A New Postfunctional Approach To Prepare Second-Order Nonlinear Optical Polyphophazenes Containing Sulfonyl-Based Chromophore

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ABSTRACT: A new synthetic strategy was developed to prepare polyphosphazenes with second-order nonlinear optical chromophore in which sulfonyl groups are the acceptors. Thus, polyphosphazenes **P1** and **P2** that contain aniline or indole groups as side chains were obtained from a highly reactive macromolecular intermediate, poly(dichlorophosphazene), by nucleophilic substitution reaction. Then a post-azo coupling of *p*-ethylsulfonylbenzenediazonium fluoroborate or *p*-octylsulfonylbenzenediazonium fluoroborate toward the aniline or indole ring in **P1** and **P2** afforded the sulfonyl-based chromophore-functionalized polyphosphazenes **P3**, **P4**, and **P5**. The polymers exhibit good solubility in common organic solvents and are thermally stable. The maximum absorption appeared at about 440 nm in **P3**, while that of **P4** was at about 393 nm, which were blue-shifted about 52 and 32 nm, respectively, compared to the corresponding chromophores with nitro acceptor and resulted in a wider transparency window. The poled films of **P3** and **P4** exhibits a resonant d_{33} value of 27 and 18 pm/V, respectively, by second harmonic generation (SHG) measurements.

Introduction

Organic polymeric second-order nonlinear optical (NLO) materials have attracted steady interest due to their potential photonics applications and many advantages over single crystals.[1−3] To meet the requirements of the practical application, the device-quality NLO materials should possess high stability and low optical loss, besides the large macroscopic optical nonlinearity.[4−7] Polyphosphazenes are inorganic polymers with a backbone of alternating phosphorus and nitrogen atoms and two side groups linked to the phosphorus atoms. In recent years, they have attracted growing attention due to their unique range of unusual properties, such as high thermal and oxidative stability, optical transparency from 220 nm to the near-IR region of the backbone, and the ease of syntheses. Compared to the ordinary polymers with only one functional side group per unit, the polyphosphazenes provide double sites for further functionalization.[8−12] Furthermore, the pioneered studies by Allcock et al. and other scientists demonstrated that polyphosphazenes could fulfill many of the requirements of the NLO active polymers and were promising candidates for the practical applications.[13−16]

On the other hand, while nitro and polycyanovinyl groups have been widely studied as acceptor groups in NLO, the sulfonyl group has not received much attention, though the sulfonyl groups possess strong acceptor properties. In addition, they are bifunctional groups, which permits greater freedom in the design of compounds for specific applications and allows more flexibility for synthetically tailoring the physical properties. According to the literature and our previous work, the chromophores exhibited similar first molecular hyperpolarizability (β) when the nitro groups were replaced by the sulfonyl groups, but the sulfonyl compounds showed much wider transparency in visible region (with hypsochromic shift of 20−40 nm) and the synthetic flexibility.[17−23] Until now, the reported polymers, which contain sulfonyl-based chromophores, were prepared by the direct polymerization or reaction of the sulfonyl-based chromophore with functional polymers.

In this paper, a new synthetic route is presented with the aim to develop polyphosphazenes containing the sulfonyl-based chromophore. Thus, polyphosphazenes that contain aniline (**P1**) and indole (**P2**) groups as side chains were obtained from a highly reactive macromolecular intermediate, poly(dichlorophosphazene), by nucleophilic substitution reaction (Scheme 1). Then a post-azo coupling of *p*-ethylsulfonylbenzenediazonium fluoroborate or *p*-octylsulfonylbenzenediazonium fluoroborate toward the aniline or indole ring in **P1** and **P2** afforded the sulfonyl-based chromophore-functionalized polyphosphazenes **P3**, **P4**, and **P5** (Schemes 2 and 3). To our knowledge, this is the first example of polyphosphazenes containing the sulfonyl-based NLO chromophore prepared by the postfunctional method. We hope that this will promote the preparation of more other polymers containing sulfonyl-based chromophore for NLO applications.

