

Novel Aromatic Polymers from Benzaldehyde and Triphenylamine Derivatives: Synthesis, Electrochromic, and Photochemical Properties

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Received 20 December 2008; accepted 24 January 2009

DOI: 10.1002/pola.23319

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of novel triphenylamine-based polymers were synthesized from benzaldehyde and triphenylamine derivatives. All the polymers having high molecular weight are readily soluble in many organic solvents and could be solution-cast into amorphous films. They had glass transition temperatures (T_g s) in the range of 193–217 °C, and 10% weight loss temperatures in excess of 475 °C. Cyclic voltammograms of all polymers showed reversible oxidation redox peaks and E_{onset} around 0.42–0.90 V, indicating that the polymers are electrochemically active and stable. In addition, all these polymers revealed photochemical characteristics in conformity with their electrochromic characteristics. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 2118–2131, 2009

Keywords: benzaldehyde; electrochemistry; electrochromic polymers; functionalization of polymers; high temperature materials; triphenylamine

INTRODUCTION

Electrochromism is an interesting property of materials that change color reversibly in different oxidation or reduction states.^{1,2} Electroactive conducting polymers such as polyanilines,³ polypyrroles,⁴ polythiophenes,⁵ and other derivatives have been investigated. Compared to small inorganic electrochromic materials (bipyridium salt, WO_3),² electroactive conducting polymers provided higher thermal stability, faster response time, and large area easy processing, which have more potential for industry application. One of electrochromic materials attractive properties

would be multicolor display. Reynolds group controlled different color changes by bipotentiostatic technique with dual polymers⁶; Wudl group also reported the full color goal by preparing a red, green, and blue (RGB) cathodic polymeric electrochromic device.⁷ Moreover, preparing electroactive polymers with multiredox states also promises as multiple colors materials.⁸

Recently, triphenylamine (TPA) derivatives materials, including small molecules and macromolecules, have extensively been investigated for hole transporters,⁹ light emitters.^{10–13} TPA can also be considered as a good electrochromic material as it easily oxidizes to form radical cation with a noticeable change of coloration.^{14–17} Therefore, we have reported many TPA-based high performance polymers such as aromatic polyarylates,¹⁸ polyamides,^{19–22} and polyimides.^{23–25} They reveal excellent reversible electrochromism

Additional Supporting Information may be found in the online version of this article.

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 47, 2118–2131 (2009)
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upon redox switching and also can reach multiple colors change between their oxidative states by applied different voltage. Although TPA has many advantages, Adams and coworkers^{26,27} reported that TPA could be easily dimerized to form tetraphenylbenzidine during the anodic oxidation pathway. For electrochromic materials, this dimerization could be considered as an undesired side reaction, which might cause irreversible defect after several redox switches. To avoid such behavior, incorporating electron-donating substituents like methyl or methoxyl at the *para*-position of TPA group could prevent the coupling reactions and afford stable cationic radicals with lower potential.²⁸ TPA-based polymers could be prepared by many methods, like Ullmann reactions,²⁹ palladium³⁰ or nickel-catalyzed³¹ coupling reactions. However, these synthetic methods required multiple steps to prepare the low-yield monomers, or might need highly cost catalysts. Our strategy in this article is to synthesize high-yield TPA-containing monomers by easier procedure, and then react with the commercially available commodity benzaldehyde through an acid catalyzed polymerization.^{32,33} Sato and coworkers^{32,33} and Shikatani et al.³⁴ reported that reaction of TPA derivatives with various aldehydes provided hole transporting materials, but the electrochromic properties of the obtained polymers were not investigated. Nishikitani et al.³⁵ also reported the similar result; however, they introduced alkyl group in *N*-position that might cause not only less conjugation cation radical form but also lower their glass transition temperatures (T_{gs}) and thermal stability. In this report, we prepared TPA-containing monomers with electron-donating group such as methyl or methoxy, and their corresponding polymers were obtained by addition condensation reaction of the TPA derivatives with benzaldehyde. The general properties such as solubility and thermal properties are described. The electrochemical and electrochromic characteristics of these polymers are also investigated herein. In addition, the photochemical reaction and photochromic phenomenon of the TPA-based polymer solutions in CHCl_3 under irradiation were also studied.

EXPERIMENTAL

Materials

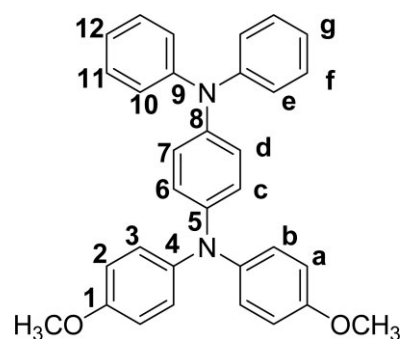
4-Methyltriphenylamine (MTPA)³² and 4-methoxytriphenylamine (MOTPA)^{13b} were synthesized by Ullmann reaction from commercially available

diphenylamine with 4-iodotoluene and 4-iodoanisole, respectively. Triphenylamine (ACROS), benzaldehyde (ACROS), chlorobenzene (TEDIA), acetic anhydride (TEDIA), *N*-methyl-2-pyrrolidinone (NMP) (TEDIA), *N,N*-dimethylacetamide (DMAc) (TEDIA), chloroform (TEDIA), and tetrahydrofuran (THF) (TEDIA) were used without further purification. Tetrabutylammonium perchlorate (TBAP) was obtained from TCI and recrystallized twice from ethyl acetate and then dried *in vacuo* prior to use. All other reagents were used as received from commercial sources.

Monomer Synthesis

N,N-Bis(4-methoxyphenyl)-*N,N'*-diphenyl-*p*-phenylenediamine (MOPD1)

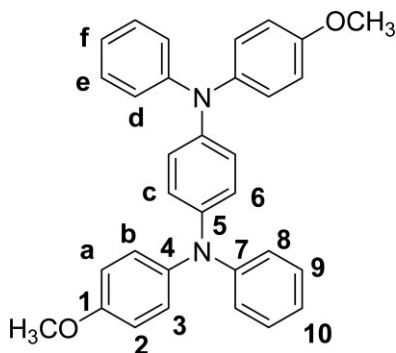
A mixture of 4-aminotriphenylamine (3.90 g, 15 mmol), 4-iodoanisole (8.66 g, 37 mmol), copper powder (2.03 g, 32 mmol), potassium carbonate (8.56 g, 62 mmol), and triethyleneglycol dimethyl ether (TEGDME) (20 mL) was heated with stirring at 160 °C for 48 h and then precipitated into 700 mL of ice water. Recrystallization from hexane yielded 3.47 g of the desired compound (MOPD1) as yellow powder in 49% yield; mp: 100–104 °C. ¹H NMR (DMSO-*d*₆, ppm): 3.71 (s, 6H, –OCH₃), 6.76 (d, 2H, *J* = 6.0 Hz; H_c), 6.87–7.01 (m, 16H, H_a + H_b + H_d + H_e + H_g), 7.24 (t, 4H, *J* = 15.0 Hz; H_f); ¹³C NMR (DMSO-*d*₆, ppm): 55.4 (–OCH₃), 115.1 (C²), 121.4 (C⁶), 122.2 (C¹²), 122.7 (C¹⁰), 126.3 (C³), 126.5 (C⁷), 129.5 (C¹¹), 139.9 (C⁵), 140.6 (C⁴), 144.7 (C⁸), 147.6 (C⁹), 155.6 (C¹). ELEM. ANAL. Calcd. for C₃₂H₂₈N₂O₂: C, 81.33%; H, 5.97%; N, 5.93%. Found: C, 81.28%; H, 5.76%; N, 5.86%. ESI-MS: calcd for (C₃₂H₂₈N₂O₂)⁺: *m/z* 472.5; found: *m/z* 472.5.



