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Λ-Type Main-Chain Polymers for Second Harmonic Generation

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A novel series of main-chain polymers from Λ-shaped molecules were synthesized by nucleophilic displacement polymerization. These polymers were prepared from bis(4-fluoro-3-nitrophenyl) sulfone with aliphatic and aromatic diamines in aprotic solvents. These main-chain polymers derived from Λ-shaped molecules are amorphous, processable, contain high density of nonlinear optical-active chromophores, and exhibit high glass transition temperatures. The corona discharge poled polymer films showed large second-order nonlinear optical coefficients and good temporal stability at elevated temperatures. Before poling, all these polymers show positive birefringence. For polymers having rigid spacer units, even after poling, the refractive indexes of n_{TE} are still larger than those of n_{TM}. The large positive birefringence indicates a preference of polymer chains to orient along the film surface.

Introduction

Poled amorphous polymers are attractive for nonlinear optical (NLO) applications due to their large NLO coefficients, fast response time, intrinsic tailorability, and processibility for integrated optics.[1–4] Three types of polymer systems have been studied for this purpose: guest–host systems,[5–7] NLO-dye grafted polymers,[8–12] and main-chain polymers.[13–15] In guest–host systems, NLO chromophores are dispersed in a polymer host matrix by dissolving polymers and NLO-active molecules in a suitable solvent, this process is very simple, but the amount of NLO dye that can be dissolved is limited to about 10%. This severely limits the optical nonlinearity. Moreover, the dissolved dye crystallizes and segregates, decreasing the second-order nonlinear optical effects as a function of time. In NLO-dye grafted polymers, large concentrations of NLO-active groups can be attached as a side chain to the polymer backbone. The side-chain polymers are attractive because they show large optical nonlinear coefficients owing to the high concentration of NLO-active chromophores. By variation of the side groups, spacer, and backbone, their mechanical, thermal, and other properties can be modified. Though NLO dye grafted polymers show better temporal stability than that of guest–host systems, they still suffer from orientation relaxation resulting into a decrease in NLO activity.

A very attractive approach to NLO polymers is constructing the head-to-tail structures. The first NLO head-to-tail main-chain polymer was reported by Hall and co-workers,[16] and shortly thereafter Lindsay and co-workers prepared other NLO main-chain polymers.[17] It was expected that such head-to-tail structure should greatly increase dipole moment and show excellent temporal stability after poling. Williams et al.[18,19] reported significant enhancement of dipole moment and hyperpolarizabilities in a series of materials based on 2-cyano-3-(4-hydroxyphenyl)-2-propenoate esters using the electric-field-induced-second harmonic generation (EFISH) method in solution, but the results on polymer films were not as expected. A variation to the head-to-tail main-chain NLO polymer approach was reported by Lindsay and co-workers.[20] In their strategy, an

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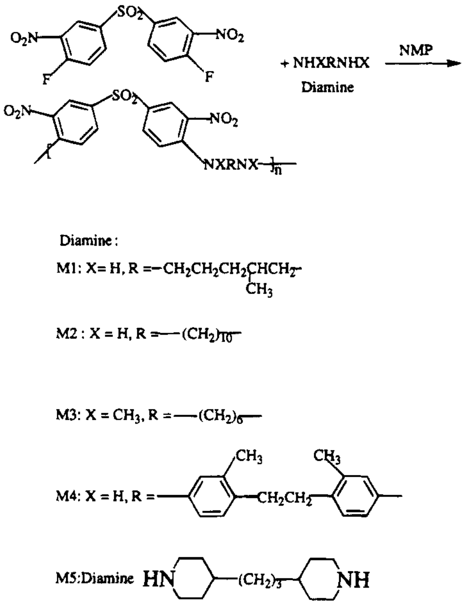

Figure 1. Schematic diagram of synthesis of poly(arylamines).

accordion (head-to-head, tail-to-tail) structure was proposed.