Experimental Section

Materials and Measurements. Tetrahydrofuran (THF) and petroleum ether (60−90 °C) were dried over and distilled from K−Na alloy under an atmosphere of dry nitrogen. *N*-Methylpyrrolindone (NMP) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. All other reagents were used as received. *p*-Ethylsulfonylaniline and *p*-octylsulfonylaniline were synthesized according to the literature.[24] *N*-(Hydroxyethyl)indole was prepared as reported before.[25] *N*-Ethyl-*N*-(2-hydroxyethyl)aniline (**3**) was synthesized from *N*-ethylaniline and 2-chloroethanol.[26] Poly(dichlorophosphazene) was obtained from the thermal ring-opening polymerization of hexachlorocyclotriphosphazene[27] and purified as we reported before.[25,28−30] Sodium hydride was weighted in the

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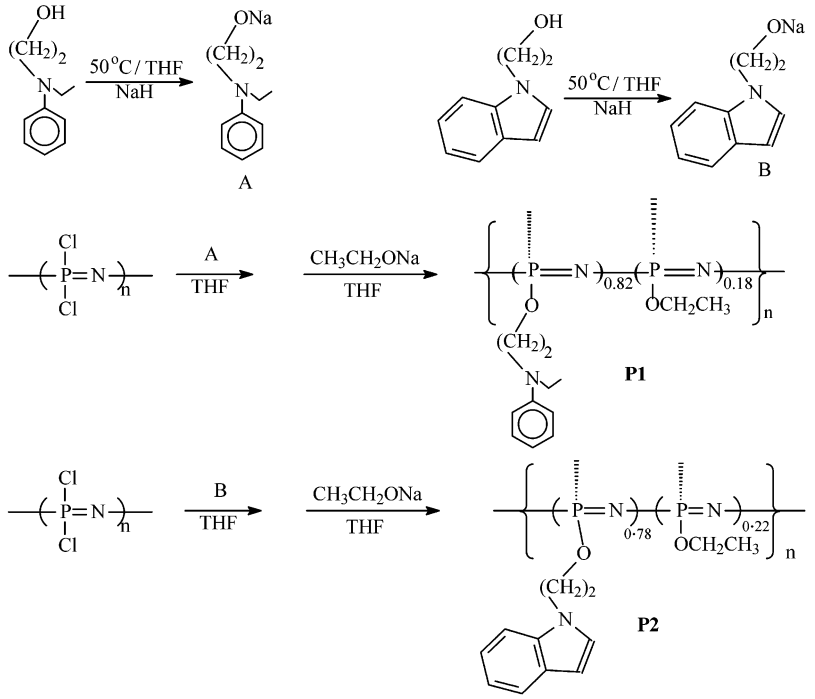
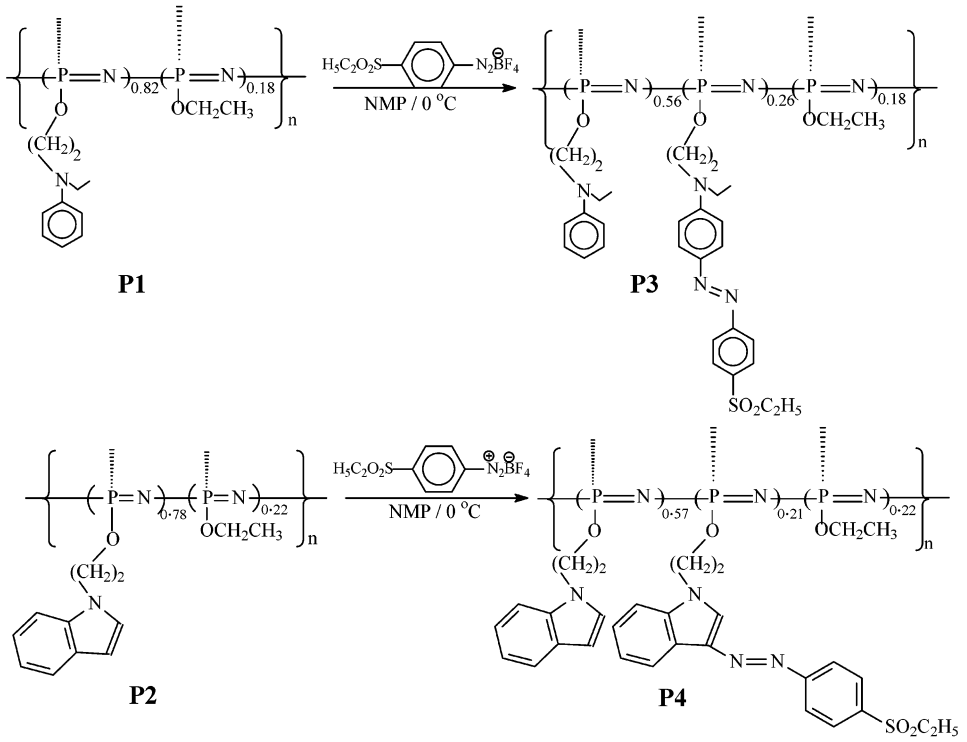
Scheme 1