N,N'-Bis(4-methoxyphenyl)-*N,N'*-diphenyl-*p*-phenylenediamine (MOPD2)

MOPD2 was synthesized by the reaction of *N,N'*-diphenyl-*p*-phenylenediamine with 4-iodoanisole

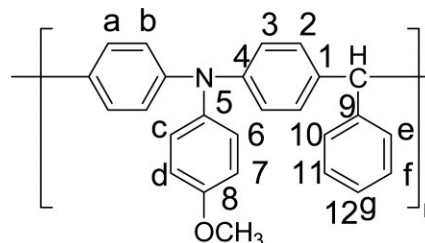
by a similar procedure described as above; yield: 56%, mp: 146–150 °C. ^1H NMR (DMSO- d_6 , ppm): 3.77 (s, 6H, $-\text{OCH}_3$), 6.91–6.96 (m, 14H, $\text{H}_a + \text{H}_c + \text{H}_d + \text{H}_f$), 7.06 (d, 4H, $J = 9.0$ Hz; H_b), 7.25 (t, 4H, $J = 15.0$ Hz; H_e); ^{13}C NMR (DMSO- d_6 , ppm): 55.2 ($-\text{OCH}_3$), 115.0 (C^2), 121.1 ($\text{C}^8 + \text{C}^{10}$), 124.3 (C^6), 127.0 (C^3), 129.2 (C^9), 139.9 (C^4), 142.2 (C^5), 147.9 (C^7), 155.9 (C^1). ELEM. ANAL. Calcd. for $\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_2$: C, 81.33%; H, 5.97%; N, 5.93%. Found: C, 80.75%; H, 6.17%; N, 5.79%. ESI-MS: calcd for $(\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_2)^+$: m/z 472.5; found: m/z 472.4.



Polymer Synthesis

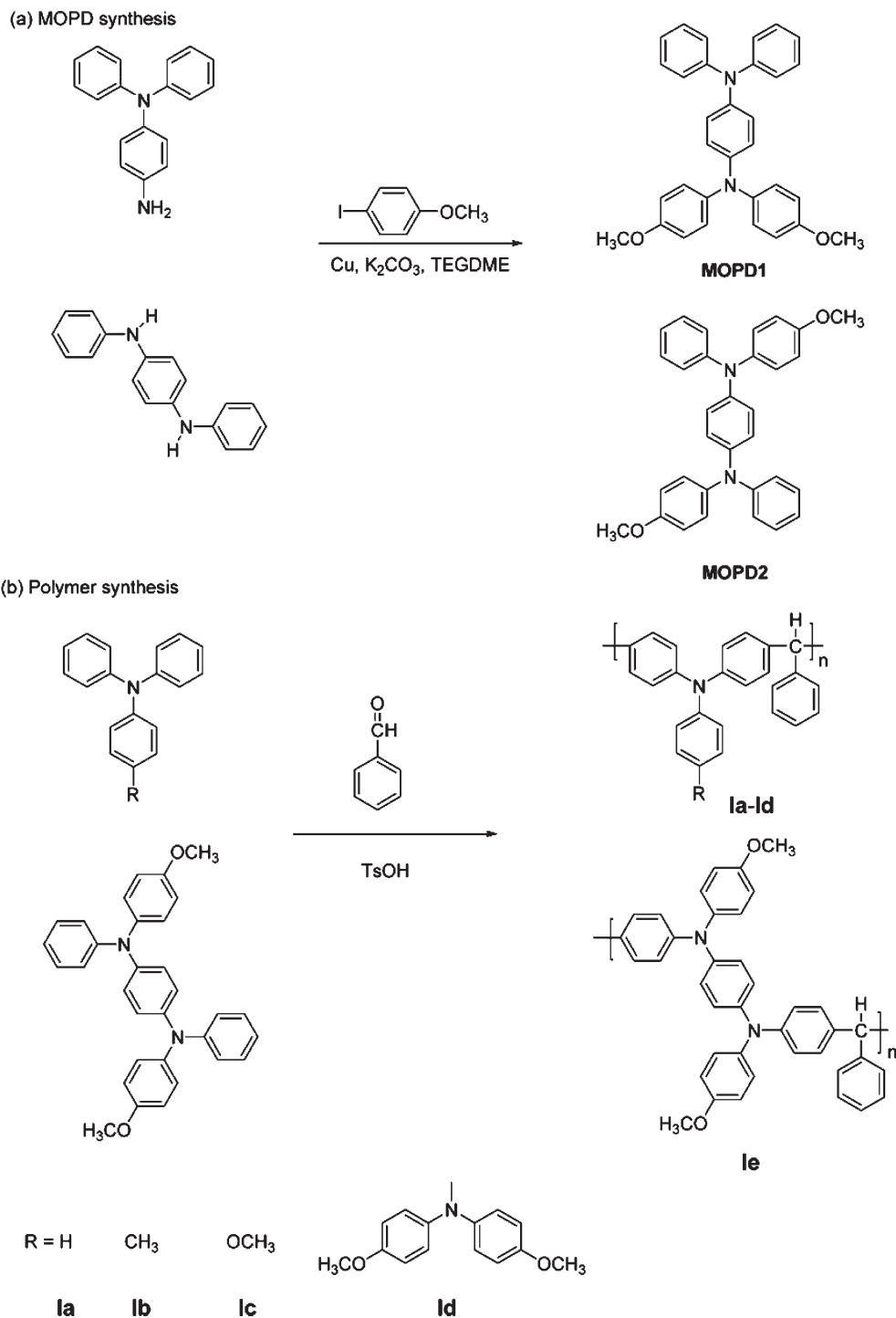
Polymerizations were carried out in sealed glass ampoules under a dry nitrogen atmosphere, and *p*-toluenesulfonic acid was used as a catalyst. The synthesis of polymer **1c** is used as an example to illustrate the general synthetic route. The typical procedure is as follows. A mixture of 1.377 g (5 mmol) of the 4-methoxytriphenylamine, 0.637 g (6 mmol) of benzaldehyde, 0.034 g of *p*-toluenesulfonic acid (0.2 mmol), and 3.9 mL of chlorobenzene was heated with stirring at 110 °C for 2 h. After polymerization, 2 mL acetic anhydride was added and refluxed for 30 min to cap hydroxyl end groups. The resulting viscous polymer solution was poured slowly into acetone and then purified by reprecipitating the polymer chloroform solution into acetone containing two or three drops of aqueous ammonia solution two or three times, followed by drying *in vacuo*. The inherent viscosity and weight-average molecular weights (M_w) of the obtained polyamide **1c** was 0.43 dL/g (measured at a concentration of 0.5 g/dL in NMP at 30 °C) and 175,600 Da, respectively. IR (film): 3025 (aromatic $-\text{C}-\text{H}$ stretch), 2949, 2833 ($-\text{CH}_2$ stretch), 1602, 1504 ($\text{C}=\text{C}$ stretch), 1242, 1034 cm^{-1} (aromatic $\text{C}-\text{O}-\text{C}$ stretch). ^1H NMR (CDCl_3 , ppm): 3.78 (s, 3H, $-\text{OCH}_3$), 5.39 (s, 1H, $-\text{CH}$), 6.82 (d, 2H, $J = 9.0$ Hz; H_d), 6.95 (s, 8H, $\text{H}_a + \text{H}_b$), 7.07 (d, 2H, $J = 9.0$ Hz; H_c), 7.20 (t, 3H,

