Synthesis and Characterization of Poly(*p*-phenylene)s with Nonlinear Optical Side Chains

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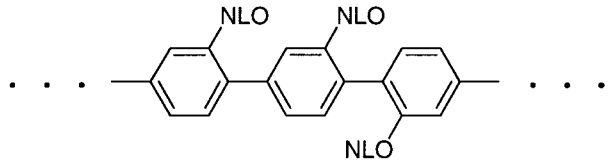
ABSTRACT: A highly substituted side chain NLO poly(*p*-phenylene) (~70.1 wt % NLOphore) has been prepared by the nickel-catalyzed coupling of 4′-(*N*,*N*-diethylamino)-2,5-dichlorobenzophenone. Poly((4′-*N*,*N*-diethylamino)-2,5-benzophenone), PDEABP, is a modest molecular weight material ($M_n = 5300$) that is thermally stable up to 400 °C with a glass transition temperature of 186 °C. The system showed virtually no decay of SHG at 100 °C hours after removal of the corona poling field. A stretched exponential was used to fit the relaxation data. At 170 °C, the SHG decayed to 1/e of its initial value with a relaxation time of $\tau = 120$ min. PDEABP exhibits a nonlinear coefficient of $d_{33} = 67.8 \pm 20$ pm/V.

Introduction

Nonlinear optically active polymers (NLOPs) exhibiting efficient second harmonic generation (SHG) rely on a noncentrosymmetric chromophore orientational distribution. The chromophores should additionally possess a large hyperpolarizability $\chi^{(2)}$ and low-lying charge-transfer excited states. Potential applications of NLOPs require exceptional thermal stability of the polymer, the chromophore, and the latter's orientational order. One synthetic strategy for making thermally robust and efficient NLOPs has been to link chromophore side chains to a stable polymer backbone. The backbone confers covalent connectivity to, and good dispersion of, the chromophore in a (glassy) environment that in turn can stabilize the chromophore orientation distribution. Current research efforts focus on processable NLOPs with high glass transition temperatures. Herein, we exploit the thermal and mechanical stability of poly(*p*-phenylene)s (**I**) as a candidate polymer backbone. Additionally, we are able to achieve a high density of NLO chromophore side chains by preparing NLO-active benzophenone monomers.



NLOPs based on polyphenylenes were previously explored by Wright and co-workers,[1] who published preliminary investigations of relatively low molecular weight ($M_n = 6000$) poly(*p*-phenylene)s with side chains consisting of 2-(4-(dimethylamino)phenyl)ethynyl phenyl sulfone NLO chromophores.

No SHG signal was observed by Wright et al. when the samples were poled, and the authors attributed this result to restricted mobility of the NLO chromophore and the high-T_g, stiff, rodlike phenylene backbone—the rotationally restricted chromophores appeared to be unable to respond to the applied field. Following methods of co-workers regarding the synthesis of high molecular weight poly(*p*-benzophenone),[2] we have prepared a poly(*p*-phenylene)-based NLOP that has a high T_g, a large d_{33}, and stable, electric field-induced, polar order.

Results and Discussion

Monomer Synthesis. Our target chromophore was the monomer 4′-(*N*,*N*-diethylamino)-2,5- dichlorobenzophenone. One of the benefits in the design of the polymers presented here is the high NLO chromophore content—70.1 wt % in the case of poly((*N*,*N*-diethylamino)-2,5-benzophenone), PBEABP. An initial effort to make the targeted monomer was adapted from the synthetic procedure for 2,5-dichlorobenzophenone, reacting 4-(*N*,*N*-diethylamino)benzoyl chloride with 2,5-dichlorobenzene.[2] However, the exploratory reaction of 4-(*N*,*N*-diethylamino)benzoic acid with thionyl chloride provided only 11% of the acyl chloride; the Friedel−Crafts condensation of the chloride was the dominate product.[3] In a second approach, only 10% of the crude desired monomer was afforded by the reaction of 2,5-benzoyl chloride with *N*,*N*-diethylaniline in the presence of catalytic amounts of aluminum chloride; the major condensation product was formed by the elimination of ethyl chloride.[4] The desired monomer could, however, be prepared in 52% yield by the condensation of 2,5-dichlorobenzanilide with *N*,*N*-diethylamiline in the presence of phosphorus oxychloride as outlined in Scheme 1. Large platelike crystals of the monomer can be recrystallized to high purity from ethanol.

