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A novel polycarbonate for high temperature electro-optics via azo bisphenol amines accessed by Ullmann coupling

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Abstract

Ullmann coupling of benzyl ether protected 4-iodophenol with 4-nitrophenylazo aniline followed by deprotection in trifluoroacetic acid affords novel 4′-(4-nitrophenylazo)-*N*,*N*-bis(4-hydroxyphenyl)aniline. Co-condensation of this azo bisphenol and 9,9′-bis(4-hydroxyphenyl)fluorene (BHPF) with phosgene gave high molecular weight polycarbonate with $T_g = 239$ °C and high thermal stability. The polymer was soluble in common organic solvents and high quality films were prepared and subjected to poling and electro-optic (EO) analysis. The copolymer exhibited a r_{33} value of 3.7 pm/V. Synthesis, characterization, and thermal properties are described.

Keywords: Ullman; Electro-optics; Polycarbonates

1. Introduction

The fabrication of electro-optic devices from non-linear optical (NLO) polymers has attracted increased attention over the last decade due to their unique balance of thermal, mechanical, optical and dielectric properties [1,2]. The use of inorganic materials is continually challenged by conjugated π-electron organic chromophores [3], as they exhibit higher NLO activity on a molecular basis, very fast switching (on the order of 10 to 100 fs), low dielectric constant (e.g. 2–5 debye at 1 MHz), lower power consumption and ease of fabrication into integrated device structures when used in polymer form [4].

While the doped polymer approach offers some advantages over organic and inorganic crystals, major limitations exist in the case of orientational stability, poor chromophore solubility, and optical loss due to aggregation of chromophores [5]. For practical applications, both chemical and orientational stability at ~125 °C is required for NLO materials [6,7]. Several strategies have focused on this goal including network formation, which suppresses the reorientation of the chromophores [8,9], or the use of high T_g polymers such as polyimides and polyquinolines [10,11]. In general, a base polymer is chosen considering its optical transparency, film forming characteristics, dielectric constant, thermal and thermo-mechanical stability. Thus polycarbonates are good candidates as electro-optic (EO) hosts and have been widely studied as such [12–14]. As for the chromophore choice, azo chromophores are well-known candidates for EO applications due to their established photo responsive ability, thermal stability and useful absorption range [15]. The evolution of chromophore design, however, has resulted in tremendous performance gains and has long surpassed simple azo dye structures [16].

Here we report a novel strategy involving protection, Ullmann coupling and deprotection for the preparation of bisphenol substituted amine monomers containing additional functionality such as the azo group. The azo bisphenol, 4′-(4-nitrophenylazo)-*N*,*N*-bis(4-hydroxyphenyl)aniline was co-condensed with 9,9′-bis(4-hydroxyphenyl)-fluorene (BHPF) and phosgene to give a novel azo containing polycarbonate with excellent thermal stability. This general strategy should allow access to a wide variety of bisphenol substituted amines containing sensitive functionality.

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2. Experimental part

2.1. Materials and instrumentation

All reagents were purchased from Aldrich or Fischer Scientific and used as received unless otherwise stated. ^{1}H NMR 300 MHz and ^{13}C NMR 63 MHz were obtained on a Varian VXR 300 NMR spectrometer. Chloroform-*d* was used as solvent, and chemical shifts reported are internally referenced to tetramethylsilane (0 ppm), $CDCl_3$ (77 ppm) for ^{1}H and ^{13}C nuclei, respectively. The GPC data were collected from an Agilent 1100 series HPLC system equipped with two PLGel mixed-C columns (300 × 7.5 mm with 5 mm particle size). The eluent was THF with a flow rate of 1 ml/min with a system temperature of 35 °C. The thermal analyses were performed on Setaram DSC-131 and TGA-DTA systems from TA instruments under a nitrogen atmosphere. High pressure flash chromatography was performed using a Biotage 75 i/12L solvent reservoir.

