Click Chemistry-Based Synthesis of Azo Polymers for Second-Order Nonlinear Optics

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ABSTRACT: Four linear polymers containing pendant azo moiety were synthesized through click chemistry for second-order nonlinear optical study. The polymers were found soluble in most of the polar organic solvents such as tetrahydrofuran (THF), chloroform, and dimethyl formamide (DMF). The polymers showed thermal stability up to 300 °C and glass transition temperatures (T_g) in the range of 120–140 °C. The molecular weights (M_w) of these polymers (measured by gel permeation chromatography) were in the range 37,900–55,000 g/mol. The polymers were found to form optically transparent films by solution casting from THF solution. Order parameters were calculated from UV–vis absorption spectra. The morphology changes in the films after poling were characterized by atomic force microscopy. The angular dependence, temperature dependence, and time dependence of second harmonic generation (SHG) intensity were obtained by using 1064 nm Nd:YAG laser. The SHG intensity remained unchanged up to 95 °C. At room temperature, it remained stable up to 8 days after initial drop of about 14%. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1572–1578, 2012

KEYWORDS: atomic force microscopy; differential scanning calorimetry; nonlinear polymer; thin films; UV-Vis spectroscopy

INTRODUCTION During the past two decades, attention has been paid by researchers for development of novel materials for second-order nonlinear optics (NLO) because of their applications in several areas including telecommunications, optical modulation, optical data storage, frequency doubling, and optical switching.[1] A good NLO polymer should have the properties, such as better optically transparency, high optical thresholds to laser power, and large NLO coefficient.[2] In this regard, several inorganic materials such as lithium niboate ($LiNbO_3$), potassium dihydrogen phosphate, and so on are used for this purpose. However, apart from stability their properties are inferior as compared with organic counterparts. At the same time, although the organic materials are superior in chemical resistivity, good processability, lighter in weight and mechanical endurance, their stability remains a concern. To address the stability problem, various approaches such as crosslinking,[3] incorporation of polyimide,[4] and polyurethane[5] linkage were also adopted. Various molecular designs for side chain NLO moiety were attempted, such as T-type,[6] Y-type,[7] H-type,[8] and so on. The T_g of polymer and interaction between the chromophores are of prime concern in enhancing the relevant properties.[9] The optimization of properties is the ultimate goal in developing a suitable NLO polymer. In our approach, attempts have been made to incorporate ring/fused aromatic ring in the main chain for enhancing rigidity.

With the above idea in mind, we tried to follow a suitable scheme so that rigid moieties are incorporated during progress of polymerization. There are several ways of synthesizing such types of polymers with various functional groups for tuning the optoelectronic properties. Percec et al. reported a series of synthetic strategies from linear to ring structure to hyperbranched polymers.[10] Further the same author elaborated a synthetic method for the preparation of linear monodisperse LC oligoethers and polyethers via a repetitive 2*n* geometric growth approach.[11] The synthesis strategy along with the phase behavior was also dealt with.[12] The synthesis of macrocyclic and hyperbranched polymers was also reported during the same period.[13] One of the reaction procedures called "Click" chemistry introduced by sharpless[14] has been popularized among the synthetic chemist due to its remarkable features such as quantitative yields, mild reaction condition, tolerance toward a broad range of functional groups etc. Another important aspect is the use of water as a cosolvent in this method. By using this methodology, various polymers are reported in various fields such as organic chemistry,[15] drug discovery,[16] dye-sensitized solar cells,[17] side chain liquid crystalline polymers,[18] and various types of linear as well as dendronized NLO polymers.[19]

In the present work, we synthesized four linear polymers containing azo chromophore as a dipole by copper-catalyzed click chemistry. Polymerization was carried out between diazido azo chromophore (which is similar to 4-*N*,*N*′-bis(2-hydroxyethyl) amino-4′-nitro azo benzene called DR19) and diyne moieties. Two of the synthesized polymers possess good film forming ability and their optically transparent films were fabricated for further analysis without blending with any other polymer like polycarbonate or PMMA. The polymers were easily soluble in common organic solvents and well characterized. In addition, their thermal, optical, and NLO properties were investigated.

