# Second-Order Nonlinear Optical Effects in Novel Polymethacrylates Containing a Molecular–Ionic Chromophore in the Side Chain

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We have synthesized new glassy methacrylate polymers containing a molecular–ionic (*N*-methylpyridinium) nonlinear optical chromophore in the side chain. A bulky tetraphenylborate (TPB) counterion was substituted at the salt unit in order to reduce the migration of the counterion during the process of poling. It was found that the poling-induced chromophore alignment of the TPB-containing polymer is significantly improved compared to that of the iodide or bromide containing polymers. The second-order nonlinear optical susceptibility, $\chi^{(2)}(-2\omega;\omega,\omega)$, of the poled TPB-containing polymer is approximately 5 times larger than that of the corresponding iodide analogue. Also, the temporal stability of the poled structure of the TPB-containing polymer is found to be considerably improved over that of the analogous iodide containing polymer.

## Introduction

The promise of extraordinary optical and mechanical properties of organic polymers have created an intense interest to utilize them in photonic and electrooptic devices.[1-7] In particular side-chain nonlinear optical (NLO) polymers have been of interest, since a higher density of NLO chromophores can be attached to the polymer backbone resulting in larger optical nonlinearities. The required noncentrosymmetry in these polymers is usually induced by external means such as the electric field poling process where by the NLO chromophores are aligned under the influence of an electric field.[8-10] Poled structures are in a thermodynamically metastable state and therefore undergo relaxation, thereby reducing the induced symmetry with a loss of optical nonlinearity. Still, in many cases, the temporal stability of a poled side-chain polymer has been found to be better than that of many poled guest–host systems.[11-14]

As a part of the research program dedicated to the development of high-efficiency NLO materials, we have designed and synthesized some novel polymethacrylates, containing molecular–ionic (*N*-alkylpyridinium) NLO chromophores in the side chain. The *N*-alkylpyridinium ion was selected as the NLO side-chain chromophore because of its remarkably larger second-order nonlinearity in the powder form.[15,16] Usually ionic polymers are difficult to pole because of their ionic–conductivity. Nevertheless, it has been shown that these molecular–ionic polymers can successfully be poled to achieve a significant chromophore alignment in them.[17,18] In our earlier paper we reported the second harmonic generation (SHG) results of corona-poled side-chain molecular–ionic NLO polymers which contained smaller counterions (bromide and iodide) at the salt unit.[18] Also, in that paper we showed that the temporal stability of those poled side-chain molecular–ionic NLO polymers was comparable to that of the poled polymethacrylates doped with guest NLO molecules such as *N*-nitrophenyl-(*s*)-prolinol (NPP) and (diethylamino)-$\beta$-nitrostyrene (DEANST). The SHG measurements made on films which were poled under approximately the same experimental conditions yielded a relatively larger $\chi^{(2)}$ value for iodide-containing polymers. The difference

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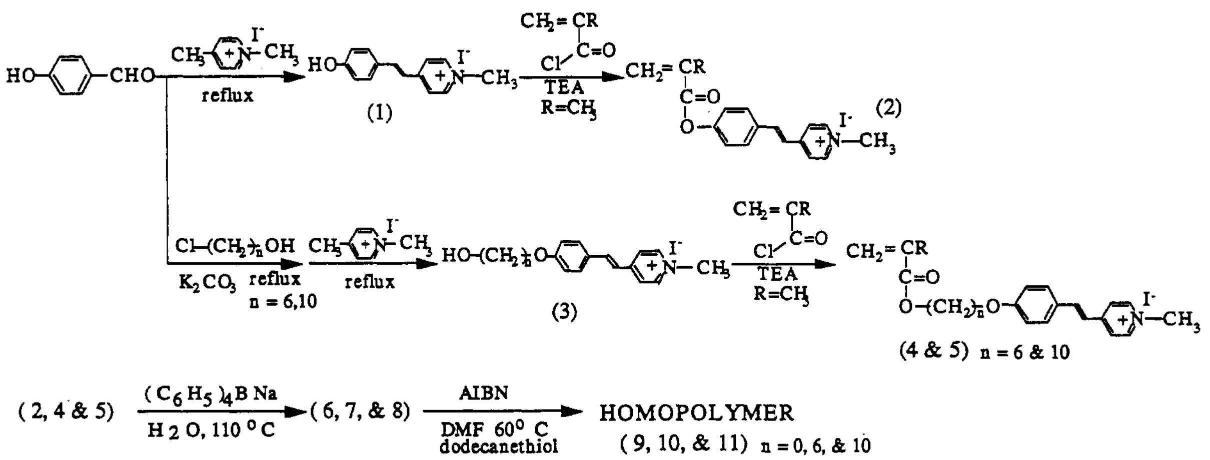