2.2. Electro-optic coefficient measurement

Films were spin coated from cyclohexanone (20% weight/volume) on patterned ITO coated glass substrates at a spin speed of 1000 rpm for 25 s. The films were carefully dried at 100 °C for 2 h in nitrogen, oven drying for 100 °C for 2 h, 150 °C for 1 h in vacuum and 225 °C for 1 h under nitrogen. A gold electrode of 25 nm thickness was deposited on the sample by DC sputtering. The samples were poled at higher temperatures than T_g in air for 5 min with 370 V (cathode to ITO) to produce an applied electric field of 100 V/μm after which the sample was cooled to room temperature with the field on. The electro-optic coefficient (r_{33}) of the poled film was measured by using a thin film reflection technique from which the r_{33} value was calculated using the equation below [17].

$$r_{33} = \frac{3\lambda I_m (n^2 - \sin^2\theta)^{1/2}}{4\pi V_m I_c n^2 \sin 2\theta}$$

where λ is the wavelength of the light, I_m the intensity of the modulated light signal, n the refractive index of the polymer, θ the angle of incidence, V_m the amplitude of the applied voltage sine wave, and I_c is the unmodulated light intensity at the intensity half point corresponding to a π/2 phase shift by a Soleil–Babinet compensator.

A Lasermax Model LAS-300-830-15 830 nm diode laser was used as the light source. A Stanford research system model SR540 chopper controller was used to chop the light at 1030 Hz. A 10 V sine wave was generated by a BK Precision Dynascan Corp 3030 sweep function generator and amplified by Lasermetrics model amplifier AF3. The I_c and I_m were measured from an amplified photodiode using 124A lock in amplifier model and 116 differential amplifier model from EG&G Princeton applied research corporation. The ratio of rms voltage was corrected by a factor of 2/π to yield a ratio of sine wave amplitudes I_c/I_m. The applied voltage V_m was measured using a digital voltmeter. In a given sample 10–12 V has been applied and the signals from the sweep generator were minimized using a 10 dB attenuator on the amplifier. The r_{33} values were determined assuming an index of refraction of 1.670 and a reflection incidence angle of 45°. The r_{33} values were measured at a second half intensity point on the other side of the chopped signal maximum yielding similar r_{33} values. The μ_β of **3** has been determined by Electric Field Induced Second Harmonic Generation (EFISH) as reported previously [22]. Refractive index (n) of **4** was measured by using a prism coupling/wave guiding method [23].

2.3. Synthesis of 4-(benzyloxy)iodobenzene (*1*)

To a 500 ml flask equipped with a reflux condenser and an addition funnel was added 50.0 g (0.277 mol, 1.0 equiv.) of iodophenol, 37.69 g (0.273 mol, 1.2 equiv.) of K_2CO_3 and 250 ml DMF. The mixture was heated at 65 °C for 20 min under nitrogen. At this point 48.61 g (0.284 mol, 1.25 equiv.) of benzyl bromide in 50 ml DMF were added dropwise over 15 min and the mixture was stirred at 45 °C for an additional 20 h. The mixture was then poured onto ice and extracted with Et_2O, dried over Na_2SO_4, reduced in vacuum and recrystallized from ethanol.

Yield: 63%, mp 55–56 °C. ^{1}H NMR ($CDCl_3$): δ 4.82 (s, 2H), 6.54 (d, 2H), 7.12–7.2 (m, 5H), 7.34 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 70.1, 89.6, 117.3, 127.4, 128.1, 128.6, 136.5, 138.2, 158.7. HRMS *m/z* (EI) calcd (found) for $C_{13}H_{11}OI = 309.9855$ (309.9851).

2.4. Synthesis of 4′-(4-nitrophenylazo)-N,N-bis(4-benzyloxyphenyl)aniline (*2*)

To a 500 ml flask equipped with reflux condenser 43.3 g (0.1392 mol, 3.0 equiv.) of benzyl ether (**1**), 11.241 g (0.0464 mol, 1.0 equiv.) of 4′-(4-nitrophenylazo)aniline (disperse orange **3**), 11.70 g (0.1856 mol, 4.0 equiv.) of Cu powder, 51.3 g (0.3712 mol, 8.0 equiv.) of K_2CO_3, 2.453 g (9.28 mmol, 0.2 equiv.) of 18-crown-6 and 100 ml 1,2-dichlorobenzene were mixed and refluxed. After 24 h, the mixture was allowed to cool to room temperature, 100 ml H_2O and 200 ml Et_2O were added and the contents were allowed to stir for 2 h before filtering over Al_2O_3 The filtrate was washed with 5 × 500 ml H_2O, dried over $MgSO_4$, filtered and reduced in vacuum giving **2** as a dark red oil. Recrystallization from acetonitrile gave **2** as a red powder.