EXPERIMENTAL

Materials

N,*N*-Bis(2-hydroxyethyl)aniline, sodium azide, sodium ascorbate, copper(II) sulfate, and thionyl chloride were purchased from Sigma-Aldrich and used without further purification. All solvents were used as received without further purifications unless otherwise stated. The compounds *N*,*N*-bis(2-chloroethyl)aniline (**1**),[16] 1-(2-ethylhexyloxy)-2,5-diethynyl-4-methoxybenzene (**4**), 1,4-bis(2-ethylhexyloxy)-2,5-diethynylbenzene (**5**), 9-(2-ethylhexyl)-3,6-diethynyl-9H-carbazole (**6**), and 9,9-bis(2-ethylhexyl)-2,7-diethynyl-9H-fluorene (**7**) were synthesized as per reported procedure.[14,20]

Instrumentation

FTIR spectra were recorded on Perkin-Elmer 1600 series Fourier Transform infrared spectrophotometer using KBr pellets. UV–visible spectra were taken on a Cary 500 Scan UV–vis–NIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz Bruker-FT NMR spectrometer using $CDCl_3$ as solvent. Molecular weights of the polymers were determined by using gel permeation chromatography (GPC; on waters 2690) with tetrahydrofuran (THF) as an eluent and polystyrene as standards. Thermogravimetric analyzer (TGA; TA instruments His Res TGA 2950) was used for determining thermal stability with a heating rate of 20 °C/min in N_2 atmosphere. Differential scanning calorimeter (DSC; TA instruments) was used to determine the glass transition temperature (T_g) with a heating rate of 10 °C/min in N_2 atmosphere. Thickness of the film was measured by using Alpha step surface profiler. Melting point of the monomers was recorded by melting point apparatus (Electro thermal 9100).

Synthesis of Monomers

Synthesis of 4-Nitro-4′-[bis(2-chloroethyl)amino]azo benzene (2)

The diazonium salt was prepared by adding aqueous sodium nitrite (1.51 g, 22.0 mmol) solution to *p*-nitroaniline (2.53 g, 18.34 mmol) in hydrochloric acid (9 N, 40 mL) at 5 °C. The diazonium salt was then added slowly to a ethanolic solution of *N*,*N*-bis(2-chloroethyl)aniline (2.53 g, 18.34 mmol) by maintaining the temperature below 10 °C. The reaction mixture was allowed to stir for 3 h after which the pH of the solution was adjusted to neutral by the addition of aqueous NaOH solution. The precipitate formed was filtered off and recrystallized in ethanol to obtain a dark red solid.

Yield: 5.4 g (80.5 %); mp: 155 °C; FTIR (KBr): ν (cm^{-1}) 1600 (—C=C—), 1510, 1350 (—NO_2), 1180 (C—N); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.42 (d, J =5.0 Hz, 2H), 8.02 (d, J = 15 Hz, 4H), 6.87 (d, J = 5 Hz, 2H), 3.96 (t, J = 5 Hz, 4H), 3.80 (t, J =5 Hz, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 156.3, 149.7, 147.7, 144.6, 126.1, 124.6, 122.8, 111.6, 53.4, 40.1.

Synthesis of 4-Nitro-4′-[bis (2-azidoethyl)amino]azo benzene (3)

The compound **2** (1 g, 2.72 mmol) and sodium azide (0.53 g, 8.1 mmol) were charged in a round-bottomed flask containing 15 mL of dimethyl sulfoxide and heated to 90 °C for 24 h. The reaction mixture was poured in to excess dilute hydrochloric acid (2 N, 50 mL) and extracted with dichloromethane. The organic phase was washed with aqueous $NaHCO_3$ solution till neutral, dried over $MgSO_4$, and evaporated *in vacuo*. The crude compound was purified by column chromatography using 10% ethylacetate in petroleum ether as an eluent to get dark red colored product.

Yield: 73%; mp: 90 °C; FTIR (KBr): ν (cm^{-1}) 2130 (—N_3), 1600 (—C=C—), 1510, 1340 (—NO_2), 1140 (C—N); ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) δ 8.36 (d, J = 5 Hz, 2H), 7.97 (d, J =6.5 Hz, 2H), 7.96 (d, J = 6.0 Hz, 2H), 6.84 (d, J = 10 Hz 2H), 3.74 (t, J = 5 Hz, 4H), 3.62 (t, J = 4.5 Hz, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 156.4, 149.9, 147.7, 144.4, 126.1, 124.4, 122.7, 111.9, 50.7, 48.7.