Our group has pointed out that organic molecules with Λ-type charge-transfer conformation easily form noncentrosymmetric crystal structure. In addition, in Λ-shaped molecules, the off-diagonal hyperpolarizability component is larger than the diagonal components, and increase the effective phase-matched second harmonic generation.[21-22] However, like other organic NLO materials, the crystal growth of Λ-shaped materials into large size and good optical quality is not easy.

Here, we describe a novel series of main-chain polymers in which Λ-shaped charge-transfer molecules have been incorporated into the polymer backbone as a part of the main chain. The Λ-shaped chromophores in the main chain can be effectively oriented by corona discharge poling and they show large SHG. In this paper, we report the synthesis, linear, and nonlinear optical properties of main-chain polyarylamines derived from Λ-shaped chromophores.

Experimental Section

Polymer Synthesis. All the reagents were commercially obtained (Tokyo kasei) and used without further purification. The solvents were distilled under reduced pressure before use. Bis(4-fluoro-3-nitrophenyl) sulfone (BFNPS) was polymerized with both aliphatic and aromatic diamines to prepare corresponding polyarylamines. In general, equimolar ratios of the desired BFNPS and diamines were mixed at room temperature in a polar aprotic solvent such as *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), or dimethyl sulfoxide (DMSO). The mixture immediately turned red and was heated over night at 50–80 °C. The schematic reaction is shown in Figure 1, where X is a hydrogen or alkyl group, and R is a spacer group. A representative example of polymerization and purification is given here for the preparation of M_1 polymer from 2-methyl-1,1-diaminopentane (MDAP) and BFNPS. A three-necked flask was charged with 1.72 g (5 mmol) of BFNPS, 0.58 g (5 mmol) of MDAP, and 20 mL of DMSO; the red solution thus obtained was stirred at 50 °C for 24 h. The polymer was purified by precipitation in water and washed thoroughly with methanol, then was further purified by extraction in a Soxhlet extractor with water, and dried at 100 °C in a vacuum oven over night. The yield of the polymer was 1.9 g (96%). All of these polymers were yellow powder and can be easily dissolved in NMP; M1 and M3 polymers were also soluble in DMSO and DMF.

The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with polystyrene as a reference and NMP as solvent ($M_w = 4.0 \times 10^4$–7.6×10^4, $M_n = 2.8 \times 10^4$ to 5.6×10^4, with $M_w/M_n < 1.5$). The chemical structures were characterized by elemental analysis and were further confirmed by ^{13}C NMR spectroscopy.

M1: Anal. Calcd for $C_{18}H_{20}N_4O_6S$: C, 51.42; H, 4.76; N, 13.33. Found: C, 51.24; H, 4.81; N,13.32. ^{13}C NMR (NMP) δ 147.8, 133.3, 130.3, 126.6, 116.8, 43.5, 32.4, 31.7, 26.4, 17.2.

M2: Anal. Calcd for $C_{22}H_{28}N_4O_6S$: C, 55.46; H, 5.88; N, 11.76 Found: C, 55.07; H, 5.85; N, 11.81. ^{13}C NMR (NMP) δ 147.9, 133.9, 131.0, 127.2, 116.8, 43.5, 41.2, 28.8, 26.9, 17.8.

M3: Anal. Calcd for $C_{20}H_{24}N_4O_6S$: C, 53.57; H, 5.36; N, 12.50. Found: C, 52.96; H, 5.39; N, 12.56. ^{13}C NMR (NMP) δ 147.9, 136.9, 131.1, 128.7, 127.6, 119.4, 53.9, 40.0, 26.8, 26.0.

M4: Anal. Calcd for $C_{28}H_{24}N_4O_6S$: C, 61.76; H, 4.41; N,10.29. Found: C, 61.02; H, 4.46; N, 10.23. ^{13}C NMR (NMP) δ 146.9, 139.1, 137.8, 136.0, 133.9, 132.4, 130.9, 129.0, 126.9, 123.9, 118.3, 33.8, 18.8.