Yield: 68%, mp 85–90 °C, ^{1}H NMR ($CDCl_3$, ppm): δ 5.08 (s, 4H), 6.75 (d, 2H), 6.8 (d, 2H), 7.14(d, 2H), 7.4 (m, 10H), 7.52 (d, 2H), 7.78 (d, 4H), 7.93 (d, 4H), 8.31 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 70.4, 115.98, 117.3, 118.0, 122.8, 124.7, 125.9, 127.4, 127.8, 128.1, 128.6, 136.8, 138.3,

Table 1
Selected properties of polycarbonate **4**

λ_{max}[a] (nm)	RI (830 nm)	N	β_o (for **3**) ($\times 10^{-30}$ esu)	T_g[b] (°C)	T_d[c] (°C)	r_{33} (pm/V)	M_w[d]	M_w/M_n
469	1.670	8.27	44	239	383	3.7	29,000	3.5

[a] UV absorption in $CHCl_3$.
[b] DSC at 10 °C/min in N_2.
[c] TGA degradation onset at 20 °C/min N_2.
[d] GPC in THF vs. polystyrene.

145.9, 147.8, 152.7, 156.4. HRMS *m/z* (EI) calcd (found) for $C_{31}H_{23}O_4 = 515.1719$ (515.1741).

2.5. Synthesis of 4′-(4-nitrophenylazo)-N,N-bis(4-hydroxyphenyl)aniline (3)

To a 1 l flask equipped with an addition funnel, 20 g (0.033 mol) of dibenzyl ether **2** and 330 ml (0.3 mol, 10 equiv.) of trifluoroacetic acid were added and allowed to stir at room temperature for 48 h. The reaction was quenched with 1 l ice water and the bisphenol was extracted into 300 ml Et_2O. The organic layer was washed 2 × 100 ml H_2O, 5 × 100 ml aq $NaHCO_3$ (sat.) and 2 × 100 ml H_2O, dried over $MgSO_4$ filtered and reduced in vacuum giving **3** as a dark red powder. All attempts to recrystallize failed and the product was purified by high pressure flash chromatography (Biotage) on silica with CH_3CN/CH_2Cl_2 (20/80%).

Yield: 25%, mp 237–240 °C. ^1H NMR (DMSO-d_6): δ 6.7 (d, 4H), 7.1 (d, 4H), 7.75 (d, 2H), 7.91 (d, 2H), 8.32 (d, 2H), 9.55 (d, 2H). ^{13}C NMR (DMSO-d_6): δ 115.5, 116.5, 122.6, 124.9, 125.5, 128.4, 136.6, 144.3, 147.4, 153.1, 155.6, 156.9. GCMS (EI) *m/z* for $C_{24}H_{18}N_4O_4 = 426$ w/276 at 100%).

2.6. Polymer synthesis

To a 250 ml flask equipped with industrially approved nitrogen/phosgene delivery inlet and mechanical stirrer was added 2.99 g (0.007 mol, 0.5 equiv.) **3**, 2.55 g (0.007 mol, 0.5 equiv.) BHPF, 100 ml CH_2Cl_2 and 3.06 ml pyridine. The dark red solution was stirred for 5 min under nitrogen and 1.4 g (0.0145 mol, 1 equiv.) of $COCl_2$ was added over 5 min and the increase in molecular weight was monitored visually by quenching samples in methanol. An additional 0.6 g phosgene was added over 45 min after which the increase in molecular weight ceased. The polymerization was quenched with 4 ml MeOH and 26 ml 0.5 M HCl and allowed to stir for 20 min before washing the solution with 2 × 25 ml H_2O, 1 × 25 ml aq. $NaHCO_3$ (0.04 g/ml), and 2 × 25 ml H_2O. The solution was then precipitated slowly into 1 l of stirring methanol giving the copolymer in essentially quantitative yield as a red fibrous powder upon filtration and drying at 80 °C for 12 h. Relative molecular weight was determined by GPC (Table 1).

^1H NMR ($CDCl_3$): δ 7.0–7.3 (m, 20H), 7.35 (m, 4H), 7.75 (m, 2H), 7.85 (m, 2H), 7.93 (d, 2H), 8.31 (d, 2H). ^{13}C NMR ($CDCl_3$, ppm): δ 64.5, 120.3, 120.6, 121.1, 122.2, 123.0, 124.7, 125.1, 126.0, 126.6, 127.9, 129.2, 129.2, 140.0, 143.8, 143.6, 144.2, 144.3, 147.2, 147.5, 148.1, 149.7, 150.4, 151.2, 151.85, 151.9, 151.95, 156.04.