Synthesis of Polymers

Synthesis of P1

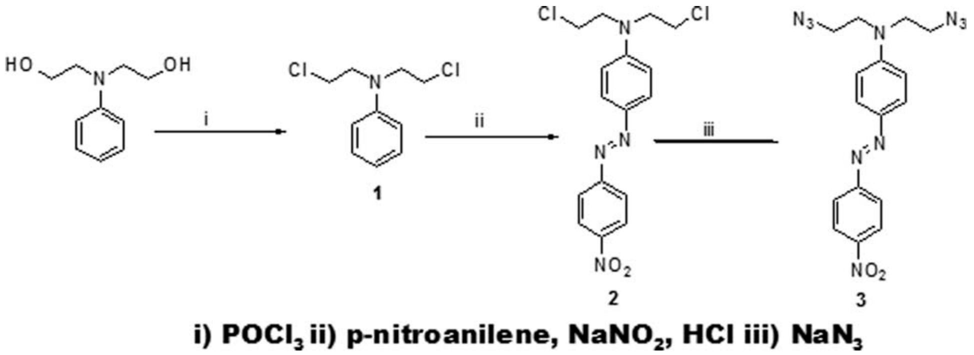
Compound **3** (0.15 g, 0.35 mmol) and diyne **4** (0.1 g, 0.35 mmol) were taken in a round-bottomed flask containing a mixture of H_2O and THF (3 mL, THF: H_2O: 1:2). The solution was degassed for 10 min followed by the addition of sodium ascorbate (0.14 g, 0.73 mmol) and then copper(II) sulfate (0.1 g, 0.38 mmol). The reaction mixture was allowed to stir at room temperature for 50 min under N_2. The polymer was precipitated in methanol and filtered. It was dissolved in THF and passed through alumina column to remove catalyst. The THF solution was concentrated and precipitated with methanol. The precipitate obtained was filtered and dried under vacuum to obtain 0.08 g of polymer P1 as a dark red solid.

Yield: 32%. FTIR (KBr): ν (cm^{-1}) 2960, 2920, 2860, 2100, 1600, 1510, 1340, 1140; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.3 (br, 2H), 8.0–7.9 (br, 6H), 7.2 (br, 1H), 6.8 (br, 2H), 4.5 (br, 3H), 4.0–3.8 (br, 4H), 3.4 (br, 2H), 1.6–0.8 (br, 17H).

Polymer P2

The polymer P2 was synthesized by similar procedure from chromophore **3** (0.137 g, 0.35 mmol) and compound **5** (0.14 g, 0.35 mmol).

Yield: 84 %; FTIR (KBr): ν (cm^{-1}) 2940, 2920, 2850, 2360, 2340, 2100, 1600, 1510, 1340, 1100; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.3 (br, 2H), 8.0–7.9 (br, 6H), 7.2 (br, 1H), 6.8 (br, 2H), 4.5 (br, 3H), 4.0–3.8 (br, 4H), 3.4 (br, 2H), 1.6–0.8 (br, 17H).



SCHEME 1 Synthesis of Diazide monomer.

Polymer P3

The polymer P3 was synthesized by similar procedure from chromophore **3** (0.128 g, 0.35 mmol) and compound **6** (0.11 g, 0.35 mmol).

Yield: 6% (only soluble fraction); FTIR (KBr): ν (cm^{-1}) 2940, 2920, 2850, 2360, 2340, 2100, 1600, 1500, 1340, 1100.

Polymer P4

The polymer P4 was synthesized by similar procedure from chromophore **3** (0.136 g, 0.35 mmol) and compound **7** (0.159 g, 0.35 mmol).

Yield: 59%; FTIR (KBr): ν (cm^{-1}) 2960, 2920, 2850, 2360, 2340, 2100, 1600, 1500, 1340, 1100; ^{1}H NMR (CDCl$_3$, 500 MHz): δ (ppm) 8.3 (br, 2H), 8.0–7.9 (br, 6H), 7.8–7.7 (br, 2H), 7.3 (s, 1H), 6.9 (br, 2H), 4.6 (br, 4H), 4.0 (br, 4H), 2.1 (br, 4H), 1.6–0.5 (br, 30H).