Polymer Synthesis and Characterization. Nickel-catalyzed coupling of the monomer in the presence of zinc provided a relatively low molecular weight poly(*p*-phenylene) derivative ($M_n = 5300$). Various attempts to increase the molecular weight—including excessive drying and optimal purity of all starting materials, rigorous exclusion of moisture and oxygen, and manipulation of the ratio of starting materials to each other—have been ineffective. The molecular weights we report here for PDEABP are similar to those reported by Wright et al. for their functionalized poly(*p*-phenylene)s. To our knowledge, only one other study reports the Ni-(0) coupling of amine-containing aryl dichlorides, and the authors also obtained modest molecular weights.[5] Table 1 summarizes the properties of PBEABP as well

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Scheme 1

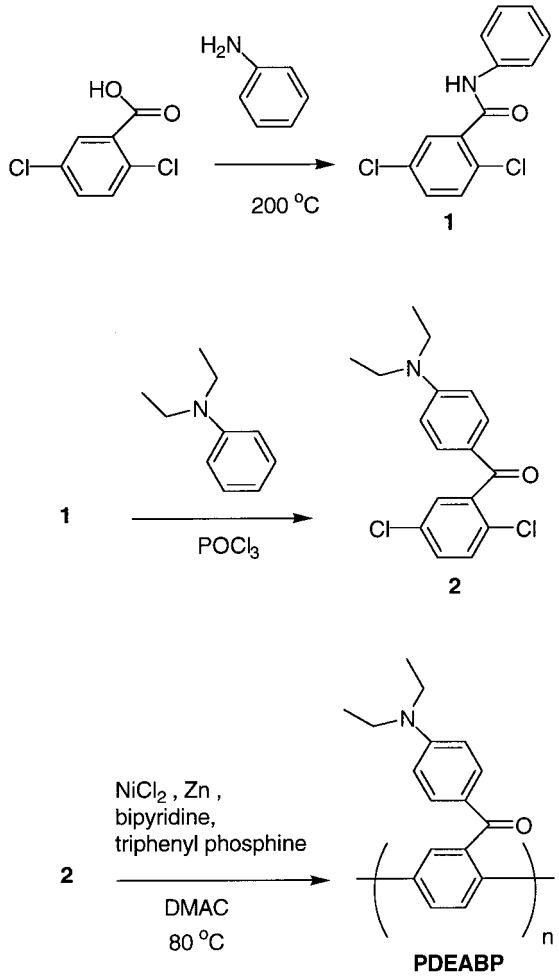

Table 1. Physical Properties of Substituted Poly(*p*-phenylene)s

polymer[a]	T_d (°C, 5%)	T_g (°C)	λ_{max} (nm)	M_n ($\times 10^3$)	PDI
PVPK		58	348		
PBP		160	365		
PDEABP	431	186	393	5.3	2.1

[a] Abbreviations: PVPK = poly(vinyl phenyl ketone); PBP = poly(*p*-benzophenone); PDEABP = poly(4′-(*N*,*N*-diethylamino)-2,5-benzophenone).

as the model compounds of poly(*p*-benzophenone) and poly(vinyl phenyl ketone).

Despite the relatively low molecular weights reported for PDEABP, contiguous solid films of high optical clarity were formed on glass substrates. Thermogravimetric analysis showed PDEABP is thermally stable up to 430 °C where a 5% weight loss was observed in nitrogen atmosphere. Decomposition data were not readily available for the model compounds used in this study, but the values are expected to be lower than 430 °C due to the more flexible backbone of PVPK and the lower transition temperature of PBP. (The T_g of PBP has been shown to scale with molecular weight and decomposition temperature.[6]) PBP reported herein was provided from the fractionation of high molecular weight polymer.[2] The T_g values are well-defined (Table 1) for the phenylene-based polymers; in addition, PVPK polymer melts at 82 °C. The phenylene backbone polymers exhibit T_g values that are an order of magnitude higher than that of PVPK.