Scheme 2

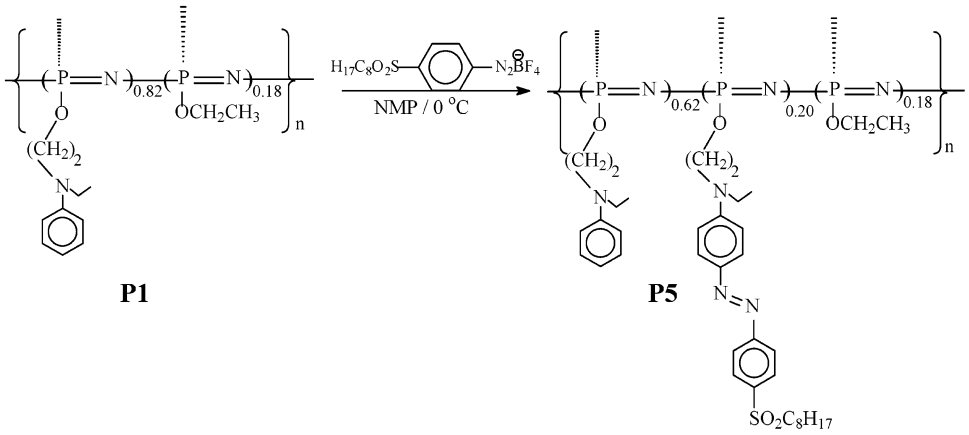


drybox. The substitution reactions of poly(dichlorophosphazene) were carried out in a dry nitrogen atmosphere using the Schlenk technique.

^{1}H NMR spectroscopy study was conducted with a Varian Mercury300 spectrometer. ^{31}P NMR spectroscopy study was conducted with a Varian Inova600 spectrometer. FT-IR spectra were recorded on a Testscan Shimadzu FT-IR 3000 series in the region of 3000−400 cm^{-1} on KBr pellets. UV−vis spectra were obtained using a Schimadzu 160A spectrometer in the polymer THF solution. Differential scanning calorimetry (DSC) analyses were performed in a Rigaku Themoflex DSC8131 at a scan rate of 10 °C/min. Molecular weights were determined in THF solution by a Waters 2960D separation module containing a Styragel HR1 THF column and a Waters 2410 refractive index detector with a calibration curve for polystyrene standards. Thermal analysis was performed on a Shimadzu DT-40 thermal analyzer at a heating rate of 20 °C/min in nitrogen at a flow rate of 50 cm^3/min for thermogravimetric analysis (TGA).

Synthesis of *p*-Ethylsulfonylbenzenediazonium Fluoroborate. *p*-Ethylsulfonylaniline (0.56 g, 3 mmol) was dissolved in fluoroboric acid (40%), and then the solution was cooled to 0 °C. A solution of sodium nitrite (0.21 g, 3 mmol) in water (1.5 mL) was added dropwise. The resultant mixture was stirred at 0 °C for half an hour. The yellow solid was filtered quickly and washed with cold ethanol and ether for

Scheme 3



several times. After this, the product (0.7 g) was stored in the refrigerator.