**Figure 1.** Synthetic scheme for side-chain molecular–ionic polymethacrylates. AIBN = 2,2′-azobisisobutyronitrile; TEA = triethylamine; BHT = 2,6-di-*tert*-butyl-4-methylphenol; DDT = dodecanethiol; HP0B = poly{1-methyl-4-[2-(4-(methacryloxy)phenyl)vinyl]pyridinium tetraphenylborate}; HP6B = poly{1-methyl-4-{2-[4-(6-((methacryloxy)hexyl)oxy)phenyl]vinyl}pyridinium tetraphenylborate}; HP10B = poly{1-methyl-4-{2-[4-(10-((methacryloxy)hexyl)oxy)phenyl]vinyl}pyridinium tetraphenylborate}.

**Table 1. Elemental Analysis Data for Polymethacrylates**

| | C% | | H% | | N% | |
|---|---|---|---|---|---|---|
| polym | calc. | found | calc. | found | calc. | found |
| HP0B | 84.14 | 81.11 | 6.39 | 6.11 | 2.34 | 2.29 |
| HP6B | 82.30 | 81.79 | 7.20 | 7.67 | 2.0 | 2.44 |
| HP10B | 82.63 | 81.04 | 7.73 | 7.69 | 1.85 | 1.83 |

**Table 2. DSC Thermal Analysis Data and the Second-Order NLO Susceptibilities of Polymethacrylates**[a]

| polym | $T_g$ (°C) | $T_d$ (°C) | thickness (μm) | $n$ ($\lambda$ = 632 nm) | $\chi^{(2)}_{zzz}$ | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|
| HP0B | 100 | 364 | 2.1 | 1.59 | 7.8 | 351 |
| HP6B | 72 | 380 | 1.3 | 1.62 | 18.1 | 390 |
| HP6I | 130 | 280 | 0.1 | 1.60 | 3.8 | 403 |
| HP10B | 69 | 325 | 1.5 | 1.61 | 10.9 | 391 |

[a] $T_d$ = decomposition temperature, $n$ = refractive index, $\chi^{(2)}_{zzz}$ = (esu) × $10^{-8}$. Thickness of the polymer HP6I was measured with a surface Profilometer and the refractive index was assumed.[18]

in the measured $\chi^{(2)}$ values between the iodide- and the bromide-containing polymers, in part, was attributed to the difference in the ionic–mobilities of the counterions. The larger the size of the counterion, the higher is the degree of difficulty in migration of the ion in the polymer matrix upon the application of an electric field. This is especially true if the poling is carried out at a temperature well below the glass transition temperature ($T_g$) of the polymer. To reduce the migration of the counterion during the poling process we have synthesized several new molecular–ionic polymers containing a bulky counterion, tetraphenylborate (TPB) at the salt unit. In this paper we describe synthesis, characterization and SHG measurements of these TPB-containing polymers. We find that the second-order NLO susceptibility, $\chi^{(2)}$, of these new TPB-containing polymers is significantly enhanced, presumably due to the improved alignment of the NLO chromophores. Also, the temporal stability of the poling-induced orientation of the NLO chromophore of TPB-containing polymers is considerably improved compared to that of the iodide- or bromide-containing polymers.

## Experimental Section

**Preparation of Materials.** A detailed description of the synthesis of side-chain molecular–ionic polymers has been reported previously.[18] Therefore details only pertinent to this work will be given here (Figure 1). The methacrylate monomer containing TPB was synthesized via a metathesis reaction as follows. The methacrylate monomer (2.4 mmol) containing the iodide salt was dissolved in hot water (100 mL), and the temperature of the solution was maintained above 100 °C. Then a hot (~110 °C) aqueous solution of sodium tetraphenylborate (0.1 M) was added in excess to this solution. The greenish yellow precipitate was filtered out and washed several times with warm (75 °C) ethanol in order to remove unconverted iodide salt. The product was further purified by precipitating it from DMF/ether.