M5: Anal. Calcd for $C_{25}H_{30}N_4O_6S$: C, 58.30; H, 5.83; N, 10.89. Found: C, 57.85; H, 5.87; N, 10.88. ^{13}C NMR (NMP) δ 148.8, 138.8, 132.2, 130.3, 127.1, 122.0, 50.9, 36.6, 35.0, 31.9, 23.5.

Film Preparation. Polymer films for refractive indexes and SHG Maker fringe measurements were prepared by spin coating on glass slides from an NMP solution with a concentration of 20% by weight. The films for absorption measurement were prepared by spin coating on a ITO glass, the spinning rate was in the range 1500–3000 rpm. The spin coated films were dried in a vacuum oven for two days. The thickness and refractive indexes of the films were determined by the *m*-line method.[23-24]

Corona Poling. These main-chain polymers were poled by corona poling method.[25] The polymers were spin coated on a slide glass, and the evaporated aluminum layer on the other side was used as the ground electrode. Corona poling discharge is a partial breakdown of air and is initiated by a discharge in an inhomogeneous electric field; ions are created and deposited on the top of the surface of polymer films. In the experiment, 5–8 kV positive electric voltage was set to the tungsten needle which was suspended about 1 cm above the ground aluminum electrode. The corona current was fixed at 2 μA; the poling temperature was kept near the glass-transition temperature (T_g) of the polymers.

Second-Harmonic Generation Measurements. The SHG experiment was conducted to determine the second-order nonlinear optical coefficients, and temporal stability of poling-induced nonlinearity at above room temperature. The setup for SHG measurement is similar to that described earlier by us.[10] The sample was mounted on a designed hot-stage which was computer controlled. A single crystal of Y-cut quartz was used as a reference ($d_{11} = 0.4$ pm/V). The polarized beam of a Q-switched Nd:YAG laser (1064 nm, 10 ns/pulse, 10 Hz) was illuminated to the sample on the stage after being polarized and focused by a polarizer and a lens, respectively. The second harmonic (SH) signal was detected by photomultiplier tube and amplified. The Maker fringe data were analyzed by fitting

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Table 1. Basic Properties of Poly(arylamines)

polymer	λ_{cutoff}[a] (nm)	T_g (°C)	T_{da} (°C)	M_w ($\times 10^{-4}$)	M_n ($\times 10^{-4}$)	M_w/M_n
M1	500	130	270	7.6	5.6	1.36
M2	500	78	275	4.0	2.8	1.43
M3	510	105	265	4.2	3.0	1.40
M4	540	192	260	5.2	3.8	1.37
M5	510	148	253	6.5	4.6	1.41

[a] The cutoff wavelengths defined as the onset wavelength of absorption peak at the longer wavelength side, the decomposition temperatures defined as the onset of exothermic peaks in DTA diagrams.

parameters to the appropriate theoretical formula. The second-order nonlinear coefficients, d_{33} and d_{31} were evaluated from these calculations. The poling voltage, temperature, and time were varied to select the best poling conditions. The temporal stability of poling-induced nonlinearlity at above room temperature was studied by in situ SHG measurements.

Results and Discussion

Synthesis Consideration. The molecular weights of poly(arylamines) are listed in Table 1 that show high molecular weight polymers. Some other polyarylamines prepared using bis(4-chloro-3-nitrophenyl) sulfone with other diamines have been reported by Imai et al.,[26] who found the best reacting temperature of about 100 °C. To get polymers with high molecular weights, several kinds of acid acceptor have been used as catalysts in their experiments. However, for the polymers prepared from aliphatic diamines, high molecular weights were not obtained in their experiment. This is because the basic properties of aliphatic diamines function as the acid acceptors. It is well-known that in such kind of nucleophilic substitution reaction, fluorine is an easier leaving group than chlorine. By using bis(4-fluoro-3-nitrophenyl) sulfone reacted with diamines under very mild conditions, high molecular weight polymers were obtained in our experiments. These polymer samples were amenable because of their amorphous morphology, and the ability to prepare optical-quality thin films on glass substrate and free standing films.