Synthesis of *p*-Octylsulfonylbenzenediazonium Fluoroborate. The preparation procedure was similar to that of *p*-ethylsulfonylbenzenediazonium fluoroborate.

Synthesis of Polyphosphazene P1. *N*-Ethyl-*N*-hydroxyethylaniline (1.94 g, 11.7 mmol) reacted with sodium hydride (0.27 g, 11.3 mmol) in THF (20 mL) at 50 °C for 10 h, then the resultant solution of the sodium salt of compound **3** was added to a solution of poly(dichlorophosphazene) (0.68 g, 5.8 mmol) in 80 mL of THF, and the mixture was stirred at 50 °C for 2 days. Then 10 mL of the solution of $NaOCH_2CH_3$ (prepared from sodium (0.27 g, 11 mmol) and ethanol (0.8 g, 17 mmol) in THF) was added, and the resultant mixture stirred at 50 °C for another 2 days. The mixture was poured into water (400 mL), and the white solid was filtered, washed with water, and air-dried. The solid was dissolved in THF, and the insoluble residue was filtered out. The filtrate was evaporated to remove the bulk of THF. Then the solid was isolated and further purified by several precipitations from THF into methanol. The solid was vacuum-dried at 40 °C to yield the product (0.70 g, 37%). ^{31}P NMR ($CDCl_3$): δ (ppm) −7.3, −1.7 (broad (br)).

Preparation of Polyphosphazene P2. The synthetic procedure was similar to the preparation of **P1** and has been reported previously.[25] ^{31}P NMR ($CDCl_3$): δ (ppm) −8.5 (br).

Preparation of Polyphosphazenes P3 and **P4.** Polyphosphazene **P1** (0.20 g) was dissolved in 1.7 mL of *N*-methylpyrrolindone (NMP), and then *p*-ethylsulfonylbenzenediazonium fluoroborate (77 mg) was added under cooling with an ice bath. The color of the solution changed to red immediately. After stirring for 8 h at 0 °C, excessive anhydrous potassium carbonate was added, and the mixture was stirred for an additional 1 h and then filtered. The residue was washed with THF, the filtrates were collected, and THF was removed under reduced pressure. Some methanol was added dropwise to precipitate the polymer. The solid was further purified by several precipitations from THF into methanol. The solid was dried in a vacuum at 40 °C to yield an orange-red product (**P3**) (0.12 g, 46%). δ (ppm): −6.2, −2 (br).

Polyphosphazene **P4** was also prepared similarly to that of **P3**, and at last 65 mg of product was obtained (51%). ^{31}P NMR ($CDCl_3$): δ (ppm) −8.6 (br).

Preparation of Polyphosphazene P5 (Scheme 3). The synthetic procedure was just as described above, but *p*-octylsulfonylbenzenediazonium fluoroborate was used instead of *p*-ethylsulfonylbenzenediazonium fluoroborate. At last, 61 mg of product was obtained (49%). δ (ppm): −6.5, −1.5 (br).

Polymer Film Preparation. Polyphosphazenes **P3** and **P4** were dissolved in THF, and the solutions (about 3 wt %) were filtered through syringe filters. Polymer films were spin-coated onto indium−tin−oxide (ITO)-coated glass substrates (which were cleaned by *N*,*N*-dimethyformide, acetone, distilled water, and THF subsequently in an ultrasonic bath) (2500 rpm). Residual solvent was removed by heating the films in a vacuum oven at 45 °C for 2 days. The film thickness was 0.55 μm for **P3** and 0.36 μm for **P4** measured by a TENCOR 500 surface profiler.

Characterization of Poled Films. The second-order optical nonlinearity of polyphosphazenes was determined by in-situ second harmonic generation (SHG) experiments using a closed temperature-controlled oven with optical windows and three needle electrodes. The film, which was kept at 45° to the incident beam, was poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature, 70 °C for **P3** and 80 °C for **P4**; voltage, 8.5 kV at the needle point; gap distance, 0.8 cm. SHG measurements were carried out with a Nd:YAG laser operating with a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

Results and Discussion

Synthesis. *p*-Ethylsulfonylbenzenediazonium fluoroborate and *p*-octylsulfonylbenzenediazonium fluoroborate were prepared by the method similar to that for *p*-nitrobenzenediazonium fluoroborate.[31] Though there was no report about the preparation of them, we still expected that they could be synthesized as both sulfonyl and nitro groups are strong acceptors, and both of *p*-alkylsulfonylaniline and *p*-nitroaniline could form diazonium salts in hydrochloric acid.