Thin Films Preparation, Poling, and Second Harmonic Generation Measurement

For preparing the polymeric films, the indium-tin oxide (ITO)-coated glass slides [(2.5 cm × 3.5 cm) ($\sigma = 10$–$15\ \Omega$/sq)] were precleaned stepwise with *N*,*N*-dimethyl formamide, distilled water, methanol, and acetone, respectively, in ultrasonic bath. The solutions of the polymers (50 mg/mL in THF) were filtered through 0.25μ PTFE filter for removing undissolved particles. The polymer solutions were then spin coated on ITO-coated glass substrates at a speed of 1000 rpm for 2 min. The spin coated films on ITO-coated glass plates were then corona poled. Poling conditions were maintained at high voltage (4.8 kV) while the tip was at a distance of 1 cm at a temperature very close to the T_g of polymer. After half an hour the film was cooled to RT while voltage was on. From poling experiment the order parameter (Φ) was calculated from their electronic absorption spectra by using the following equation[21]

$$\Phi = 1 - A_1/A_0,$$

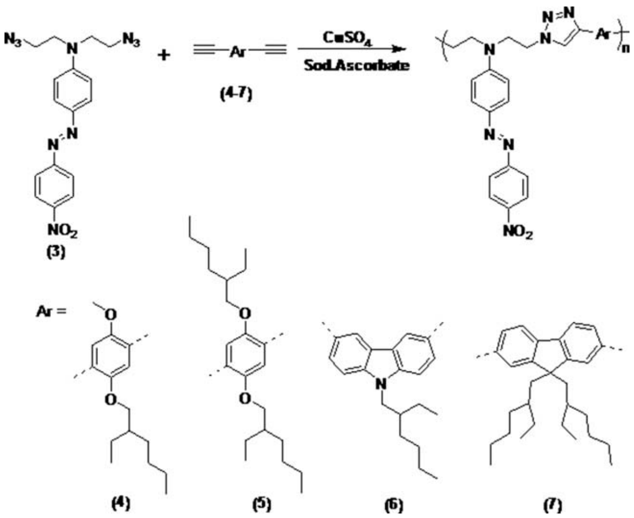
where A_1 and A_0 are the absorbance of poled and unpoled films, respectively.

The second-order optical nonlinearity of the linear click polymers were then determined from their second harmonic generation (SHG). In this process, poled films were mounted on rotational stage. For measuring the SHG intensity, 1064-nm pulsed Nd:YAG laser of pulse width 5 ns and 10 Hz repetition rate with laser energy 5 mJ was passed through poled films. The fundamental beam was blocked after passing through the film by an IR filter. The SHG signal was detected by a photomultiplier tube (PMT) and the signal averages by using an oscilloscope.

RESULTS AND DISCUSSIONS

Synthesis and Characterization of Polymers

In this study, one of the monomer was widely varied by changing the aromatic unit as well as the type of substitution for finding the effect on NLO property. The synthesis of monomers and the polymerizations were performed as shown in Schemes 1 and 2, respectively. The monomers were synthesized by adopting the standard diazotization procedure. Initially, *N*,*N*-bis(2-hydroxyethyl)aniline was chlorinated in presence of POCl$_3$ to obtained compound **1** in quantitative yield.[22] Then compound **1** was treated with *p*-nitro aniline under diazotization condition to obtained compound **2** in good yield. Compound **2** was then reacted with sodium



SCHEME 2 Click polymerization of diazide and diynes.

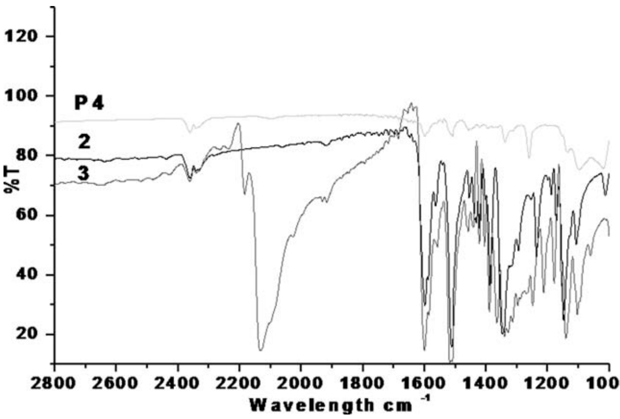


FIGURE 1 FTIR spectra of dichloroazo compound(2), diazide azo monomer (3) and polymer (P4).