$J = 18.0$ Hz; $\text{H}_f + \text{H}_g$), 7.26 (d, 2H, $J = 9.0$ Hz; H_e). ^{13}C NMR (CDCl_3 , ppm): 55.4 ($-\text{OCH}_3$), 55.6 ($-\text{CH}$), 114.7 (C^7), 122.4 (C^3), 126.1 (C^{12}), 127.3 (C^6), 128.2 (C^{10}), 129.3 (C^{11}), 129.9 (C^2), 137.4 (C^1), 140.7 (C^9), 144.5 (C^5), 146.2 (C^4), 156.0 (C^8). ELEM. ANAL. Calcd. for $(\text{C}_{26}\text{H}_{21}\text{NO})_n$: C, 85.92%; H, 5.82%; N, 3.85%. Found: C, 85.03%; H, 5.66%; N, 3.76%. Other polymers were synthesized by a similar procedure described as above.



Measurements

Infrared spectra were recorded on a PerkinElmer RXI FTIR spectrometer. ^1H and ^{13}C NMR spectra were measured on a Bruker Avance 300 MHz FT-NMR system. Elemental analyses were run in an Elementar VarioEL-III. A Finnigan LCQ Advantage MAX LC/MS/MS ion trap mass spectrometer (ESI-MS; Thermo Finnigan, San Jose, CA) was used in the electrospray ionization (ESI) mode. The spray voltage was 2.4 kV with a current of about 20 mA. Samples were introduced to the source by direct insert probe. Gel permeation chromatographic (GPC) analysis was performed on a Lab Alliance RI2000 instrument (two column, MIXED-C and D from Polymer Laboratories) connected with one refractive index detector from Schambeck SFD GmbH. All GPC analyses were performed using a polymer/THF solution at a flow rate of 1 mL/min at 40 °C and calibrated with polystyrene standards. Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer Pyris 1 TGA. Experiments were carried out on ~6–8 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris Diamond DSC at a scan rate of 20 °C/min in flowing nitrogen (20 cm^3/min). Electrochemistry was performed with a CHI 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downward. Cyclic voltammetry was performed with the use of a three-electrode cell in which ITO (polymer films area about 0.7 $\text{cm} \times 0.5$ cm) was used as a working electrode.



Scheme 1. Synthesis routes of monomers and polymers in this study.

A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (sat.) reference electrode. Absorption spectra in the spectroelectro-

chemistry experiments were measured with a HP 8453 UV-visible spectrophotometer and Jasco V-570 UV/Vis/NIR spectrophotometer. Irradiation of the photochemical reaction system with light also

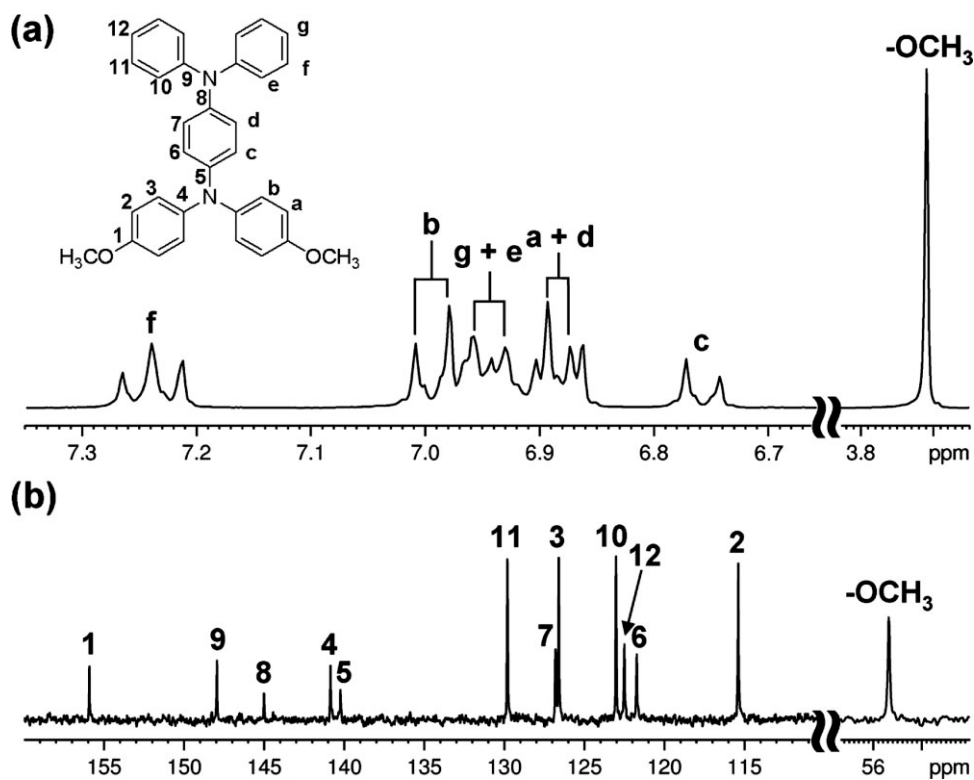


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of **MOPD1** in $\text{DMSO-}d_6$.