The synthetic routes to polyphosphazenes are shown in Schemes 1−3. **P1** and **P2** were obtained from the highly reactive macromolecular intermediate, poly(dichlorophosphazene), by nucleophilic substitution reaction. At the end of the substitution reaction, an excess of $NaOCH_2CH_3$ was added into the reacting mixture to replace all the remaining chlorine atoms completely, since indole and aniline groups could not react with all the chlorine atoms because of the steric shielding effect.[32]

P3 and **P4** were synthesized via a post-azo coupling reaction (Scheme 2). In the previous literature, there were reports about the postderivatization of organic groups on polyphosphazenes to prepare new functional polyphosphazenes.[15,33,34] The azo coupling reaction has been previously carried on polyphosphazene side groups by the diazotization of high-polymeric phosphazenes, followed by coupling to phenol, naphthol, etc., to prepare polymer-bound dyes.[35] Now the azo coupling reactions between the polymers and diazonium salts enable the introduction of NLO chromophore, which was first used by Katz et al. to functionalize a copolymer of methyl methacrylate and methacrylate ester of *N*-ethyl-*N*-(hydroxyethyl)aniline in acetic acid.[36] As an acid medium was not a favorite solvent medium for most polymers, Tripathy et al. developed this method by

using polar organic solvent such as dimethylformamide or dimethylacetamide.[37] In our previous studies, we easily synthesized DR-1 containing polysilanes by the azo coupling reaction in *N*-methylpyrrolidone (NMP) with the use of *p*-nitrobenzenediazonium fluoroborate.[38] And in 2002, this method was further developed by us to prepare indole azo chromophore functionalized polymers.[25] However, in all the above cases, the acceptors are nitro groups, and there are no reports about other acceptors. Here, *p*-ethylsulfonylbenzenediazonium fluoroborate was synthesized and used to attack the aniline and indole rings to prepare polymers containing sulfonyl-based NLO chromophores; besides, there were reports about the polyphosphazenes containing sulfonated aryl side groups.[39,40]

The overall synthesis of **P3** and **P4** was carried out through two steps. The synthetic route was simple, and the purification of the products was easy. Another advantage of this method was that the concentration of the sulfonyl-based chromophore in **P3** and **P4** could be controlled to some extent by adjusting the quantity of the compound of *p*-ethylsulfonylbenzenediazonium fluoroborate in the azo coupling reaction. Furthermore, the sulfonyl groups are bifunctional groups, and the alkyl group can be adjusted. Also, **P5** with octyl groups instead of ethyl groups linked to the sulfonyl groups was prepared successfully as shown in Scheme 3. So, other groups including those containing end functional groups could be there instead of ethyl or octyl groups, and then some other *p*-alkylsulfonylbenzenediazonium fluoroborate might be prepared and used to synthesize the polymers containing the corresponding sulfonyl-based chromophore. This research is still under study in our lab.

Structural Characterization of P1−P5. In the IR spectra of **P1**−**P5**, the 1250−1200 cm^{-1} bands were attributed to an intense P═N stretching vibration and the 750 cm^{-1} band to an in-phase P−N−P stretch. The new strong absorption bands appeared at about 1128 cm^{-1} in the IR spectrum of **P3**−**P5** were assignable to the absorption of the sulfonyl groups. This confirmed that the *p*-ethylsulfonylbenzenediazonium fluoroborate or *p*-octylsulfonylbenzenediazonium fluoroborate had reacted with the aniline or indole rings, and the sulfonyl groups were introduced into the polymer side chains successfully.