3. Results and discussion

The preparation of triarylamine chromophores containing the azo linkage by Ullmann coupling has been described previously by IBM workers and others [13,14]. We adopted this general strategy and successfully identified the benzyl ether-protecting group as one which is stable to Ullmann conditions yet can be removed in high yield. The azo bisphenol monomer **3** was synthesized in three steps as shown in Fig. 1 in an overall isolated yield of 10%. Other protecting groups including methyl ether and TMS ether were attempted but were not successful due to the sensitivity of the chromophore to harsh deprotection methods for methyl ether deprotection and the sensitivity of the TMS ether to Ullmann coupling as also observed previously [14].

After purification by high pressure flash chromatography, monomer **3** was copolymerized with BHPF and phosgene to give 50:50 (mol:mol) copolycarbonate **4** shown in Fig. 2. The molecular weight of the copolymer was measured by GPC in THF (vs. polystyrene) and gave $M_w = 29,000$ with molecular weight distribution (M_w/M_n) of 3.5

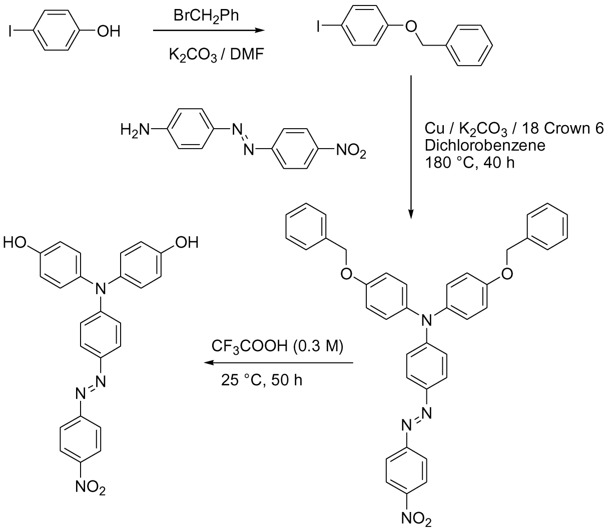

Fig. 1. Synthesis of bisphenol monomer **3**.

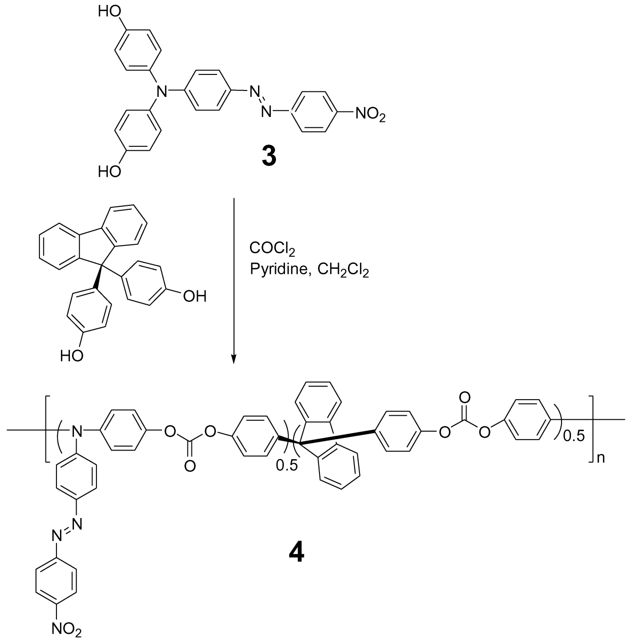

Fig. 2. Synthesis of polycarbonate copolymer **4**.

after precipitation. The ^{1}H and ^{13}C NMR spectra of the polymer are shown in Figs. 3 and 4.

The chromophore content in copolymer **4** can be tailored in this random step-growth condensation reaction, however a 50:50 ratio demonstrates a high chromophore loading in the polymer. The copolymer ratio was confirmed by ^{1}H NMR (Fig. 3) integration of the *ortho* fluorene proton signals at 8.3 ppm compared to the integration of the chromophore aromatic proton signals ($\delta = 7.7$, 7.85, 7.95, 2H signals, respectively). The integration can be further confirmed by the well-resolved *meta* and *para* protons of the fluorene group (7.4 δ, 4H) in comparison with the two protons adjacent to the nitro group in the chromophore (7.95, 2H). The ^{13}C NMR spectrum of copolymer **4** in pyridine-d_5 exhibits the polycarbonate carbonyl carbon signal at 156.6 ppm.