The monomer was polymerized at 60 °C in dry DMF by free-radical polymerization. Freshly recrystallized AIBN (7.5 × $10^{-2}$ mmol) was added to a mixture of monomer (1.5 mmol) and a trace amount of dodecanethiol (a chain-transfer reagent which prevents cross-linking of the polymer[19]) in dry DMF. The mixture was subjected to several freeze–thaw cycles and stored under argon atmosphere at 60 °C for 48–72 h. The thin-layer chromatography was carried out in order to make sure that no trace of the monomer was present in the reaction mixture. All polymers were precipitated by pouring the reaction mixture into vigorously stirring ether. The structures of the synthesized polymers were confirmed with the spectroscopic measurements. The proton NMR spectra of these polymers indicate the presence of the —HC═CH— group in the stilbene unit confirming that cross-linking has been prevented. Also, the NMR coupling constant (~15.5 Hz for ethylenic protons) suggests that the stilbene units in these polymers are in the trans configuration.

Elemental analyses of polymers (Table 1) were carried out at Atlanta Microlab Inc. Absorption spectra of polymer films were recorded with a Shimadzu UV-3101PC scanning spectrometer. Thin layer chromatography was performed on the precoated hard-layer plate with a fluorescent indicator (J. T. Baker, Phillipsburgh). DSC thermograms were recorded under nitrogen atmosphere with a Shimadzu DSC-50 differential scanning calorimeter. NMR spectra were recorded on a Varian Gemini-300 spectrometer. Thermogravimetric data were taken with a Shimadzu TGA-50 thermal analyzer (Table 2).

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**Material Processing.** Polymer films were spin coated (at 1000 rpm) onto borosilicate glass slides using filtered solutions (~5 wt %) in DMF. All films were dried in vacuum at 100–110 °C for more than 96 h to remove the solvent residue. The thickness and the refractive index (at $\lambda$ = 632 nm) of the film were determined by the prism coupling technique.[20] All films were poled using the corona poling technique in a wire-to-plane geometry as described previously.[21,22] The films were placed on a grounded planar aluminum electrode which was heated (~5 °C/min) by two cartridge heaters. The temperature of the samples was continuously monitored with a thermocouple. When the temperature was higher than the glass transition temperature ($T_g$), a large positive voltage was applied to the top electrode which was situated 1 cm above the planar electrode. The current from the cathode was monitored by measuring the voltage drop across at 10-MΩ resistor. All polymers were poled at 105 °C at a poling current of 3 μA for a period of 15 min. The typical corona current was 3 μA. The samples were slowly (~5 °C/min) cooled to room temperature in the presence of the applied electric field.

All films were examined by optical microscopy and spectroscopy, in order to check whether the polymers were damaged in the process of poling. In the previous work[18] (polymers containing iodide and bromide counterions) it was evident that if poling was performed at temperatures above $T_g$, irreversible changes and visible damages (whitening of the films underneath the corona source) occurred in films even at a poling current of 1 μA. On the other hand, the polymers studied in the present work could be successfully poled at temperatures above their $T_g$'s, at a poling current of 3 μA, without damage. We attribute the success of poling above $T_g$ and the resulting higher degree of alignment (enhanced $\chi^{(2)}$, see below) to the reduced ionic mobility of bulky tetraphenylborate ions.

**SHG Measurements.** The second harmonic generation (SHG) measurements of poled samples were carried out with the experimental setup described previously.[18,22] In the case of in situ poling, the samples were mounted on a grounded planer aluminum electrode at the center of which a hole was carved in order to clear the path for the laser beam. The sample was kept at a fixed angle of incidence (45°). The corona source was kept 1 cm away from the planer electrode. The temperature of the sample was continuously monitored with a thermocouple which was carefully glued on to the film surface. The SHG behavior of samples were recorded as a function of applied voltage, temperature, and time. Once optimum poling conditions were formulated, films were poled according to the previously described procedure.