The component concentrations in the polymers could be calculated by analyzing the ^{1}H NMR peak integration carefully and are shown in Schemes 1−3. For **P1**, the ratio of aniline and ethoxy groups was calculated from the integration area of three phenyl protons of the aniline group in the range 6.4−6.8 ppm and three protons of the methyl group in the range 0.9−1.2 ppm. Figures 1 and 2 show the ^{1}H NMR spectrum of **P1** and **P3** for examples and the assignment of peaks downfield for comparison. Some resonance peaks appearing downfield in Figure 2, which were due to the *p*-ethylsulfonyl phenyl moieties, also confirmed that the azo coupling reaction was successful and the azo chromophore really formed. The ratio of the two kinds of aniline groups in **P3**, aniline and sulfonylazoaniline moieties, was estimated to be 2.2:1 by analyzing the peaks of two protons in the range 6.4−6.8 ppm and six sulfonylazo chromophore protons in the range 7.6−8.0 ppm. By the same method, the ratio of the two kinds of aniline groups in **P5**, aniline and sulfonylazoaniline moieties, was estimated to be 3.1:1. The preparation of **P2** has been

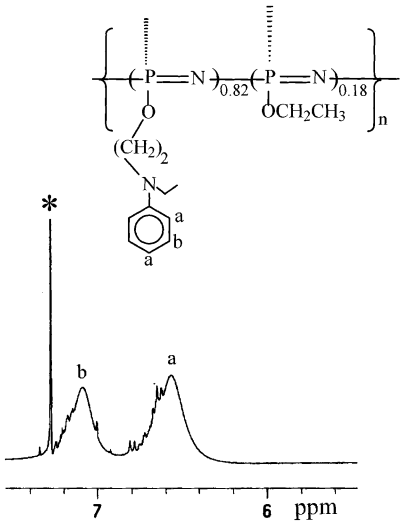


Figure 1. ^{1}H NMR spectrum of polyphosphazene **P1** (* solvent).

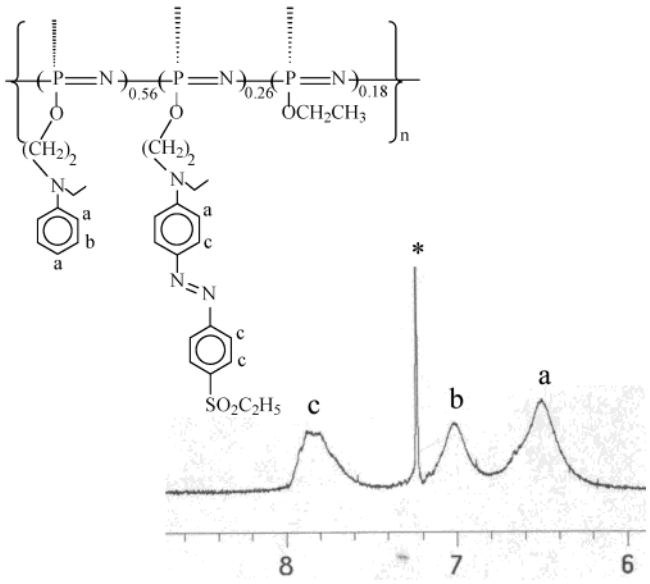


Figure 2. ^{1}H NMR spectrum of polyphosphazene **P3** (* solvent).

reported previously. The ratio of the two kinds of indole units in **P4**, indolyl and sulfonylazoindolyl moieties, was estimated to be 2.7:1 by analyzing the spectrum carefully.

^{31}P NMR study was conducted with a Varian Inova600 spectrometer, and the data are presented in the experimental part. In **P1**, **P3**, and **P5**, there are peaks at about −1.7 ppm, which extend to 0 ppm, indicating that there was rearrangement of the polyphosphazene to a phosphazane. This might be due to the long reaction period and the relatively high synthetic temperature for the preparation of **P1**. However, the peaks around 0 ppm seem to be absent in the spectra of **P2** and **P4** though the reaction period of **P2** was also relatively long. The further study is needed to seek the reasons.

