × 10^5 V/cm. However, it is not certain how this field is distributed between the polymer film and the nonconducting substrate. We are unable to evaluate the strength of the electric field inside the film during the process of poling. The point to note here is that we have calculated reported $\chi^{(2)}$ values from the SHG measurements that were performed after complete decay of surface static charges. Therefore, the contribution to the SHG signal from the third-order process can be neglected.

(D) Measurement of $\chi^{(2)}$. The second harmonic generation (SHG) measurements of poled samples were carried out with a Q-switched mode locked, Nd^{3+}:YAG laser (λ = 1064 nm) operating in the TEM$_{00}$ mode. Each Q-switched pulse contains about 40 mode-locked pulses having a pulse width of approximately 100 ps. The entire pulse train was utilized for the SHG measurements.

The laser beam was lightly focused onto the sample with a 100-cm focal length lens. The samples were mounted on a motor-driven rotational stage which could be rotated around an axis perpendicular to the surface normal. The SHG signal was passed through a series of interference filters to reject the fundamental wavelength and focused onto the photocathode of a photomultiplier tube. The output from the PMT was amplified and recorded with a boxcar integrator. The desired polarizations of the fundamental and second harmonic beams were achieved by a polarizer–analyzer combination in conjunction with a half-wave plate. The second harmonic signal was normalized with respect to that of a calibrated quartz crystal for which a value of d_{11} = 5.0 pm/V was assumed.[23]

Results and Discussion

(A) Synthetic Considerations. A general synthetic route to these moleucular–ionic polymers is illustrated in reaction schemes shown in Figures 1 and 2. Neither the monomers nor the polymers show any distinct liquid-crystalline phase transitions in DSC thermograms (Table I). Monomers were polymerized by free-radical polymerization in dried chloroform. To prevent cross-linking of the polymer, a phase-transfer reagent, dodecanethiol, was used in polymerization.[24] The proton NMR spectra of these polymers indicate the presence of —HC=CH— group in the stilbene unit; therefore, the cross-linking has been prevented. Also, the NMR coupling constant (~15.5 Hz for ethylinic protons) suggests that the stilbene units in these polymers are in the trans configuration. It was found that 1–2 mol % of AIBN is sufficient to convert the monomers to homopolymers in 48–72 h. In the case of copolymerization the monomer feeding ratio was 1:5. The fraction of NLO units in the copolymer was calculated (using NMR data) to be ~22%.

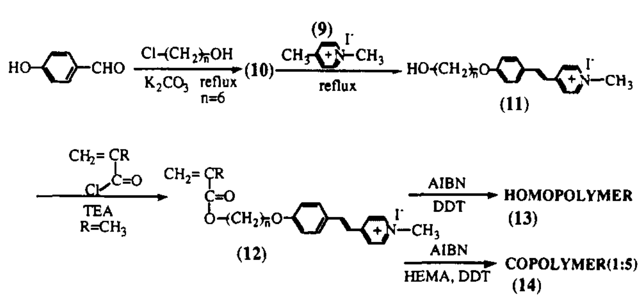

Figure 2. Synthetic scheme II. DDT, dodecanethiol; HEMA, 2-hydroxyethyl methacrylate; TEA, triethylamine; HPBr15, poly{1-hexadecyl-4-[2-(4-methacryloxyphenyl)vinyl]pyridinium bromide]; HPBr21, poly{1-docosyl-4-[2-(4-methacryloxyphenyl)vinyl]pyridinium bromide}; CP6I-HEMA, poly(1-methyl-4-{2-[4-(6-methacryloxyhexyloxy)phenyl]vinyl}pyridinium iodide-*co*-2-hydroxyethyl methacrylate). HP6I, poly(1-methyl-4-{2-[4-(6-methacryloxyhexyloxy)phenyl]vinyl}pyridinium iodide).