Poled polymers possess a $C_{\infty V}$ symmetry, and, therefore, the second-order NLO susceptibility tensor for SHG can be given as[23]

$$\chi^{(2)} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \chi^{(2)}_{xxz} & \chi^{(2)}_{xxz} & 0 & 0 \\ 0 & 0 & 0 & \chi^{(2)}_{xxz} & \chi^{(2)}_{xxz} & 0 & 0 & 0 & 0 \\ \chi^{(2)}_{zxx} & \chi^{(2)}_{zxx} & \chi^{(2)}_{zzz} & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{1}$$

If one assumes the Kleinman symmetry[24] (i.e., $\chi^{(2)}_{zxx} = \chi^{(2)}_{xxz}$), the number of independent nonzero components in the above $\chi^{(2)}$ tensor further reduces to two, namely, $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$. The $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$ can be evaluated by measuring the p-polarized SHG intensity generated in the sample by the p- and s-polarized fundamentals respectively. Since the thickness of the films used in our experiments is less than the coherence length [$I_c = 0.25\lambda/(n_{2\omega} - n_\omega)$], no Maker fringes[25] were observed in the SHG pattern. The $\chi^{(2)}_{zzz}$ values given in Table 2 were extracted by using a 1-mm-thick quartz plate as a reference for which a value of $d_{11}$ = 5.0 pm/V was assumed.[26] The error in reported $\chi^{(2)}_{zzz}$ values is estimated to be ~30%.

## Results and Discussion

A general synthetic route to these new polymethacrylates was reported previously.[18] The monomer containing TPB is stable and does not polymerize in water up to a temperature as high as 110 °C. However, if the temperature of the solution is raised to 120 °C, after a few minutes, a yellowish greasy material is formed due to severe cross-linking. Since the solubility of the monomers in hot water is very low, excess of water has to be used in the metathesis reaction. Also, the larger the number of methylene groups in the spacer, the lower is the solubility of the monomer in water. Therefore, a complete dissolution of some monomers may take up to 30 min. We obtained a percent yield of 85% in the metathesis reaction.

Neither the monomers nor the polymers show a distinct liquid-crystalline behavior as examined by DSC. The thermal behavior of a particular monomer is very similar to that of the analogous polymer. The DSC thermograms of all polymers show the presence of two endothermic peaks, beyond the glass transition temperatures. These endothermic peaks are assigned to elimination of the TPB unit and decomposition of the compounds, respectively. The elimination temperatures are consistent with the results of thermogravimetric analysis. For example, in the case of the polymer HP10B percent weight loss in the sample at 320 °C is about 38–42%. The percent weight of the TPB in the polymer is 41%. Therefore, the TPB$^-$ unit is completely eliminated from the polymer at 325 °C.

The polymer with no methylene spacer, HP0B (poly{1-methyl-4-[2-(4-(methacryloxy)phenyl)vinyl]pyridinium tetraphenylborate}) has the highest glass transition temperature (Table 2). When a spacer is introduced in the polymer between the backbone and the NLO chromophore, the $T_g$ decreases due to the enhanced motion of the main chain facilitated by the flexibility of the side chain. As described in the Experimental Section, all the polymers were poled at the same temperature (105 °C) and at the same poling current. It was seen that the SHG signal in polymers HP10B (poly{1-methyl-4-{2-[4-(10-((methacryloxy)hexyl)oxy)phenyl]vinyl}pyridinium tetraphenylborate}) and HP6B (poly{1-methyl-4-{2-[4-(6-((methacryloxy)hexyl)oxy)phenyl]vinyl}pyridinium tetraphenylborate}) saturated within 5–10 min at 105 °C, whereas the SHG signal in polymer HP0B never reached the saturation limit even after poling for a period of 3 h. It is known that in side-chain NLO 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.[11] It is necessary to perform poling at temperatures well above $T_g$'s in order to decouple the motion of the NLO chromophore and the main chain. Although the poling temperature (105 °C) is well above the $T_g$'s of polymers HP6B and HP10B it is very close to the $T_g$ of HP0B (100 °C). Moreover, in polymers HP6B and HP10B the NLO unit is separated from the main chain by flexible methylene spacers. Therefore, it is reasonable to assume that the degree of poling induced NLO chromophore alignment in polymer HP0B is less compared to that of polymers HP6B and HP10B.