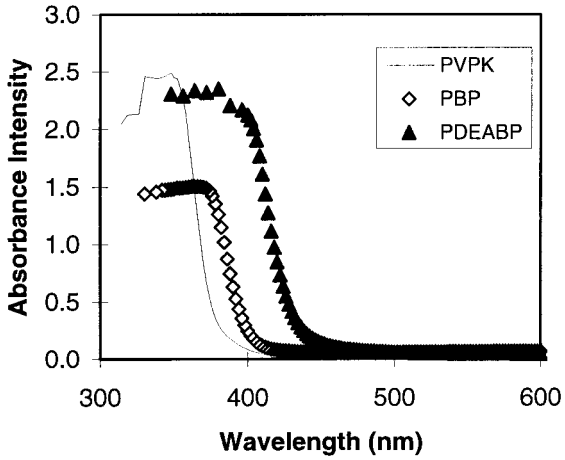

Figure 1. UV−vis spectra of PDEABP, PBP, and PVPK films.

Table 2. Second-Order NLO Properties of Substituted Poly(*p*-phenylene)s

polymer	sample thickness, μm	chromophore density, wt %	d_{33}, pm/V	poling temp, °C
PVPK	82	79.5	1.1 ±0.1	62
PBP	1	58.0	3.7 ± 0.2	156
PDEABP	1.5	70.1	67.8 ± 20	182

The second harmonic generation (SHG) wavelength utilized in this study (532 nm) is well beyond the absorption regime for the polymers as shown in Figure 1. Hence, only nonresonant effects are expected to contribute to the SHG signal. From UV−vis analysis of PDEABP films, the absorption maximum is around 393 nm. PBP has an absorption maximum of 365 nm while that of PVPK is 348 nm.

Nonlinear Optical Properties. The NLO chromophore is the same in PVPK and PBP; the only difference between the two NLOPs is the degree of flexibility in the respective backbones. The d_{33} value for PBP is 3.7 ± 0.2 pm/V—a factor of 2 higher than that of PVPK (see Table 2). (The error in the nonlinear coefficient is due to the uncertainty in the refractive indices.) The addition of the diethyl amino group to the benzoyl chromophore increases the d_{33} coefficient by more than an order of magnitude, from 3.7 pm/V for PBP to 67.8 ± 20 pm/V for PDEABP. Previous reports[2] have shown that the regiochemistry of substituted *p*-phenylenes changes as a function of the synthetic procedure. When the polymerization involves a bipyridine ligand (as in the current study), a more regular head-to-tail polymer microstructure is obtained. Thus, the d_{33} value of 67.8 pm/V reported herein most likely reflects the NLO properties of the more stereoregular polymer—a value subject to increase at higher poling temperatures and DC poling fields. The d_{33} value reported is comparable to "state of the art" side chain NLO polymers.[9] The dialkylamine is a better donor than the benzene ring alone, and the conjugation length has been extended in the case of PDEABP. By replacing the carbonyl oxygen of PDEABP with a better acceptor group such as vinyldicyano and exchanging the alkyl groups on the amine for phenyl groups, the hyperpolarizability of the monomer would presumably increase.

Polar Order Stability Measurements. The temporal stability of the polar chromophore orientational distribution after removal of the external poling electric field was examined at sub-T_g temperatures by monitoring the SHG intensity versus time. The polar distribu-