Table I. Second-Order NLO Susceptibilities of Novel Ionic Polymethacrylates

polymer	T_g (°C)	thickness (μm)	$\chi^{(2)}_{zzz}$ (pm/V)
HPBr15	142	0.3	5.9
HPBr21	134	0.1	5.4
CP6I-HEMA	93	0.5	10.0
HP6I	138	0.1	15.9

(B) Second-Order NLO Effects in New Polymethacrylates. The macroscopic polarization induced in the sample by the probing radiation can be written as

$$P_i^{NL} = d_{ijk}(-\omega_3;\omega_1,\omega_2):E_j(\omega_1)E_k(\omega_2)$$

where d_{ijk} ($2d_{ijk} = \chi^{(2)}_{ijk}$) is the contracted, macroscopic second-order NLO susceptibility tensor. Poled materials possess $C_{\infty v}$ symmetry,[20] and therefore the second-order optical susceptibility tensor for SHG has only three independent nonzero tensor elements, namely, d_{33}, $d_{31} = d_{32}$, and $d_{24} = d_{15}$.

We calculated $\chi^{(2)}_{zzz}$ of poled samples, using a calibrated quartz plate as a reference (Table I). The errors encountered in the measurement of $\chi^{(2)}_{zzz}$ is about 30%. In calculating $\chi^{(2)}_{zzz}$ we have assumed a refractive index of 1.50 for n_ω and 1.60 for $n_{2\omega}$ for all the polymers. It should be noticed that the given $\chi^{(2)}_{zzz}$ values were obtained from SHG measurements that were performed after the surface charge had completely decayed. The calculated $\chi^{(2)}_{zzz}$ value of the homopolymer, HP6I is approximately 1.5 times larger than that of the copolymer, CP6I-HEMA. In fact this is expected since the portion of NLO chromophores

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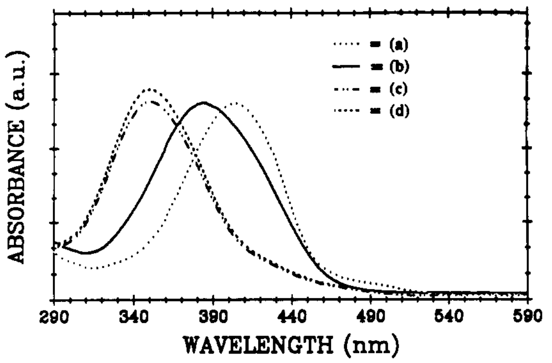

Figure 3. UV-visible spectra of polymer films: (a) HP6I, (b) CP6I-HEMA, (c) HPBr15, and (d) HPBr21.

in our copolymer (~22%) is lower than that in the homopolymer. It has been shown that in a copolymer saturation of $\chi^{(2)}$ occurs as the molar fraction of the NLO side-shain chromophore in the polymer exceeds a certain value (~25%).[26] The saturation of $\chi^{(2)}$ in a copolymer suggests that the effect of poling field is diminished due to the interaction between the side chains as the side-chain content in the polymer increases. Therefore, the lower $\chi^{(2)}$ value of the copolymer, compared to that of the homopolymer, suggests that the molar fraction of the NLO side chains in our copolymer is below the saturation limits.

As, seen in Figure 3, the absorption at the second harmonic wavelength by these polymers is negligible and, therefore, the $\chi^{(2)}_{zzz}$ values are unlikely to be resonance enhance.d However, the role of preresonance enhancement of $\chi^{(2)}$ for the polymers HP6I and CP6I-HEMA for which the absorption bands are considerably red shifted cannot be ruled out. The $\chi^{(2)}_{zzz}$ values of these polymers indicate that the ionic polymers can successfully be poled to achieve a significant molecular alignment in them. The calculated $\chi^{(2)}$ value of the homopolymer HP6I is approximately 3 times larger than that of homopolymers HPBr15 and HPBr21. However, the temporal stability of the poled structures of HPBr15 and HPBr21 was found to be somewhat better than that of HP6I. For example, when measured 10 days later, we observed 65–70% of the initial SHG signal for polymers HPBr15 and HPBr21, whereas in the case of HP6I the SHG signal was about 55% of that of the initial signal. In the case of guest–host systems, such as polymethylmethacrylate doped with NPP and DENST, only 30–40% of the initial SHG signal remained after 10 days.[28] The higher glass transition temperature of HPBr15 and HPBr21 may be the reason for the improved stabilities of the poled structure in these two polymers.