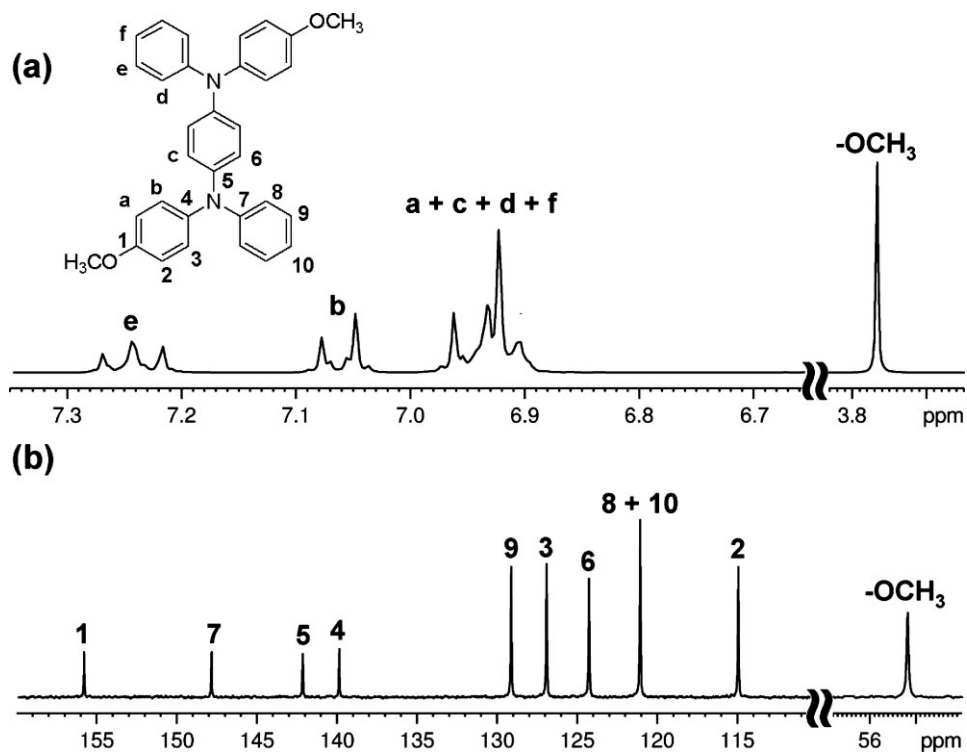


Figure 2. (a) ^1H NMR and (b) ^{13}C NMR spectra of **MOPD2** in $\text{DMSO-}d_6$.

Table 1. Reaction Conditions^a and Molecular Weights^b of Polymers

Polymer Code	Catalyst mol %	Reaction Temp (°C)	Reaction Time (h)	M_n	M_w	PDI M_w/M_n
Ia	4	65	2.0	25,200	73,300	2.9
Ib	4	110	2.0	13,800	37,500	2.7
Ic	4	110	2.0	23,700	175,600	7.4
Id	8	110	12.0	10,300	33,200	3.2
	4	110	25.0	1,600	2,600	1.5
Ie	8	110	3.0	12,300	30,500	2.5
	4	110	10.0	3,700	7,600	2.0

^a Conditions: solvent, chlorobenzene; benzaldehyde/TPA (or MOPD) mole ratio, 1.2; TPA (or MOPD) mole concentration, 1.3 mol l⁻¹.

^b Values estimated by GPC using THF as an eluent (polystyrene standards).

was carried out by using Jasco FP-6300 as the source of light.

RESULTS AND DISCUSSION

Monomer Synthesis

The synthetic route of monomers is outlined in Scheme 1. **MOPD1** and **MOPD2** were prepared by Ullmann reaction from 4-iodoanisole with 4-aminotriphenylamine and *N,N'*-diphenyl-*p*-phenylenediamine, respectively, according to our previous study.³⁶ Elemental analyses and NMR spectroscopic techniques were used to confirm the structures of the obtained monomers. The ¹H and ¹³C NMR spectra of **MOPD1** and **MOPD2** were illustrated in Figures 1 and 2. Assignments of each proton and carbon were assisted by the two-dimensional H–H COSY (Correlation Spectroscopy) and C–H HMQC (Heteronuclear Multiple Quantum Correlation) spectra given in Supporting Information Figures S(1–4), and the results agreed well with the proposed molecular structure of **MOPD1** and **MOPD2**.

Polymer Synthesis

A series of polymers were prepared from various aromatic TPA derivatives and benzaldehyde by using *p*-toluenesulfonic acid as a catalyst (Scheme 1). All the polymerizations proceeded homogeneously throughout the reaction and afforded dark-green and viscous polymer solutions. Table 1 summarizes all the polymerization conditions, and all obtained polymers **Ia–Ie** were in almost quantitative yield. The GPC results indicated that weight-average molecular weights (M_w)

values and polydispersity values (PDI) were in the range of 30,500–175,600 and 2.5–7.4, respectively. The average molecular weight of polymers decrease in the order of **Ic**>**Ib** that could be attributed to the different electron-donating effect between methoxy and methyl group, which increases the reactivity of electrophilic substitution process because of higher electron density for **Ic** moieties. Polymer **Ia** with high molecular weight was also obtained because TPA could be considered as a trifunctional groups monomer which might enhance the reactivity. The low reactivity of **Id** and **Ie** is probably caused by the MOPD structure which has higher conjugation system than TPA. The resonance effect with more conjugation may reduce the electrophilicity of the phenyl rings that need double catalyst amount to get higher molecular weight polymer **Id** and **Ie**.

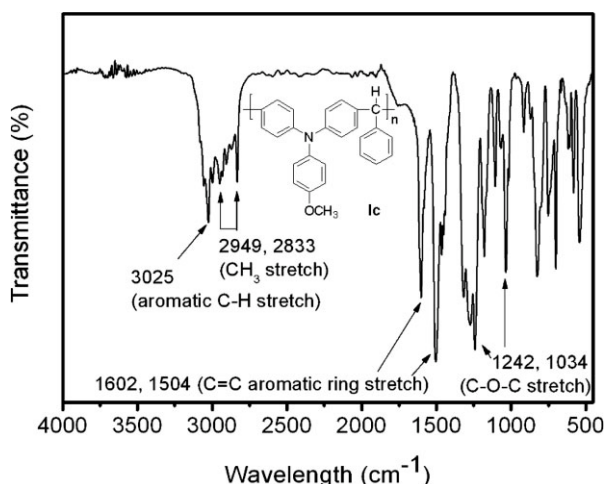


Figure 3. The FTIR spectrum of **Ic**.