TABLE 1 Polymeric Characterization Data

Polymer	λ_{max}[a] (nm)	M_w [b]	PDI[b]	T_g[c] (°C)	l_s[d] (μm)	ϕ[e]
P2	445	55,000	2.1	120	0.54	0.10
P4	445	37,900	2.3	140	0.46	0.18

[a] Wavelength at which maximum absorption observed for polymer in thin film on ITO.
[b] Determined by GPC in THF (polystyrene standard).
[c] Glass transition temperature of polymers detected by DSC.
[d] Film thickness measured by profilometer.
[e] Order parameter measured by UV–vis spectra.

azide to get the diazide monomer **3**, which was used for synthesizing polymers. All the triple-bonded compounds (diynes) containing different aromatic moiety were synthesized following the reported procedure and shown in Scheme 2. The diazide and diynes monomers were then polymerized by using copper-catalyzed 1,3-cycloaddition to get the polymers in quantitative yield. Most of the polymerization reactions were found to be completed within 50 min. It was observed that the polymerization reaction continued for longer time results in the formation of insoluble product, which may be due to the formation of high molecular weight polymers.

Polymerizing through click chemistry is not only helpful in synthesizing novel polymers within shorter reaction time but also introduce a triazole ring between the chromophores and the aromatic ring. The formation of ring structure in stepwise synthesis was also reported by Percec et al.[10–13] The ring structure in the main chain obviously enhances the rigidity which is very much desired in such type of materials to have better thermal stability.

From the FTIR spectroscopy (Fig. 1) for compound 3, a sharp peak near 2130 cm^{-1} indicates the presence of azide group. This peak almost disappeared after the 50 min of polymerization duration. During polymerization, the intensity of the peak gradually decreased and finally disappeared indicating the progress of polymerization reaction. The structure of the polymer was confirmed from ^{1}H NMR spectra, which showed broad peaks having different chemical shift than that of the monomers (Fig. 2). The molecular weight of polymer was determined by GPC using THF as solvent and was found to be in the range of 37,900–55,000 g/mol. Polymerization beyond 50 min lead to polymer, which could not be analyzed as it was not soluble in solvents. This may be due to high molecular weight. For most of the polymers synthesized thermal stability (by TGA; not shown) was found to be quite reasonable as only 3 wt % loss is observed above 290 °C. The higher thermal stability of the polymers could be due to the presence of large number of nitrogen atom as well as the triazole ring. DSC study of the polymers showed glass transition temperatures (T_g) in the range of 120–140 °C (Table 1).

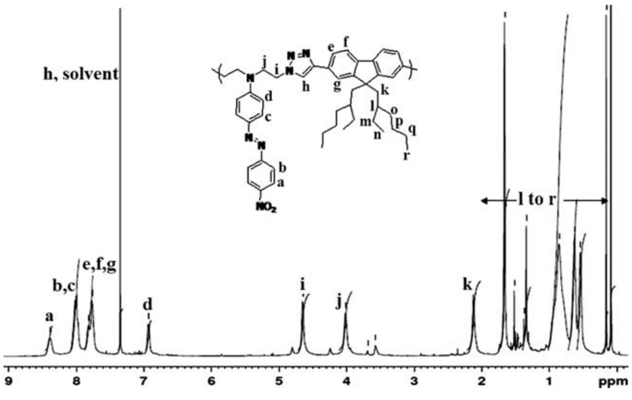


FIGURE 2 1H NMR spectra of polymer P4.

For studying the SHG activity, the polymers were cast on ITO-coated glass. It is observed that polymers P2 and P4 form good quality film, whereas polymers P1 and P3 form poor quality film. The formation of bad quality film for polymers P1 and P3 could be due to the presence of less branches making the polymer more rigid having restricted solubility. These kinds of observations were also reported by Chen et al. for the click polymers containing carbazole in the main chain.[23]

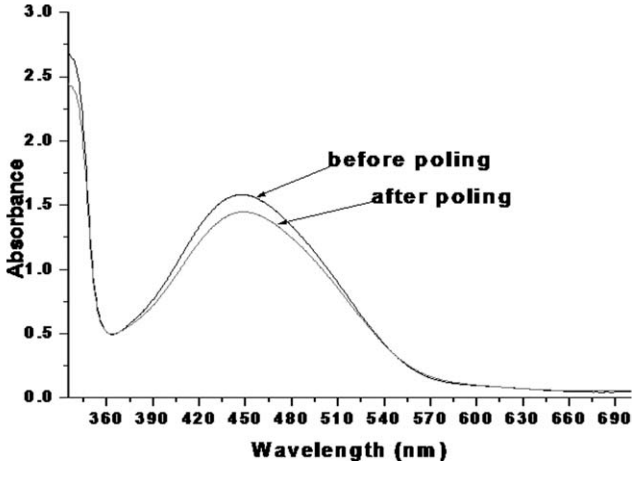


FIGURE 3 UV–vis absorption spectrum of polymer P4.