The glass transition temperature for copolymer **4** was determined by DSC and a reproducible value of 239 °C was measured after multiple cycles to 300 °C (Fig. 5). Typically the T_g of polymers with doped chromophores decreases with increase in chromophore loading [18]. In this case, however, the chromophore is covalently attached to the main chain and therefore thermal stability is enhanced. Chromophore functionalized polycarbonate **4** can be poled at and above T_g without degradation as shown in Fig. 5. The high T_g of polymer **4** provides a larger difference between use temperature and poling temperature when compared to most other polycarbonate and polyimide NLO systems [19].

The thermal stability of copolymer **4** was assessed by TGA where the onset of catastrophic decomposition in an inert atmosphere was found to be above 385 °C at 20 °C/min (Fig. 6). Clearly, the covalent incorporation of the azo chromophore into BHPF based polycarbonates does not significantly limit the thermal stability while maintaining reasonable optical absorption [20].

In general, polymeric electro-optic wave guide device fabrication involves deposition of a lower electrode layer (ITO), a lower cladding layer, an active guiding layer (copolymer 4), an upper cladding layer, and an upper electrode layer. The λ_{max} of 4 is below 700 nm (Table 1) and

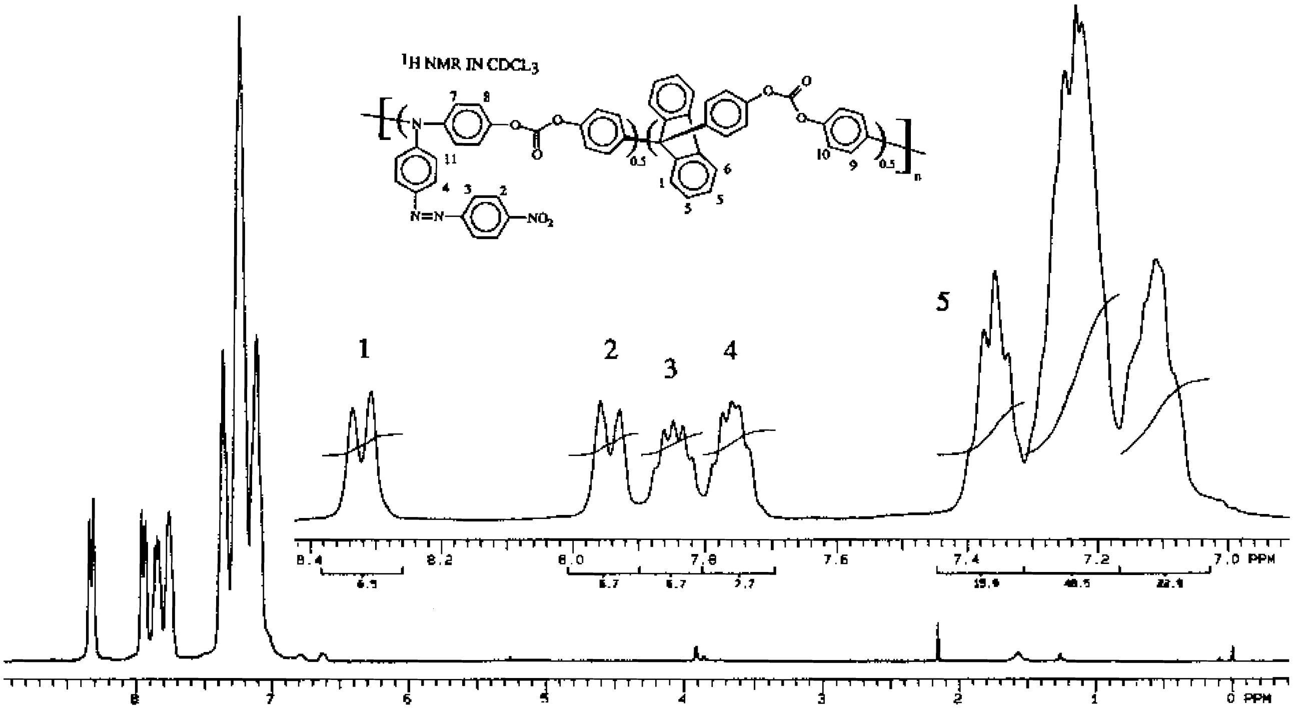

Fig. 3. ^{1}H NMR spectrum of polycarbonate **4** in CDCl$_3$.