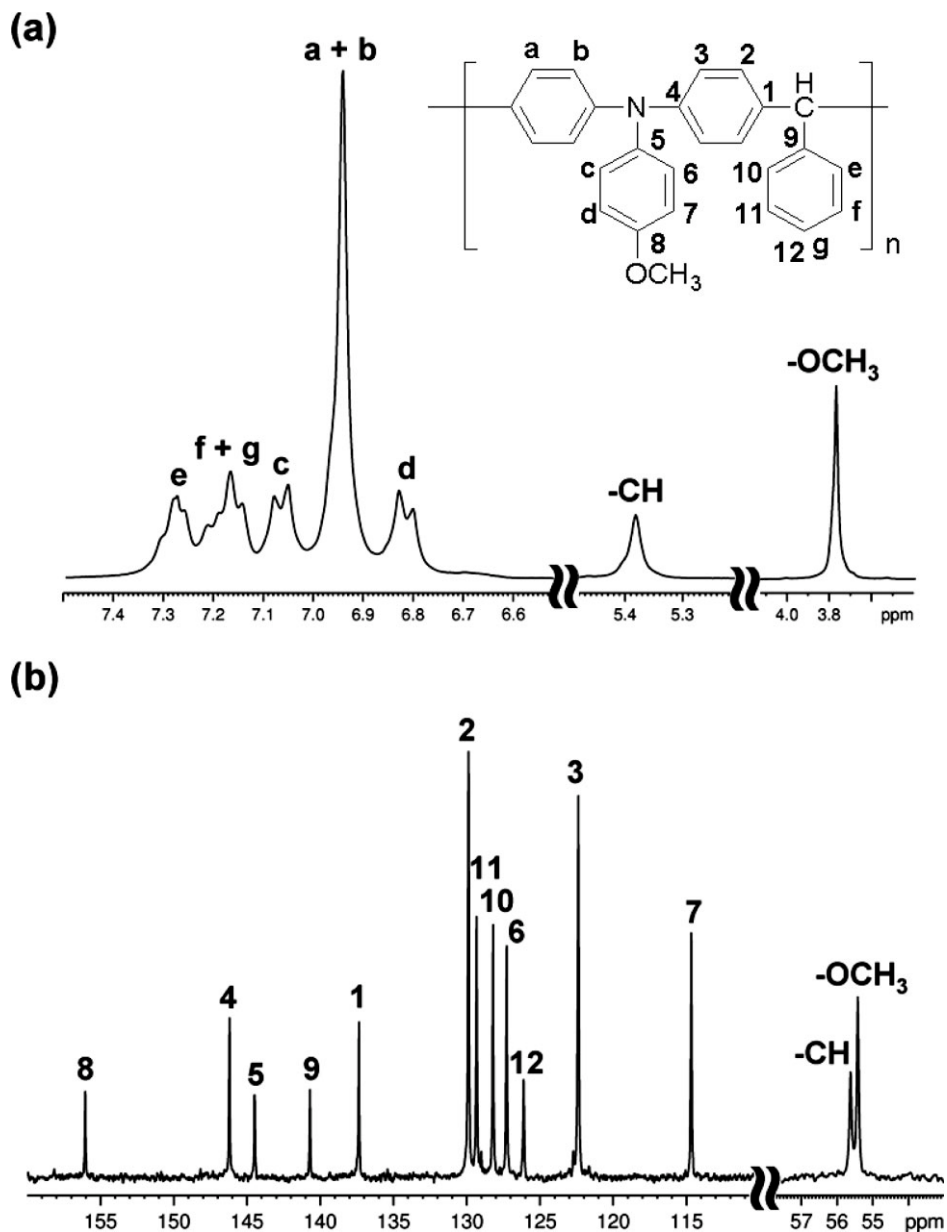


Figure 4. (a) ^1H NMR and (b) ^{13}C NMR spectra of **Ic** in chloroform-*d*.

The formation of polymers was confirmed by means of IR and NMR spectroscopy. The typical FTIR spectrum of **Ic** (Fig. 3) exhibited characteristic absorption band in the region of 1242 and 1034 cm^{-1} (C—O—C stretching). Figure 4 illustrates the ^1H and ^{13}C NMR spectra of the polymer **Ic**. The signal at 5.39 ppm is assigned to methine proton and another signal at 3.78 ppm could be attributed to the methoxy proton. Assignment of each carbon and proton were assisted by the two-dimensional H—H COSY and C—H HMQC spectra showed in Figures 5 and 6, respectively, and

all these spectra revealed that the polymerization occurred only at *p*-position of phenyl group.

Polymer Properties

Basic Characterization

The solubility behavior of **Ia–Ie** was tested qualitatively, and the results are summarized in Table 2. All these polymers were highly soluble in common solvents such as NMP, toluene, and even in chloroform and THF. Polymer **Id–Ie** showed

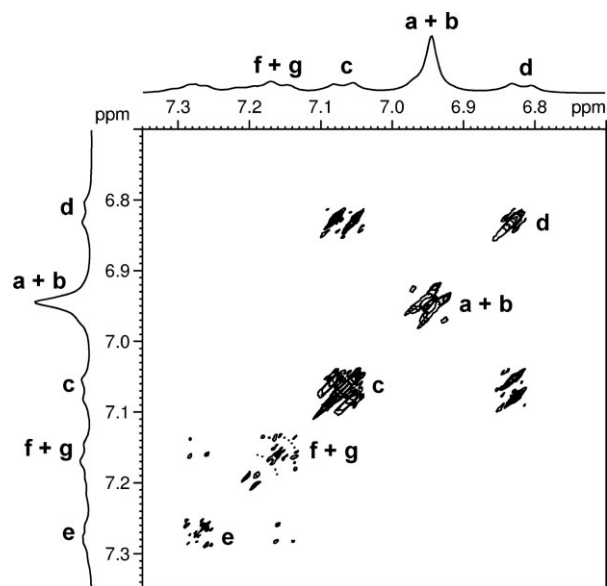


Figure 5. H–H COSY spectrum of polymer **Ic** in chloroform-*d*.

the excellent solubility could be attributed to the introduction of the bulky pendent MOPD moiety into the repeat unit. Thus, the excellent solubility makes these polymers potential candidates for practical applications by spin- or dip-coating processes.