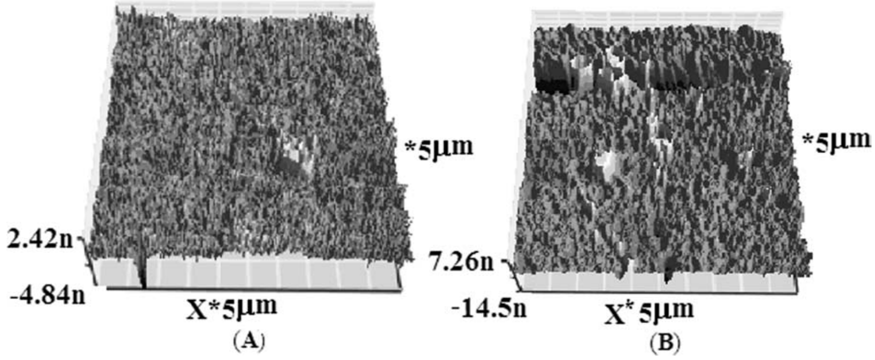


FIGURE 4 Atomic force micrography of polymer P4. (A) Before poling and (B) After poling.

NLO Properties of Polymers

As polymers P1 and P3 did not form good quality films, only polymers P2 and P4 were taken for NLO characterizations. Films of both the polymers P2 and P4 were cast using 5 wt % (w/v) THF solutions over ITO substrate. For achieving noncentrosymmetric environment, polymer films were corona poled by applying 4.8 kV. After applying the field, the temperature was raised to T_g, that is, 135 °C (which is very close to T_g) for polymer P4 and maintained for 30 min. The noncentrosymmetric arrangements of the dipoles are confirmed by checking their absorption spectra, which shows decrease in the intensity of absorption due to poling. Figure 3 shows the change in absorption for polymer P4 due to poling. From the change in absorption, the order parameters (Φ) calculated are found to be 0.1 and 0.18 for P2 and P4, respectively. Figure 4 shows atomic force microscopy image of a spin-coated film, before and after poling for polymer P4. It is found that the smoothness of the surface reduces after poling which is due to the alignment of dipoles along the field direction.

By using Nd:YAG laser of fundamental wavelength 1064 nm, angular dependence of SHG intensity was measured. Figure 5 shows the angular dependence of SHG intensity for polymer P4. The SHG intensity gradually increases with the incident angle, which is followed by a decrease. It means that at a particular angle (36°) for P4 the dipoles interact to maximum extent with the fundamental frequency. After confirming the maximum SHG intensity at a particular angle (θ), same angle was maintained for further measurements.

Dynamic thermal stability of SHG intensity for polymers P2 and P4 was studied by increasing the temperature at a rate of 4 °C/min. Figure 6 shows the dynamic thermal stability of SHG intensity for polymers P2 and P4. From the figure it is clear that polymer P4 shows better dynamic thermal stability than P2. For polymer P2, the drop of SHG intensity started at 70 °C where as for polymer P4 it started at 95 °C. This could be due to the presence of a large condensed aromatic ring (fluorine) in case of P4 when compared with P2 where benzene is the aromatic ring present. However, after 100 °C, a sharp decrease in SHG intensity was observed for

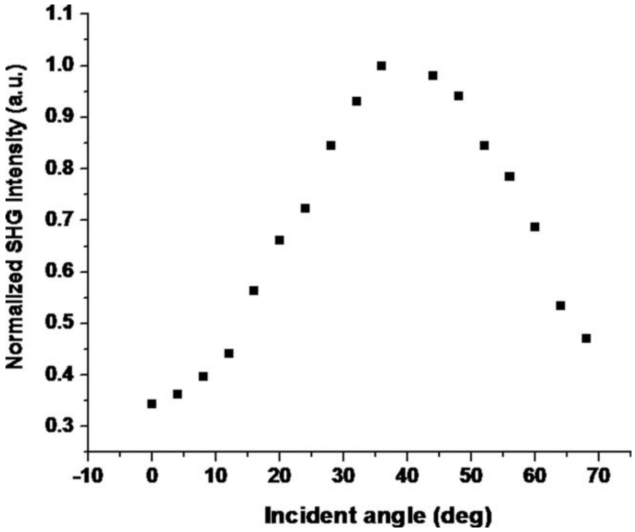


FIGURE 5 SHG Intensity of poled polymer P4 as a function of incident angle.