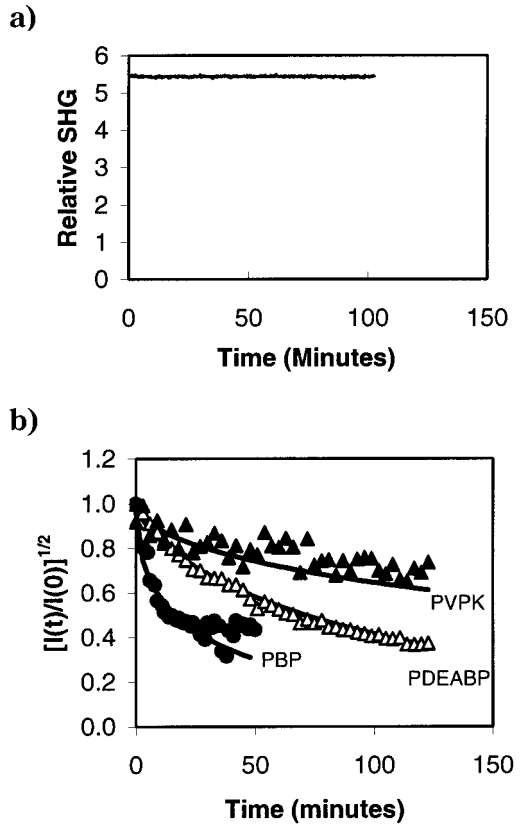

Figure 2. (a) Temporal stability of NLO chromophores in PDEABP observed at 100 °C. (b) Relaxation of NLO chromophores in PDEABP (observed at 170 °C), PVPK (observed at 38 °C), and PBP (observed at 144 °C). The experimental relaxation curves were fit to eq 1 (solid line) to determine σ and β. (The SHG relaxation data for PDEABP were acquired on the same sample after conducting a stability experiment at 100 °C for 100 min and a relaxation experiment at 143 °C for 400 min.)

tion of chromophores in PDEABP is clearly stable at elevated temperatures (100 °C) on a time scale of tens of hours (Figure 2a); 100 °C is 86 °C below the T_g of PDEABP (T_g = 186 °C). The relaxation of the chromophore orientations in PVPK, PBP, and PDEABP was compared by monitoring the decay of the SHG signal at two temperatures. A relaxation time τ was obtained by fitting the SHG decay to the stretched exponential function (1) where $I(t)$ is the SHG signal intensity at observation time t for a set temperature.[7,8]

$$[I(t)/I(0)]^{1/2} = \exp[-(t/\tau)^{\beta}] \qquad (1)$$

The magnitude of $[I(t)/I(0)]^{1/2}$ reflects the degree of chromophore orientational order in the sample. The time τ is a measure of the rate of decay of orientational order; β describes the breadth of the distribution of relaxation time where $\beta = 1$ implies simple exponential decay and $\beta < 1$ implies that the second 1/e decay period is longer than the initial 1/e decay (used to determine τ). There are other functional forms used in the literature, and the optimum functional form is still a matter of discussion.[9]

Figure 2b shows the SHG decay observed for PDEABP at 170 °C, PBP at 144 °C, and PVPK at 38 °C as well as the corresponding stretched exponential fits. The observed stabilities as determined from fitting the decay curves are quite different for the three polymers. In Table 3 we show relaxation times for PDEABP, PBP, and PVPK. The tabulated τ values are obtained either by fitting the SHG decay curves measured at $T_g - 16$ (shown in Figure 2b) or by extrapolating the measured τ values to 25 °C. Within the phenylene-type polymer series, a higher T_g value corresponds to a longer τ (25 °C) value; PDEABP displays the longest relaxation time at ambient temperatures. Contrasting τ values for our polymers with the polyimides reported by Verbiest et al., we note that the latter polyimides are 2 or more orders of magnitude more stable than the polyphenylenes (PBP and PDEABP) at 25 °C. On the other hand, at elevated temperatures the $\tau(T_g - 16$ °C) value for PDEABP is slightly longer than the extrapolated $\tau(T_g - 16$ °C) for the polyimidies PI-3 and PI-1 (see ref 9); the polyimides generally have T_g values above 225 °C. The thermal stability of the SHG near T_g for the polyphenylenes is undoubtedly related to the restricted backbone mobility in this class of NLOPs in conjunction with the conformationally restricted linkage of the NLO chromophore to the polyphenylene backbone. Restricted chromophore mobility in PVPK must similarly account for its unusually long τ values near T_g.

Table 3. Sub-T_g Relaxation Times τ for Phenylene-Type NLOPs and Polyimides

NLOP	T_g, °C	τ (25 °C), s	τ (T_g − 16 °C), s
PVPK	58	5.5	4.9
PBP	160	7.5	3.3
PDEABP	186	8.8	3.8
PI-1	228	30.6 ± 0.25	0.0 ± 0.25
PI-2	252	26.3 ± 0.25	3.4 ± 0.25
PI-3	350	15.2 ± 0.25	2.4 ± 0.25

Conclusions

The poly(*p*-phenylene)-based nonlinear optical polymer, PDEABP, prepared in this study exhibits a large second-order nonlinear optical value as well as impressive stability of the electric-field-induced polar state. At 170 °C, the polymer system relaxes to 1/e of its initial value in τ = 120 min. Advances in identifying chromophores with large hyperpolarizabilities and thermal stabilities have already taken place,[10,11] and this knowledge could be exploited with the more rigid backbone structures of poly(*p*-phenylene)-based NLOPs considered here.