The thermal properties of all the obtained polymers were investigated by TGA and TMA. The results are summarized in Table 3. The softening temperatures (T_s) values of the polymers films were determined from the onset temperature of the probe displacement on the TMA traces. Typical TGA curves of polymer **Ia** in both air and nitrogen atmospheres are shown in Figure 7. These polymers exhibited good thermal stability with insignificant weight loss up to 300 °C in

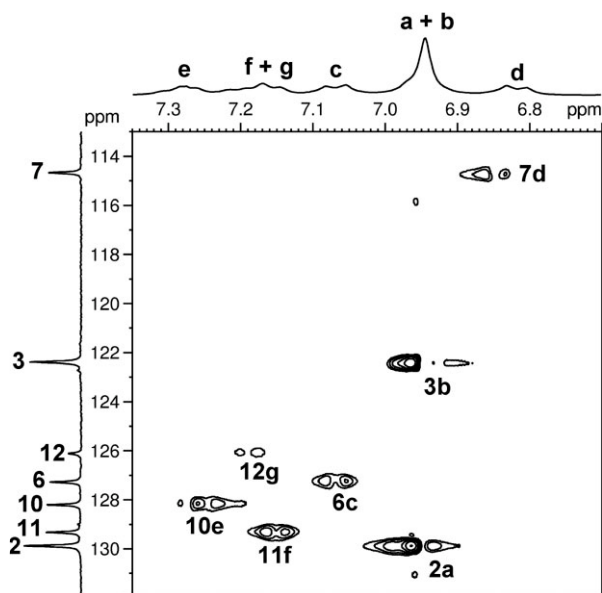


Figure 6. C–H HMQC spectrum of polymer **Ic** in chloroform-*d*.

nitrogen. Their 10% weight-loss temperatures in nitrogen and air were recorded at 480–565 and 475–565 °C, respectively. The carbonized residue (char yield) of these aromatic polymers was more than 40% at 800 °C in nitrogen atmosphere. The glass-transition temperatures (T_g s) of polymers **Ia–Ie** could be easily measured in the DSC thermograms; they were observed in the range of 193–217 °C, depending upon the stiffness of the polymer chain. Our previously study indicated that TPA-based polymers showed decreased T_g value while substitutes becoming more bulky.²⁴ However, in the case of this series of polymer **Ia–Id**, no obvious T_g changes could be observed but only **Ie** with a slightly decreased T_g at 193 °C. All polymers indicated no clear melting endotherms

Table 2. Inherent Viscosities^a and Solubility of Polymers^b

Code	Polymer	η_{inh}^a (dL/g)	Solvent						
			NMP	DMAc	DMF	THF	CHCl ₃	CH ₃ CN	Toluene
Ia		0.31	+	–	–	++	++	–	++
Ib		0.22	+	–	–	+	++	–	+
Ic		0.43	++	–	–	++	++	–	++
Id		0.18	++	++	++	++	++	–	++
Ie		0.43	++	++	++	++	++	–	++

^a Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.

^b The solubility was determined with a 1 mg sample in 1 mL of a solvent.

++, soluble at room temperature; +, soluble on heating; –, insoluble even on heating.

Table 3. Thermal Properties of Polymers^a

Code	T_g (°C) ^b	T_s (°C) ^c	T_d at 5% Weight Loss (°C) ^d		T_d at 10% Weight Loss (°C) ^d		Char Yield (wt %) ^e
			N ₂	Air	N ₂	Air	
Ia	212	197	400	385	485	490	60
Ib	217	214	480	500	565	565	40
Ic	213	213	475	485	505	515	52
Id	211	215	470	460	495	490	57
Ie	193	210	455	445	480	475	52

^aThe polymer film samples were heated at 200 °C for 30 min prior to the TGA and TMA analyses.

^bMidpoint temperature of baseline shift on the second DSC heating trace (rate: 20 °C/min) of the sample after quenching from 300 °C.

^cSoftening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C/min.

^dDecomposition temperature, recorded via TGA at a heating rate of 20 °C/min.

^eResidual weight percentage at 800 °C under nitrogen flow.

up to the decomposition temperatures on the DSC thermograms. This result supports the amorphous nature of these polymers.

Electrochemical Properties

The electrochemical and optical properties of these polymers were investigated by cyclic voltammetry and UV-vis spectroscopy; the results are summarized in Table 4. The electrochemical behavior of these polymers in CH₂Cl₂ solution

(10⁻³ M) was conducted by using ITO-coated glass substrate as working electrode with 0.1 M TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammograms for polymers **Ia-Ic** are shown in Figure 8. Except polymer **Ia**, all other polymers **Ib-Ie** exhibited reversible oxidation redox couples at $E_{\text{onset}} = 0.42\text{--}0.84$ V and $E_{1/2} = 0.52\text{--}0.93$ V, respectively. As mentioned above,^{26,27} TPA-based polymer **Ia** also could be oxidized to form an unstable cationic radical at first scan, then dimerizes (couples) to form

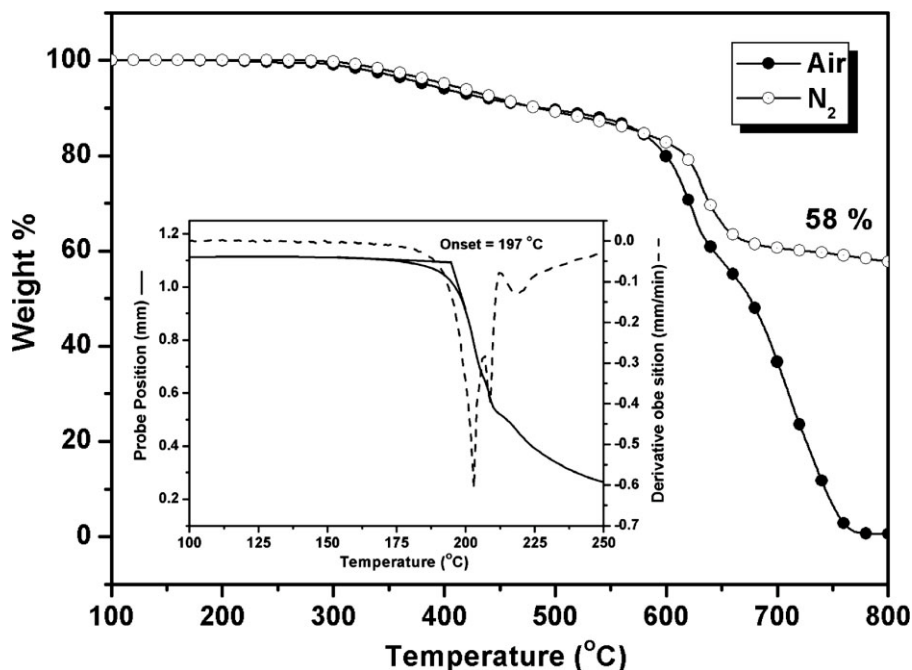


Figure 7. TGA and TMA curves for **Ia** (TGA: at a scan rate of 20 °C/min; TMA: heating rate = 10 °C/min; applied force = 10 mN).

Table 4. Redox Potentials and Energy Levels of Polymers

Index	UV-Vis Absorption of the Polymer Films (nm)		Oxidation (V) (vs. Ag/AgCl)			E_g^a (eV)	HOMO ^b (eV)	LUMO ^c (eV)
	Abs max	Abs onset	First E_{onset}	First $E_{1/2}$	Second $E_{1/2}$			
Ia	312	355	0.90	1.06	–	3.49	5.16	1.67
Ib	313	358	0.84	0.93	–	3.46	5.10	1.64
Ic	308	360	0.76	0.86	–	3.44	5.02	1.58
Id	319	385	0.42	0.52	1.00	3.22	4.68	1.46
Ie	315	385	0.44	0.52	0.96	3.22	4.70	1.48

^aThe data were calculated by the equation: $\text{gap} = 1240/\lambda_{\text{onset}}$ of polymer films.