Optical Absorption Properties. The absorption spectra of polyarylamine films spin coated on ITO glass were measured with a UV–visible spectrometer in the wavelength 300–800 nm. The cutoff wavelengths of these polymers are summarized in Table 1. Figure 2 shows the absorption spectrum of M1 polymer. The results indicate that after poling, a decrease in absorbance (hypochromic shift) was observed in all polymers, though the shapes of absorption spectra before and after poling were similar. When the poled M1 polymer film was heated at 130 °C for 48 h, absorbance increased to 0.9 of that of unpoled films, which indicates that the decrease of absorbance is due to the reversible alignment of chromophores.

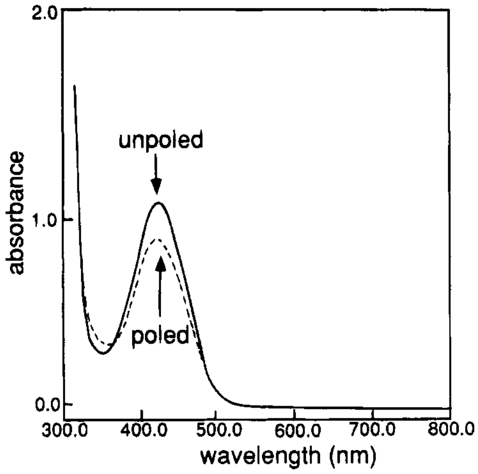

Figure 2. UV–vis absorption spectra of the M1 polymer before and after poling.

During corona poling, a surface charge is accumulated on the surface of the polymer films with opposite charge at the planar electrode,[27] this introduces a large electrostatic field in the film that interacts with the chromophores of the polymer. The static field aligns the dipoles in the direction of the poling field, which leads to a change in the intensity of the absorption spectrum, i.e., to dichroism. The poling-induced absorption decreases for polymers containing long flexible spacer groups. They are reaching easier the poling equilibrium states than polymer with rigid spacer units. One parameter to express the extent of poling-induced orientation is order parameter shown in eq 1. Here A_p

$$\Theta = 1 - A_p/A_0 \qquad (1)$$

is the absorbance of the poled sample measured with electric poling field perpendicular to the polymer film, A_0 is the absorbance of an unpoled sample. The largest order parameter was observed in M3 polymer. The absorption maxima and cutoff wavelengths are related to the strength of donor groups and the length of the π-conjugation system. For M_1 and M_2 polymers, the donor is an N-substituted amino group, which has a cutoff wavelength of about 500 nm, while M_3 and M_5 polymers have a stronger N,N-disubstituted amino donor group, their cutoff wavelength was 510 nm. The longest cutoff wavelength is 540 nm in M_4 polymer, since an aromatic diamine was used as a spacer unit, forming a longer π-conjugated system over other poly(arylamines).

Thermal Analysis and X-ray Spectra. Thermal properties of these polymers are summarized in Table 1. The glass transition temperatures of these poly(arylamines) have a large difference due to the spacer groups. The polymers with longer spacer units have relative lower T_g since the long flexible spacer groups are easy to rotate. DTA and TG show that the decomposition temperatures of these polymers do not have large difference in a nitrogen atmosphere, this may be related to the dissociation of the bonds between nitrogen and benzene carbon atoms or the bonds with sulfone groups. Before decomposition, no melting point was observed in these polymers, indicating that they are amorphous. Furthermore, wide-angle X-ray diffraction of the films obtained by using nickel-filtered Cu Kα radiation revealed a broad halo that confirms they are completely amorphous.