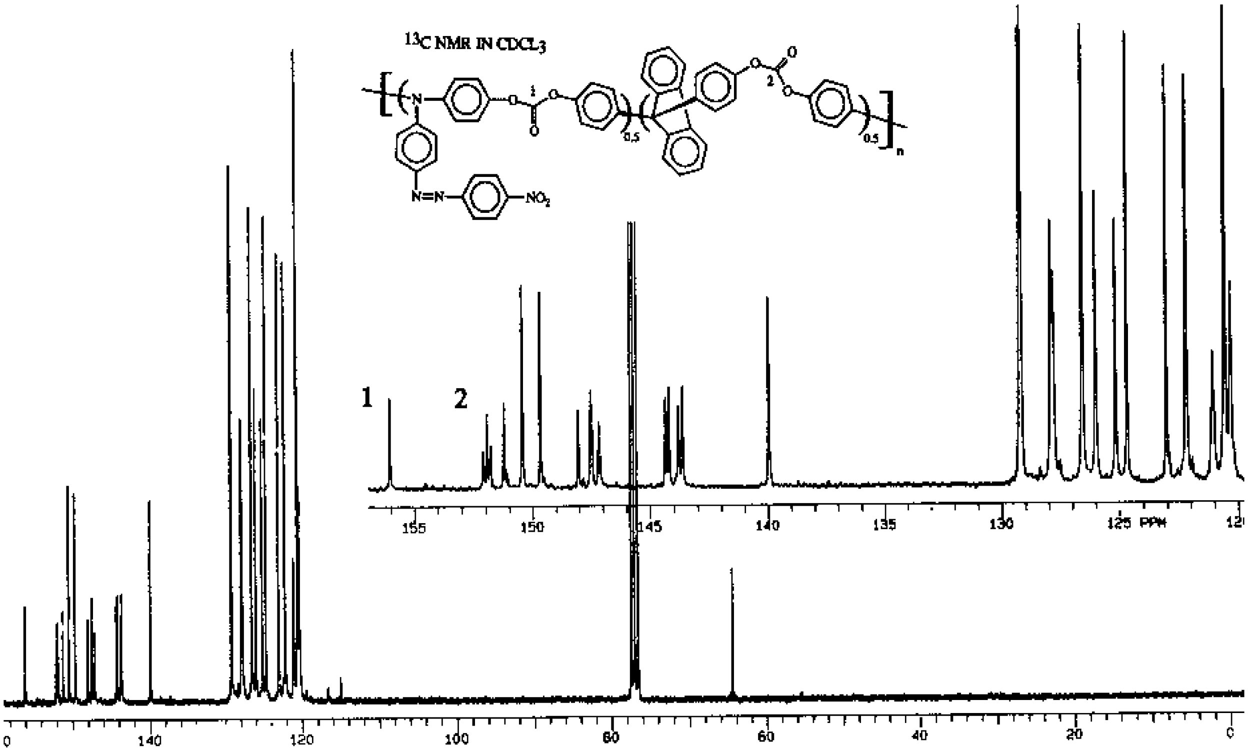

Fig. 4. ^{13}C NMR spectrum of polycarbonate **4** in CDCl$_3$.