The difference in the $\chi^{(2)}$ values of these homopolymers, to a certain extent, may be attributable to the degree of poling induced molecular alignment in these polymers.[17,27] The lower $\chi^{(2)}$ value in polymers, HPBr15 and HPBr21, may be indicative of that the orientational order induced in them by poling is smaller than that in HP6I. The NMR spectra indicate that the electron pulling strength of the salt unit of these three polymers are identical. Although the films were poled at the same poling currents, the strength of the effective poling field inside the film may be different for different polymers (the surface potential measurement yields approximately the same filed for these polymers, i.e., 7.8×10^5 V/cm for polymer HP6I and 7.6×10^5 V/cm for polymer HPBr21); hence, the degree of molecular alignment.

Also, in polymer HP6I, the NLO unit is separated from the polymer backbone by six methylene spacer units. In polymers HPBr15 and HPBr21 the NLO group is directly connected to the polymer backbone. In addition, these two polymers contain bulky hydrocarbon chains in the chromophore. It is known that the side-chain polymers with less than three spacer methylene units, the chromophore, and the polymer backbone tend to move as one unit upon application of an electric field. It is required to perform poling at temperatures well above T_g's in order to decouple the motion of the NLO unit and the main chain.[11] We had to maintain our poling temperatures in the vicinity of T_g's in order to prevent any break down in films during poling. Therefore, the structural constraints in polymers HPBr15 and HPBr21 also may account to a certain extent for the observed lower $\chi^{(2)}$ value in them.

All the polymers studied in this paper are molecular ionic compounds and contain smaller counterions (Br^- or I^-) in the salt unit. Although the intrinsic conductivities of these polymeric salts are very low, there is a possibility that these anions can migrate (especially since the poling was performed in the vicinity of T_g) in the polymer matrix under the applied field thereby reducing the poling efficiency. Polymers HPBr15 and HPBr21 contain Br^- ion, whereas polymers HP6I and CP6I-HEMA contain I^- ion. Perhaps, the relatively smaller size of the Br^- ion may allow it to migrate more easily than the I^- ion when the field is applied. Therefore, the different mobilities of these anions may account to a certain extent for the difference in $\chi^{(2)}$ values of homopolymers. Finally since the absorption spectra of the iodide containing polymers (HP6I and CP6I-HEMA) are considerably red-shifted with respect to the bromide-containing polymers (HPBr15 and HPBr21), a preresonance enhancement to give a larger $\chi^{(2)}$ value for the iodide polymer is another strong possibility. Presently we are investigating the effect of the anion on $\chi^{(2)}$ of poled molecular–ionic polymers.

Conclusion

We have synthesized and successfully poled the methacrylate polymers containing *N*-alkylstilbazolium salt units in the side chain. A large second-order susceptibility was achieved by using *N*-alkylstilbazolium dye salt chromophore with high second-order hyperpolarizability β. The temporal stability of poled new polymer films is better than that of some guest–host systems. The poling efficiency, hence the resulting second-order NLO susceptibilities, and the temporal stability of poling-induced orientation of these polymers can be largely improved by varying the counterion in the polymer. In our laboratory, we are currently pursuing these endeavors.

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Registry No. 1, 2315-40-4; 2, 143745-39-5; 3, 143745-40-8; 4, 143745-41-9; 5, 143745-42-0; 5 (homopolymer), 143745-47-5; 6, 143745-43-1; 6 (homopolymer), 143745-48-6; 9, 2301-80-6; 10, 143745-44-2; 11, 143745-45-3; 12, 143745-46-4; 12 (homopolymer), 143745-49-7; (12)(HEMA) (copolymer), 143745-50-0; 1-bromodocosane, 6938-66-5; 4-picoline, 108-89-4; 1-bromohexadecane, 112-82-3; 4-hydroxybenzaldehyde, 123-08-0; iodomethane, 74-88-4; 6-chloro-1-hexanol, 2009-83-8; methacryloyl chloride, 920-46-7.

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