Experimental Section

Methods. The preparation of poly(*p*-benzophenone) has been reported elsewhere.[2] Poly(vinyl phenyl ketone) was purchased from Aldrich. Triphenylphosphine (Aldrich) was purified by crystallization from hexane, and 2,2′-bipyridine (Aldrich) was recrystallized from ethanol. Nickel chloride and zinc powder, purchased from Cerac, were both of high purity (>99%) and used as received.

All intermediates were characterized by a 400 MHz Varian instrument for ^{1}H and ^{13}C NMR. Monomer purity was determined by Hewlet Packard GC/MS with a 5972 series mass selective detector. Thermal stabilities of the polymers were determined by TGA (Seiko SSC/5200) heating at a rate of 10 °C/ min. DSC analyses (Seiko SSC/5200) were performed by heating at a rate of 20 °C/min under nitrogen flushing, cooling at 40 °C/min, and heating a second time at 10 °C/min. The middle point of the inflection area detected on the second heat was taken to be T_g. Molecular weights of the polymers were determined by GPC size exclusion chromatography where polystyrene standards were used as references.

The second-order NLO efficiencies of the spin-coated polymeric thin films were measured by using the second harmonic generation technique in which a Q-switch ND:YAG laser beam, operating at 1064 nm with a pulse width of ~10 ns and a 10

Hz repetition rate, was used as the fundamental source. All measurements were made relative to a quartz reference, which also monitors the laser power stability. The second-order NLO coefficients, d_{33}, were determined by nonlinear least-squares regression analysis of the Maker Fringe pattern[12] using the ASYST computer program ANALYSIS.TXT.[13]

Analysis of the relaxation data was performed using commercially available software (Microsoft Excel, Version 6.0). A simple stretched exponential model has been used with the best fit resulting in the largest statistical correlation value. For poled polymer films, the experimentally monitored SHG intensity normalized to unity at $t = 0$ is related to the second harmonic coefficient, via eq 2:

$$\frac{d_{33}(t)}{d_{33}(0)} = \left(\frac{I^{2\omega}(t)}{I^{2\omega}(0)}\right)^{1/2} \quad (2)$$

Preparation of 2,5-Dichlorbenzanilide (1). 2,5-Dichlorobenzoic acid was commercially available as a white lumpy solid that was purified by crystallization from ethanol. Aniline (Aldrich) was distilled under vacuum from potassium hydroxide. According to the modified procedure of Webb,[14] 2,5-dichlorobenzoic acid (29.97 g, 0.156 mol) was added to a round-bottom flask with aniline (25.58 mL, 0.280 mol) and heated quickly to 200 °C in an oil bath. At approximately 210 °C, aniline distilled over to a collection flask. The reaction flask was cooled below 180 °C, and an additional 12 mL of aniline was added. The temperature was again raised until excess aniline condensed in the collecting flask. The hot reaction mixture was then poured into an evaporating dish and allowed to cool. The light purple solid material was grounded with a mortar and pestle, stirred in 5% hydrochloric acid solution for 1 h, and filtered to collect the solids. This procedure was repeated three times with dilute hydrochloric acid, twice with 1 M sodium hydroxide, and once with water. The crude solids were left to air-dry overnight before drying in a vacuum oven until a constant weight measurement was obtained (18.67 g, 45% yield); mp 132.2 °C (DSC). ^{1}H NMR ($CDCl_3$): σ (ppm) 8.00 (s,1,-CON*H*Ar) 7.90 (s, 1, aromatic-H) 7.78 (d,1, ortho aromatic −H of anilide) 7.54 (t,1, meta aromatic −H of anilide) 7.40 (s, 2, aromatic-H) 7.34 (t,1, para aromatic-H of anilide). ^{13}C NMR ($CDCl_3$): σ (ppm) 137.1 (C-1) 136.5 (C-1′) 133.2 (C-2) 131.5 (C-6) 130.0 (C-2′) 129.1 (C-3, C-4) 125.1 (C-3′) 120.5 (C-4′).