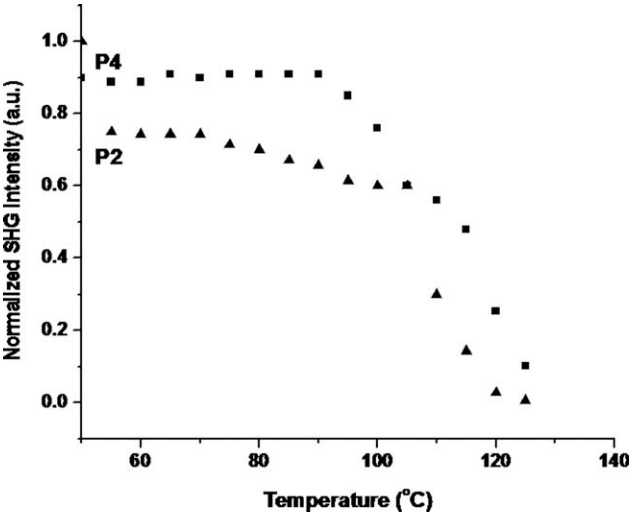


FIGURE 6 SHG Intensity of poled polymer P2 and P4 as a function of temperature.

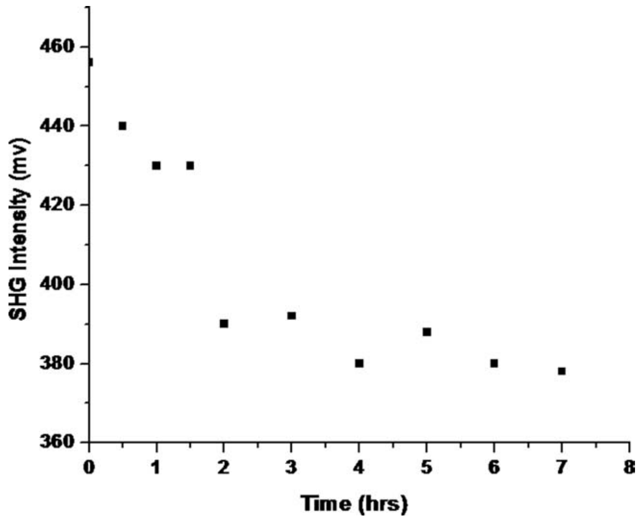


FIGURE 7 Temporal stability of SHG signals of polymer P4 at room temperature.

both the polymers. Here, the decrease for P4 is also less sharp than that of P2. A similar trend of decreasing in SHG value was also observed by Li et al.[24] where same types of isolation groups were used. When temperature above their T_g was approached, the SHG intensity starts disappearing rapidly due to relaxation at higher temperature and tends toward minimum. However, when the same sample was repoled on same area where previous poling was carried out (as it was relaxed due to temperature), the SHG signal returned back to similar intensity. This indicates that the polymers do not undergo any kind of damage at high experimental temperature. Figure 7 shows the temporal stability of polymer P4. The poled film shows long term stability at room temperature. Up to 8 days of study there was no change in the SHG intensity with an initial drop of upto 14% (approximately).

CONCLUSIONS

The NLO polymers containing azo chromophore as side chain and aromatic ring in the main chain were synthesized through copper-catalyzed click chemistry. The polymers formed good optically transparent films from THF solution. The T_g of the polymers was found to be above 100 °C, which ensured reasonable stability of poled polymer at RT. UV–vis spectra showed decrease in absorbance after poling, which confirms the alignment of dipoles in the polymer film. Dynamic thermal stability of P4 recorded continuous SHG intensity versus temperature and a fall started after 95 °C. Temporal stability of these polymers were studied at RT up to 8 days. It showed about 14% initial drop in SHG intensity that remained stable over the time studied.

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