^bThe HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

^cLUMO = HOMO- E_g .

tetraphenylbenzidine (TPB). TPB formation during oxidation of the polymer **Ia** was also proved by spectroelectrochemistry using an optically transparent thin-layer electrode (OTTLE) cell

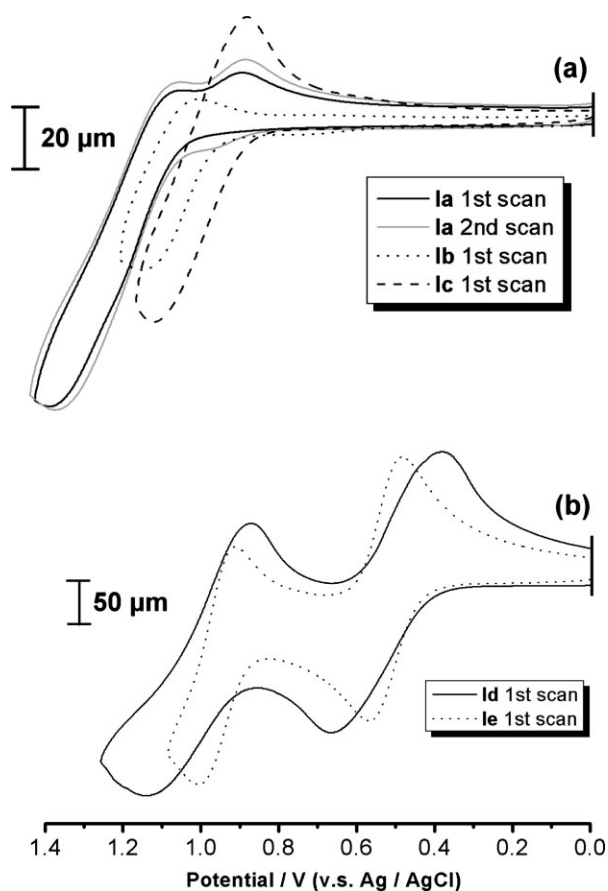


Figure 8. Cyclic voltammograms of (a) polymer **Ia-Ic** (b) polymer **Id** and **Ie** in CH_2Cl_2 solution (10^{-3} M) containing 0.1 M TBAP. Scan rate = 0.05 V/s.

coupled with UV/Vis/NIR spectroscopy, and the results are shown in Figure 9. The characteristic peak of TPA at 310 nm decreased and three new bands at 484, 686 and 1444 nm grew up. The new bands at 484, and 1444 nm are corresponding to the one-electron oxidation form of TPB⁺.²⁸ The electron-donating substituent's effect is also clearly identified from the E_{onset} values by the decreasing order **Ic** < **Ib** < **Ia**. The first electron removal for polymer **Id** was assumed to occur at the N atom on the pendent 4,4'-dimethoxydiphenylamine groups, which was more electron-rich than the N atom on the main chain TPA unit. For polymer **Ie**, the first electron removal should occur at either one of the N atoms due to the two nitrogen sites have the same chemical condition. Although polymers **Id** and **Ie** have different molecular geometries, their electrochemical properties do not notably different. This result is also similar in our previous study.³⁶ The energy of the HOMO and LUMO levels of the investigated polymer **Ia-Ie** could be determined from their oxidation onset potentials and the onset absorption wavelengths, and the results are tabulated in Table 4.

Electrochromic Characteristics

Electrochromism of the polymer was conducted in CH_2Cl_2 solution (5×10^{-4} M), and the electrochromic absorption spectra were also examined by an OTTLE coupled with UV-vis spectroscopy at different applied potentials. Figure 10 showed the spectral changes for **Ie** at various electrode potentials. After one-electron oxidation, the peak at 314 nm decreased gradually while new peaks at

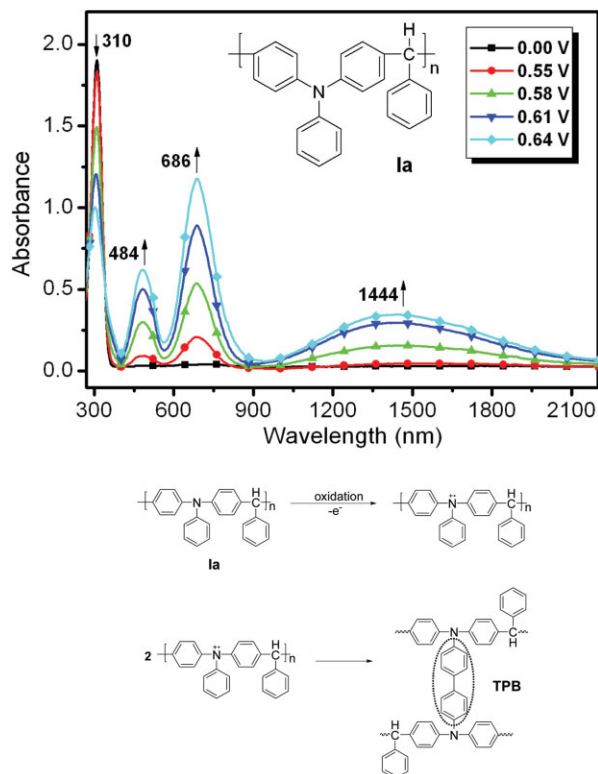


Figure 9. Electrochromic behavior of **Ia** in CH_2Cl_2 solution (5×10^{-4} M) containing 0.1 M TBAP. $E_{\text{appl.}} = 0.00$ (■), 0.55 (●), 0.58 (▲), 0.61 (▼), and 0.64 (◆) (V vs. Ag/AgCl).

420 and a very intense broad with peak at 992 nm appeared due to the first stage oxidation. The spectrum of **Ie** could be recovered when the

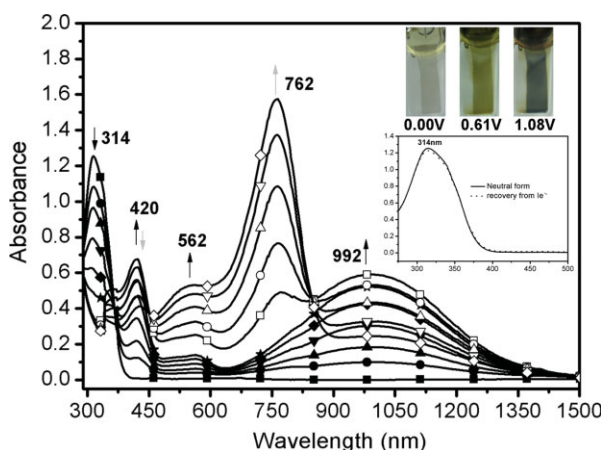


Figure 10. Electrochromic behavior of **Ie** in CH_2Cl_2 solution (5×10^{-4} M) containing 0.1 M TBAP. $E_{\text{appl.}} = 0.00$ (■), 0.46 (●), 0.52 (▲), 0.55 (▼), 0.58 (◆), 0.61 (★), 0.96 (□), 0.99 (○), 1.02 (△), 1.05 (▽), and 1.08 (◇) (V vs. Ag/AgCl).