P1−**P5** have good solubility in common organic solvents, such as $CHCl_3$, THF, DMSO, and DMF. Figure 3 showed the UV−vis spectra of them in the solution of THF. After the post-azo coupling reaction, a new strong absorptions maximum of the $\pi-\pi^*$ transition of indole-based chromophore appeared at about 440 nm in **P3**,

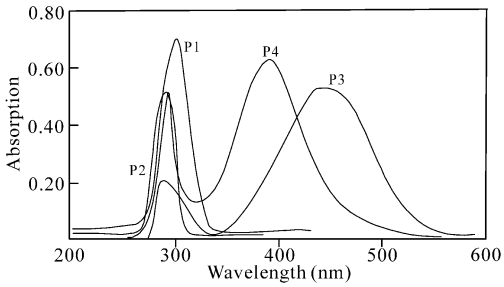


Figure 3. UV-vis spectra of polyphosphazenes **P1**−**P4** in THF.

Table 1. Characterization Data for Polymers

polymer	T_g (°C)	M_n ($\times 10^5$)	M_w ($\times 10^5$)
P1	*a*	0.24	1.0
P2	37	0.26	0.42
P3	98	0.34	1.3
P4	110	0.25	0.65
P5	*a*	0.41	1.2

[a] Not obtained.

while that of **P4** was at about 393 nm. The maximum absorptions were blue-shifted about 52 and 32 nm, respectively, compared to the corresponding chromophore with a nitro acceptor. This resulted in a wider transparency window and should contribute to the low optical loss of polyphosphazenes.

The polyphosphazenes did not show any significant low-temperature weight loss. The high-temperature weight loss for the polymers commenced at about 290 °C and increased gradually at high temperature. Some physical properties of **P1**−**P5** are listed in Table 1. The T_g of **P4** is higher than that of **P2** due to the rigid indole-based chromophore side chains in **P4** after the azo coupling reaction. After the azo coupling, the molecular weights of polymers increased a little, and the difference between **P1** and **P2** was due to the usage of the different batch of poly(dichlorophosphazene).

To evaluate the NLO activity of the poled polymer films, thin films of polyphosphazenes **P3** and **P4** were prepared for SHG measurement. Calculation of the d_{33} values has been reported previously.[25] The d_{33} values of **P3** and **P4** were calculated to be 27 and 18 pm/V, respectively, at 1064 nm fundamental wavelength. The values were relatively high, similar to those of polymers containing Dispersed Red-1 (DR-1) or similar chromophores reported in the literature[41,42] but lower than that of polyphosphazene with Dispersed Red-1 side groups reported by Allcock in 1991.[13] However, the d_{33} value of the same NLO polymer could be different when tested by different method or different testing system. Compared with the values of our other polymers containing Dispersed Red-1 (DR-1) or nitro-based indole azo groups as NLO chromophores tested at the same testing equipment,[25,38,43] the d_{33} values were similar though the sulfonyl groups were in place of the nitro groups as the acceptor groups.

Conclusion

Three new polyphosphazenes **P3**−**P5** with a high density of the sulfonyl-based chromophore are prepared by a novel two-step method. First, polyphosphazenes **P1** and **P2** that contain aniline and indole groups as side chains were obtained. Then a post-azo coupling of *p*-ethylsulfonylbenzenediazonium fluoroborate or *p*-octylsulfonylbenzenediazonium fluoroborate toward the aniline and indole ring in **P1** and **P2** afforded the sulfonyl-based chromophore-functionalized polyphosphazenes **P3**−**P5**. This synthetic route is simple, and the purification of the products was easy. It is believed that many other polymers containing sulfonyl-based chromophores for nonlinear optical applications could be prepared by this new and simple synthetic strategy. The polymers exhibit good solubility in common organic, such as $CHCl_3$, THF, DMSO, and DMF. The maximum absorptions appeared at about 440 nm in **P3**, while that of **P4** was at about 393 nm, which were blue-shifted about 52 and 32 nm, respectively, compared to the corresponding chromophores with nitro acceptor. The poled film of **P3** and **P4** exhibits a resonant d_{33} value of 27 and 18 pm/V, respectively, by second harmonic generation (SHG) measurements.

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