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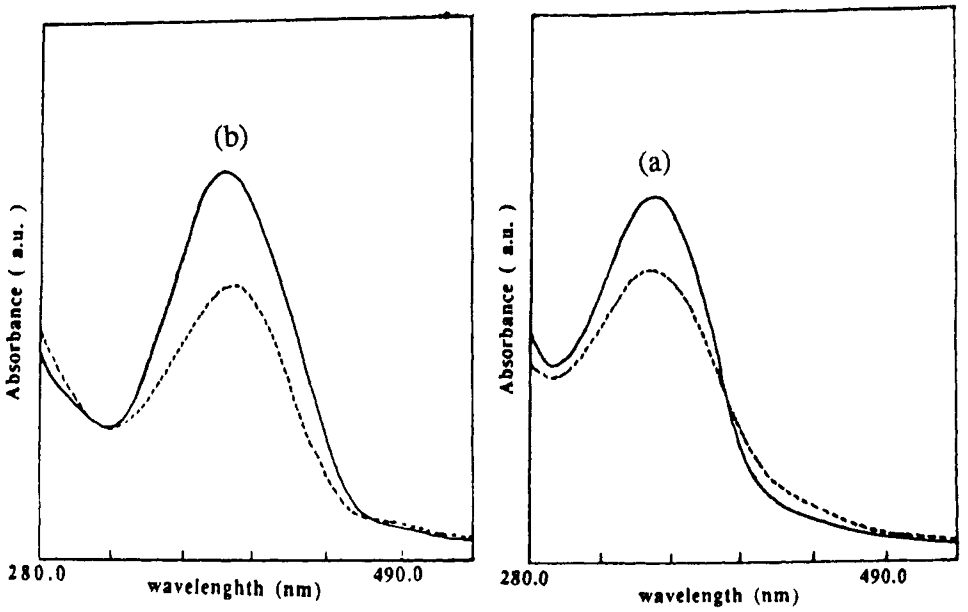

**Figure 2.** Optical spectra of polymers (a) HP0B and (b) HP10B before (solid lines) and after (broken lines) poling.

It should be noted that all the $\chi^{(2)}_{zzz}$ values of the poled polymers were calculated by assuming that $n_\omega \approx n_{2\omega} \approx n_{632}$ for each polymer. Therefore, the reported $\chi^{(2)}_{zzz}$ values should be considered approximate and good only for relative comparison. The calculated $\chi^{(2)}_{zzz}$ value of polymer HP6B is approximately 2 times larger than that of polymer HP0B. It is important to take into account the strength of the poling field when comparing the $\chi^{(2)}_{zzz}$ values of poled polymers. We are unable to measure the electric field inside the film during the process of poling. The surface potential measurements, yield similar poling fields for polymers HP0B and HP6B. However, it is not known how this field is distributed between the polymer film and the substrate. The larger $\chi^{(2)}_{zzz}$ value of polymer HP6B, in part may be attributable to improved alignment of NLO chromophores in this polymer compared to that of polymer HP0B. Also, in the case of polymer HP6B the frequency of the first electronic excited state is closer to SHG frequency than that of HP0B. Although the absorption cutoffs are at wavelengths that are well bellow the SHG wavelength, we cannot rule out the role of preresonance enhancement in polymer HP6B (Figure 2). Furthermore, in the case of polymer HP0B the donor group is a part of an ester unit (relatively weaker donor), whereas in the case of polymer HP6B donor group is a part of an ether unit (relatively stronger donor). Therefore, the relatively larger $\chi^{(2)}_{zzz}$ value in polymer HP6B compared with HP0B may also be attributed to the improved electron-donating strength of the ether group. However, this possibility seems less favorable since the $\chi^{(2)}_{zzz}$ value of polymer HP0B is 2 times larger than that of polymer HP6I which also has an ether linkage.