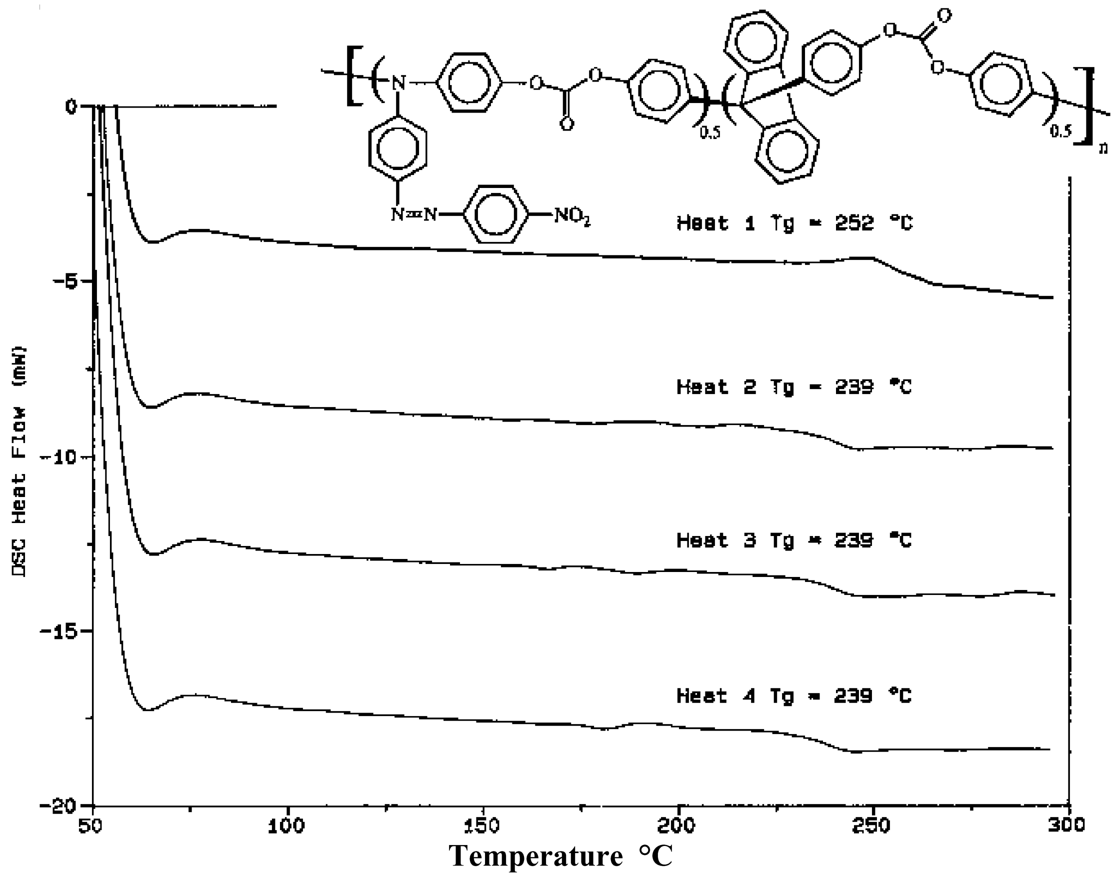

Fig. 5. DSC overlay of copolymer **4** at the rate of 10 °C under N$_2$.

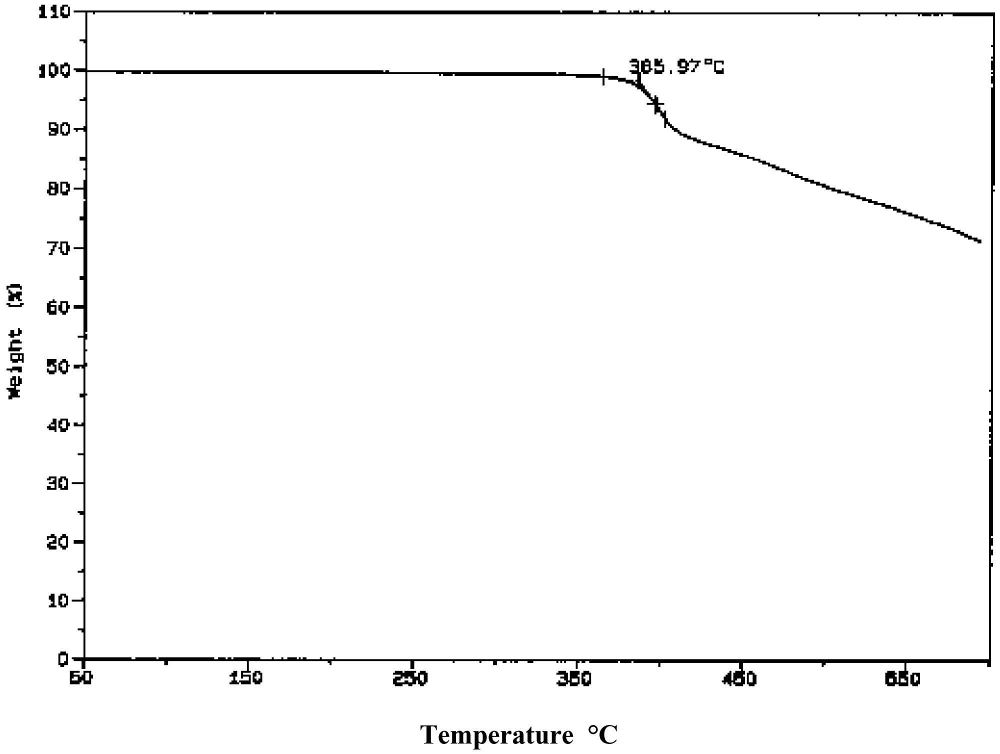

Fig. 6. TGA of polycarbonate copolymer **4** at the rate of 20 °C under N_2.

therefore adequate for electro-optic applications as there is no significant second harmonic optical absorption at the telecommunication wavelengths of 1.33 or 1.55 μm [16]. Polymer **4** is soluble in many common organic solvents and was spin coated onto ITO glass substrates from cyclohexanone solution (20% w/v) giving high quality defect-free films. A gold electrode was then deposited on top of the film and the film was poled at 240 °C to induce a non-centrosymmetric orientation. The electro-optic coefficient, r_{33} value, was calculated to be 3.7 pm/V which compares well with other reported azo based NLO polymers [21]. Selected properties for the copolymer are given in Table 1.