Refractive Indexes. The knowledge of refractive indexes is very important parameter in evaluation of the suitability of a given material for nonlinear optical applications. Refractive indexes are necessary for the determination of phase-matching conditions and for the

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Table 2. Refractive Indexes of Poly(arylamines) before and after Poling at Different Wavelengths

sample	wavelength (nm)	n_{TE} (unpoled)	n_{TM} (unpoled)	n_{TE} (poled)	n_{TM} (poled)
M1	532	1.7466	1.7377	1.7427	1.7485
	632.8	1.6968	1.6896	1.6887	1.6912
	1064	1.6504	1.6424	1.6474	1.6483
M2	532	1.7090	1.7062	1.7073	1.7103
	632.8	1.6682	1.6602	1.6654	1.6685
	1064	1.6401	1.6365	1.6381	1.6385
M3	532	1.7109	1.7059	1.7027	1.7038
	1064	1.6415	1.6337	1.6386	1.6340
M4	632.8	1.7302	1.7015	1.7289	1.7059
	832.5	1.6942	1.6689	1.6873	1.6699
	1064	1.6729	1.6512	1.6654	1.6541
M5	532	1.6973	1.6749	1.6966	1.6868
	632.8	1.6588	1.6413	1.6551	1.6442
	832.5	1.6415	1.6286	1.6369	1.6223
	1064	1.6318	1.6140	1.6268	1.6164

calculation of nonlinear optical coefficients. Several phase-matching methods have been developed based on the nature of refractive indexes, such as the phase matching by birefringence in single crystals,[28] phase-matching by the anomalous dispersion of refractive indexes in some special systems;[29] and phase matching by modal dispersion in thin films.[30] In our experiment, the refractive indexes of polymers were measured by the *m*-line method in a slab waveguide configuration;[31] the results are listed in Table 2. It is well-known that the refractive indexes of materials are determined by the nonresonant background n_0 and the two-level charge transfer-resonance enhancement δn.[32] In these poly(arylamines), the refractive indexes are related to the spacer group lengths, chromophore density, and charge-transfer absorption wavelengths. For example, the M2 polymer has 10 methylenes as the spacer group, the refractive indexes of n_{TE} of unpoled polymer at 1.064 μm is 1.6401. For the M1 polymer, the spacer group is five methylenes; the chromophore density of M1 polymer is higher than that of M2 polymer, therefore the M1 polymer has higher refractive indexes than those of M2 polymer. The spacer group of the M4 polymer contains two methylenes and two substituted benzene rings; the M4 polymer has the longest cutoff wavelength and the highest refractive indexes among these polymers. A very interesting behavior of these poly(arylamines) is that positive birefringence are observed in all unpoled polymers. The values of birefringence are also related to the chromophore density and the steric constraints. The birefringence of a material is defined as the difference between the two refractive indexes in the directions of parallel and perpendicular to the film plan, which is a result of a physical ordering of optically anisotropy elements along some preferential direction:

$$\Delta n = n_{\parallel} - n_{\perp} \qquad (2)$$

$n_{\parallel}$ is the refractive index of the sample in the direction along the film plan, and $n_{\perp}$ is the refractive index in the direction perpendicular to the film plan. In the waveguide technique the birefringence can be expressed as the difference between n_{TE} and n_{TM}. The value of birefringence was determined by the orientation of the chromophores and the steric constraints in the films. In this series of poly(arylamines), the main structural difference is their spacer group that determines the values of birefringence. M2 polymer has a long and flexible spacer group $(CH_2)_{10}$, before poling the birefringence (n_{TE} - n_{TM}) is 0.0036 at 1.064 μm. At the same wavelength, the birefringence of M4 is 0.0217 since M4 has a more rigid spacer group. When poled by corona discharge at temperature just lower than T_g, for polymers with more flexible groups such as M1, M2, and M3, large order parameters have been introduced by poling and the refractive indexes of $n_{\perp}$ becoming larger than $n_{\parallel}$. When the spacer group is more rigid such as in M4 and M5, even after poling the refractive indexes of $n_{\parallel}$ are still larger than those of $n_{\perp}$. The thermal analysis and wide-angle X-ray spectra have shown that these poly(arylamines) are completely amorphous; such a kind of large positive birefringence may be related to the special molecular structures. Such optical anisotropic properties have also been observed in polyimide films.[33] In these poly(arylamines), before poling, the polymer chains are preferentially stretched along the film plan, when a strong field such as a corona discharge is applied to the films, the chromophores are aligned along the field direction. For polymers with flexible spacer groups, the chromophores are oriented perpendicular to the film, so that the refractive indexes of $n_{\perp}$ become larger than those of $n_{\parallel}$; however, for the polymers with very rigid space groups, there is very large steric constraints, it is difficult to reach the equilibrium orientation by poling, and the chromophores are still preferentially oriented along the film plane. Such type of positive birefringence may exist in other main-chain polymers with Λ-shaped charge-transfer conformation, therefore, this work not only opens the way to a new class of second-order NLO polymers but also indicates the new possibility of phase matching in polymer films by using positive birefringence.

Nonlinear Optical Properties. The second-order optical nonlinearity of these main-chain polymers was measured by the Maker fringe method.[34] The NLO coefficients were calculated following the method of Jerphagnon and Kurtz as well as Singer et al.,[35] using the obtained second harmonic intensity, thin-film thickness, and refractive indexes at fundamental and harmonic wavelengths. Figure 3 shows the dependence of SH intensity as a function of the incidence angles in the range −70° to 70° for P and S polarization of fundamental beam (1.064 μm) of the M4 polymer, respectively.

The nonlinear optical coefficients of these polymers are summarized in Table 3. The difference in the d_{33} values may be mainly attributed to the degree of molecular alignment induced by poling, i.e., the order

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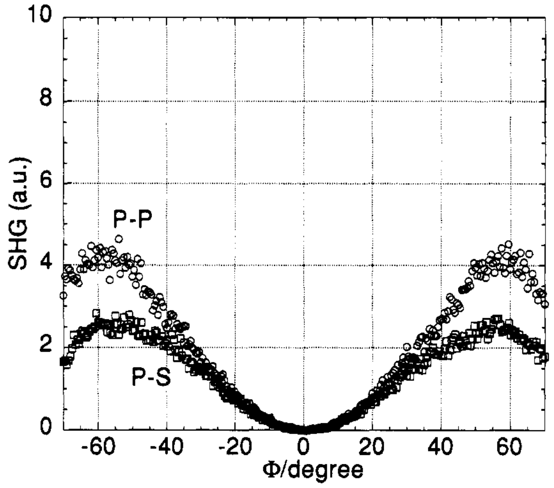

Figure 3. Maker fringes of the M4 polymer for P and S polarization at a fundamental wavelength of 1.064 μm.

Table 3. Nonlinear Optical Coefficients of Poly(arylamines)[a]

polym	d_{33} (pm/V)	d_{31} (pm/V)	poling temp (°C)
M1	12	4.2	100
M2	7.6	2.5	70
M3	17.6	5.4	130
M4	9.2	3.0	170
M5	8.0	2.4	135

[a] d_{11} (quartz) = 0.4 pm/V.

parameters. The best poling conditions, such as the poling temperature and time were determined by in situ SHG measurement. The corona discharge current was fixed at 2 μA. The largest d_{33} value is obtained in M3 polymer. This is because the poling temperature was higher than its T_g, and a higher orientation order was obtained. For other polymers the poling temperatures were lower than their T_g; when the poling temperatures were higher than Tg, large ionic conductivity currents were observed. In this situation, the chromophores cannot be effectively aligned by poling. If we can successfully eliminate the ions by the electrolysis, larger nonlinear coefficients should be obtained in these polymers.