The calculated $\chi^{(2)}_{zzz}$ value of polymer HP6B is approximately 5 times larger than that of its iodide analogue (HP6I). However, it should be noted that these two polymers have been poled at two different temperatures. In the case of polymer HP6I poling was performed at 120 °C which is below its glass transition temperature (130 °C). It was impossible to pole this polymer, above its glass transition temperature without damage. On the other hand the polymer, HP6B, was poled at 105 °C, which is well above its glass transition temperature (72 °C). Both polymers were poled at the same poling current for the same period of time. Furthermore, the surface potential measurements yield comparable poling fields for both polymers. Again, we attribute the larger $\chi^{(2)}_{zzz}$ value of polymer HP6B to enhanced poling-induced NLO chromophore alignment, because of the ability to pole above $T_g$ and consequently to the effect of the bulky counterion, TPB. In the case of polymer HP6I a smaller counterion (iodide) can migrate relatively easily in the polymer matrix upon application of the poling field, especially at elevated temperatures, and thereby reduce the poling efficiency. It should be noted that the HP6I film (thickness = 0.1 μm) used in the previous corona poling study[18] was considerably thinner than the HP6B film (thickness = 1.3 μm) used in the present study. It is our experience that a thin film is more efficiently poled than a relatively thick film. This contrary observation again supports the role of a bulky counterion providing improved poling condition to pole above $T_g$. However, the interaction of different counterions with the chromophore may also affect the product of $\mu\beta$ and hence the value of $\chi^{(2)}_{zzz}$.

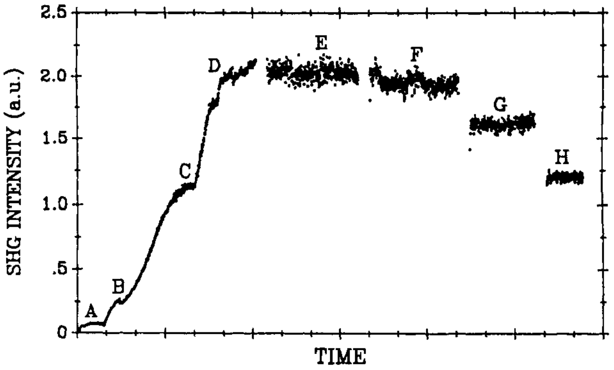

**Figure 3.** Temporal behavior of the SHG intensity of poled polymer, HP0B: (A) 37 °C, poling field on, (B) 60 °C, (C) 100 °C, (D) 105 °C, cooled to room temperature in the presence of the poling field and ultimately poling field switched off, (E) 1 week after poling, (F) 2 weeks after poling, (G) 3 weeks after poling, and (H) 1 month after poling.

The SHG measurements performed 1 month after poling (poled polymers were store inside a desiccator at ambient temperature) showed ~45% of the initial signal for

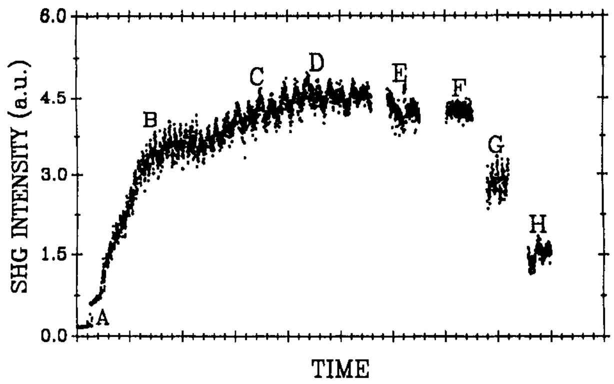

**Figure 4.** Temporal behavior of the SHG intensity of poled polymer, HP10B: (A) 60 °C high voltage on, (B) 105 °C, (C) cooled to room temperature in the presence of the applied voltage, (D) room temperature and the voltage was switched off, (E) 1 week after poling, (F) 2 weeks after poling, (G) 3 weeks after poling, and (H) 1 month after poling.

polymer HP0B and ~30% of the initial signal for polymer HP6B (Figures 3 and 4). In the case of the polymer HP6I only 55% of the initial SHG signal could be detected when measured 10 days after poling. In contrast, both the polymers HP0B and HP6B retain ~95% of the initial SHG signal during the first 2 weeks after poling. Therefore, the temporal stability of the poling-induced orientation of TPB-containing polymers is considerably improved compared to that of the iodide- or bromide-containing polymers.

## Conclusions

We have synthesized and successfully poled novel methacrylate polymers containing molecular–ionic chromophores in the side chain. The present work shows that the use of a bulky counterion (tetraphenylborate in the present study) leads to a reduced ionic mobility and then allows the polymer to be efficiently poled above its $T_g$. The poling efficiency, and hence the resulting second-order NLO susceptibility and the temporal stability of poling-induced chromophore orientation of these polymers, can be significantly improved by increasing the size of the counterion.

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