Preparation of 4′-(*N*,*N*-Diethylamino)-2,5-dichlorobenzophenone (2). 2,5-Dichlorobenzanilide (18.00 g, 0.067 mol) was reacted with *N*,*N*-diethylaniline (35,17 mL, 0.227 mol) and phosphorus oxychloride (8.58 mL, 0.092 mol) according to a procedure adapted from the literature.[4,15] The resulting dark green material was purified by repeated crystallization from ethanol to afford pale green plates (8.99 g, 41.1% yield); mp 73 °C (DSC). ^{1}H NMR ($CDCl_3$): σ (ppm) 7.66 (d,1) 7.35 (m, 3) 6.62 (d, 1) 3.45 (q, 2, CH_2) 1.23 (t, 3, CH_3). ^{13}C NMR ($CDCl_3$): σ (ppm) 190.9 (C═O) 152.0 (C-1′) 141.36 (C-1) 132.9 (C-6) 132.6 (C-2) 131.0 (C-3) 130.1 (C-2′) 129.36 (C-5) 128.6 (C-4) 122.74 (C-4′) 110.36 (C-3′) 44.68 (CH_2) 12.52 (CH_3), GC/MS (CH_3-$COCH_3$) t(min) 12.441 (100%).

Polymerization. Ni(0) coupling chemistry was used to polymerize the rigorously purified monomer.[2,16−18] 4′-(*N*,*N*-Diethylamino)-2,5-dichlorobenzophenone (12.0 g, 37.4 mmol), nickel chloride (0.0482 g, 0.374 mmol), triphenylphosphine (3.80 g, 14.5 mmol), 2,2′-bipyridine (0.0700 g, 0.448 mmol), and zinc powder (6.71 g, 103.2 mmol) were added to a three-arm 100 mL long neck flask inside an argon atmosphere drybox. The flask was equipped with a stirring rod and two rubber septa. After removal from the drybox, the flask was connected to an argon bubbler and a mechanical stirrer. Approximately 50 mL of dry DMAC (freshly distilled from calcium hydride) was added by syringe into the flask, and the whole solution was heated to 80 °C in an oil bath. After 18 h, the reaction was cooled and precipitated into acetone. The resulting solid was filtered and washed with dilute HCl, water, and acetone to afford a yellowish green material (7.23 g, 77.1% yield). UV−vis (film) λ_{max}/nm 393; T_g (DSC) = 186.2 °C; M_n(SEC, polysytrene calibrations) = 5.293×10^3; $M_w/M_n = 1.8$. ^{1}H NMR (400 MHz, $CDCl_3$): σ 8.41 (br m, 3H), 6.80 (br s, 1H), 3.92 (br, 2H, CH_2), 1.45 (br s, 3H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$): σ 196 (C═O), 152 (C-1′), 141 (C-1), 133.3 (C-6), 133 (C-2), 132 (C-3), 130 (C-2′), 129.2 (C-5), 127.2 (C-4), 125 (C-4′), 110.1 (C-3′), 44.7 (CH_2), 12.9 (CH_3). Under a polarizable microscope, shear-induced birefringence was observed around 295 °C; further heating lead to complete decomposition around 350 °C.

Polymer Thin Films. Polymer thin films were prepared by two methods: (1) Poly(vinyl phenyl ketone) was manually pressed into a film at 90 °C between a microscope coverslip and indium tin oxide (ITO) pretreated glass substrate; the film was quickly quenched to room temperature, and the coverslip was removed. (2) Solutions of poly(*p*-benzophenone), thiophene, and 2,5-benzophenone copolymers and PDEABP were prepared by dissolving ∼40 mg of the respective polymer in ∼2 mL of chloroform (2.7 wt %). After passing through a 0.4 μm filter, the solution was spin-coated onto ITO glass substrates. As a typical example, the films were spun at 1500 rpm for 100 s and then dried under vacuum close to their respective T_g values for 24 h.

Film thickness measurements were performed by a profilometer. These measurements were then used to roughly determine the refractive index of each film at 543 and 1100 nm by the M-line waveguide technique (Metricon Instruments). The refractive indices of PVPK were taken from the literature.[19]

For poling experiments, the thin films were heated close to their respective T_g over a 30 min period with the application of a −9.02 kV dc electric field to a tungsten needle 2.6 cm from the sample surface. After a 30 min poling period, the samples were cooled to room temperature over a 30 min period in the presence of the dc field. The polymer films were allowed to sit at room temperature for several hours and grounded with a second ITO-coated glass plate before SHG characterization studies were conducted. This procedure ensured that surface charge effects induced by the electric field were removed.[20]

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