Other factors affecting the NLO coefficients of these poly(arylamines) are their dipole moments and hyperpolarizabilities related to the amines structures. Mitchell et al.[36] have reported a series of *p*-aminophenyl sulfone oligomers with a head-to-tail arrangement. They found with different amine structures, the dipole moment and the $\mu\beta_z$ values of oligomers were different, but the expected enhancement of the hyperpolarizability was not observed despite the head-to-tail structure. The theoretical calculation and experiment measurement of dipole moments and hyperpolarizabilities of our Λ-type main-chain poly(arylamines) as well as a comparison to those of 2-nitroaniline will be discussed in another paper.

Aabsorption at the second harmonic wavelength (2ω) of these polymers is negligible, and the $\chi^{(2)}$ values are not resonantly enhanced. However, the role of resonance enhancement of $\chi^{(2)}$ for M4 polymer cannot be ruled out since it has a considerable red shift of cutoff wavelength compared with other poly(arylamines). The $\chi^{(2)}$ values of these poly(arylamines) indicate that main-chain polymer with Λ-shaped chromophores can be successfully aligned by corona poling. The electric-field-induced dynamic phase-matching of M1 polymer waveguide is reported elsewhere.[37]

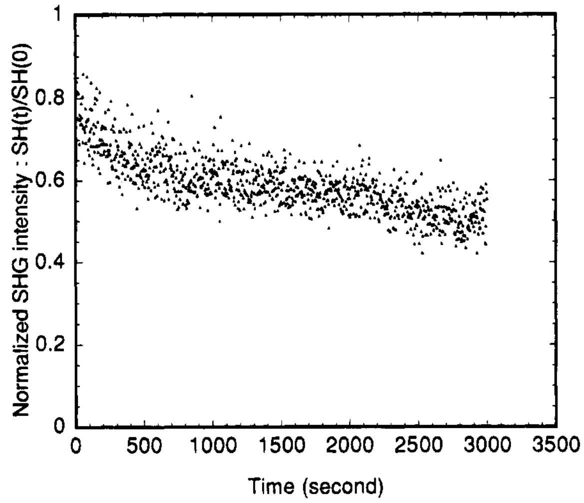

Figure 4. Second harmonic generation (SHG) temporal characteristics at 100 °C of the M4 polymer.

Temporal Stability of Poling-Induced NLO Effects. The long-term stability of nonlinear optical properties in poled polymers at higher temperature is critical for practical applications since devices are frequently exposed to high temperatures during fabrication process. To investigate the SHG stability, in situ SHG experiments were poformed. The M4 polymer was heated to 175 °C and kept at this temperature for 30 min, then the temperature was brought down to 100 °C, and the poling field was take off. The relationship of the SHG intensity versus time is shown in Figure 4 by monitoring the SHG intensity continuously at a fixed angle (Φ = 60°). From this figure, we can see that after 50 min, the SHG intensity remained approximately 60% of the original value, indicating that even at high temperatures the temporal stability of poling-induced SHG of main-chain polymer with the Λ-shaped chromophore is apparently better than other NLO dye-grafted polymers.[38]

Conclusions

In conclusion, we have synthesized a novel series of second-order NLO main-chain polymers having a bidirectional charge-transfer chromophore. Alignment of the nonlinear optical chromophores by corona discharge in these main-chain polymers is relatively easy since we need only rotate part of the dipole moments to obtain the noncentrosymmetric structure. Poly(arylamines) were found to be amorphous from thermal analysis and wide-angle X-ray diffraction spectra. Before poling, a large birefringence was observed in all these polymers,

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indicating those chromophores have a preferential orientation in the polymer systems.

Films were poled by corona discharge at temperatures below their glass transition temperatures except M3. We obtained the d_{33} in the range 7−18 pm/V. The temporal stability of poling-induced NLO effects were studied by in situ SHG measurements at elevated temperatures. The results indicate that these polymers have good temporal stability even at high temperatures.

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