4. Conclusion

A new triarylamine azo bisphenol has been prepared by Ullmann coupling using a benzyl ether protection strategy. Co-condensation of the bisphenol **3** and 9,9′-bis(4-hydroxyphenyl)fluorine (BHPF) with phosgene gave high molecular weight polycarbonate with $T_g = 239$ °C and good thermal stability. The copolymer was soluble in common organic solvents and high quality films were prepared and subjected to poling after which the copolymer exhibited a r_{33} value of 3.7 pm/V. The high glass transition temperature and high thermal decomposition temperature indicates that this strategy may be promising for EO applications requiring high processing and use temperatures.

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References

[1] Dalton LR, Steier WH, Robinson B, Zhang C, Ren A, Garner S, Chen A, Londergan T, Irwin L, Carlson B, Fifield F, Phelan G, Kincaid C, Amend J, Jen A. J Mater Chem 1999;9:1905.
[2] Marder SR, Kippelen B, Jen AK-Y, Peyghambarian N. Nature 1997; 388:845.
[3] Burland DM, Miller RD, Walsh CA. Chem Rev 1994;94:31.
[4] Bales SE, Bremann DJ, Gulotty RJ, Haag AP, Inbasekharan MN. US Patent 5,208,299.
[5] Hampsch HL, Yang J, Wong GK, Torkelson JM. Macromolecules 1988;21:526.
[6] Starhelin M, Burland DM, Ebert M, Miller RD, Smith BA, Tweig RJ, Volksen W, Walsh CA. Appl Phys Lett 1992;61:1626.
[7] Weder C, Neuenschwander P, Suter UW, Pretre P, Kaatz P, Gunter P. Macromolecules 1995;28:2377.
[8] White KM, Francis CV, Isackson AJ. Macromolecules 1994;27:3619.
[9] Tsutsumi N, Yoshizaki S, Sakai W, Kiyotsukuri T. Macromolecules 1995;28:6437.
[10] Petre P, Kaats P, Boheren A, Gunter P, Zysset B, Ahlheim M, Starhelin M, Lehr F. Macromolecules 1994;27:5476.
[11] Ma H, Jen AK-Y, Wu JY, Wu XM, Liu S, Shu CF, Dalton LR, Marder SR, Thayumanavan S. Chem Mater 1999;11(8):2218.
[12] For a recent example, see: Ermer S, Lovejoy SM, Bedworth PV, Leung DS, Warren HB, Epstein JA, Girton DG, Dries LS, Taylor RE,

Barto RR, Eades WV, Timothy E, Moss AS, Anderson WW. Adv Funct Mater 2002;12(9):605.

[13] Miller RD, Lee VY, Twieg RJ. J Chem Soc, Chem Commun 1995;2:245.

[14] Martin EH, Brittain WJ. Polym Prepr 1999;40:1304.

[15] Natansohn A, Rochon P. Adv Mater 1999;11:1387.

[16] Dalton LR. Adv Polym Sci 2002;158:1.

[17] Levy Y, Dumont M, Chastaing E, Robin P, Chollet PA, Gadret G, Kajzar F. Mol Cryst Liq Cryst Sci—Sect B Nonlinear Opt 1993;4:1.

[18] Zhao M, Bautista M, Ford WT. Macromolecules 1991;24:844.

[19] Liu YG, Sui Y, Yin J, Gao J, Zhu ZK, Huang DY, Wang ZG. J Appl Polym Sci 2000;76:290.

[20] Thayumanavan S, Mendez J, Marder SR. J Org Chem 1999;64:4289.

[21] Huang D, Zhang C, Dalton LR, Webber WP. J Polym Sci Part A 2000;38:546.

[22] Levine BF, Bethea CG. J Chem Phys 1975;63:2666.

[23] Tien PK, Ulrich R. J Opt Soc Am 1970;60(10):1325.