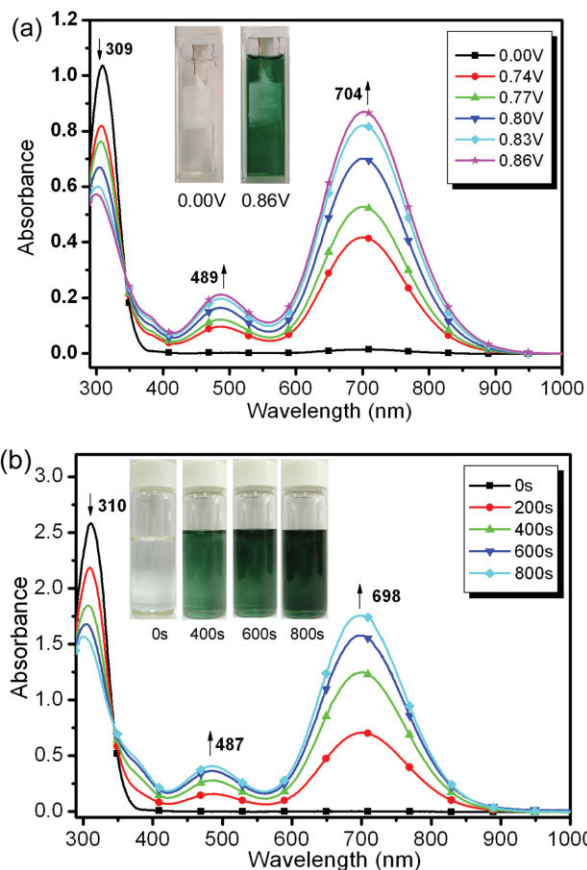


Figure 11. (a) Electrochromic behavior of **Ic** in CH_2Cl_2 solution (5×10^{-4} M). $E_{\text{appl.}} = 0.00$ (■), 0.74 (●), 0.77 (▲), 0.80 (▼), 0.83 (◆), and 0.86 (★) (V vs. Ag/AgCl). (b) Photochromism of **Ic** in CHCl_3 solution (10^{-4} M) after UV irradiation (Excited 330 nm); irradiation time = 0 s (■), 200 s (●), 400 s (▲), 600 s (▼) and 800 s (◆).

applied potential was stepped back to 0.00 V. The reversibility was 98% based on the absorbance at 314 nm. When the potential was adjusted to more positive values, it was corresponding to the second electron oxidation. The characteristic peak at 992 nm for **Ie**⁺ decreased and new bands at 562 and 762 nm appeared. When the applied potential was stepped back to 0.00 V, still 96% absorbance remained at 314 nm, implying electron-donating methoxy groups could effectively contribute to the stability of corresponding dications.

Photochromic Characteristics

An interesting photochromic phenomenon was observed when a freshly prepared CHCl_3 solution

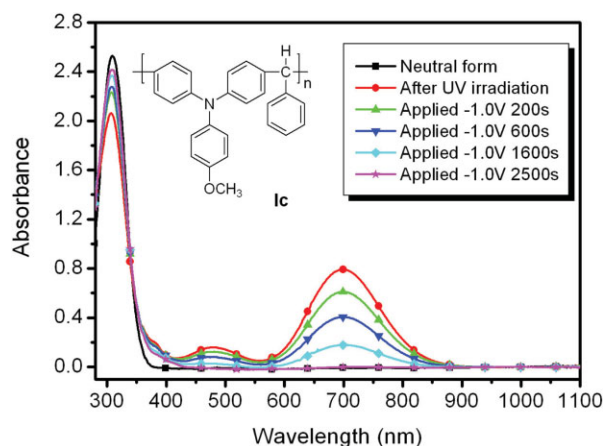


Figure 12. Photochromism and electrochromism of **Ic** in CH_2Cl_2 solution containing 0.1 M TBAP, and hold at -1.0 V (V vs. Ag/AgCl) for 200 s (\blacktriangle), 600 s (\blacktriangledown), 1600 s (\blacklozenge), and 2500 s (\blackstar). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of polymer **Ic** was irradiated by UV light. Figure 11(b) showed changes of the UV-vis spectra during the photochemical reaction of **Ic** with CHCl_3 under 330 nm UV irradiation, we find that original peak at about 310 nm decreased with time, while two new peaks around 487 and 698 nm gradually increased which was in conformity to the electrochromic behavior shown in Figure 11(a). After UV irradiation of **Ic** in CH_2Cl_2 solution for 800 s, the spectrum of **Ic** could be reversible by holding at -1.0 V for 2500 s as showed in Figure 12.

To understand this photochromism, the structurally related polymer (**PMeOTPA**)³¹ prepared by oxidation coupling with FeCl_3 was also studied for comparison. The photochromic phenomenon of **PMeOTPA** is likely due to the reaction between excited state of TPA moiety and the halogenated solvent as known for aromatic compounds containing the amino, hydroxy, and mercapto substituents in halogenated solvents.³⁷ However the color of **PMeOTPA** solution in chloroform was only slightly changed to light yellow after UV irradiation as shown in Figure 13, and its UV-vis spectrum was not similar with polymer **Ic** perhaps due to the radical cation of TPA easily decomposes after it is formed photochemically, and was unavailable to produce stable TPA oxidation form in the room temperature.³⁸ Therefore, the photochemical phenomenon of polymer **Ic** appreciably not only involved TPA unit. Considering the methine group of polymer **Ic**, we believe

the highly stable triphenylmethyl (or trityl) cation formation during UV irradiation.³⁹ The high stability of the trityl cation in polymer **Ic** may be contributed to the extensive delocalization of the charge onto the phenyl rings and TPA via resonance as shown in Scheme 2. The halocarbon-sensitized photooxidation mechanism of triphenylmethane have already be described.^{40,41} The new absorption band at 698 nm of **Ic** in Figure 11(b) is another strong evidence that the methine protons of TPA derivatives-benzaldehyde polymers could be completely eliminated by UV light, which Sato also reported the similar absorption result by the reaction of polymer **Ib** with oxidant.⁴²

CONCLUSIONS

TPA and MOPD derivatives containing electron-donating group could be easily polymerized with benzaldehyde in the presence of *p*-toluenesulfonic acid. Soluble polymers containing TPA units in the main chain were successfully prepared with molecular weight over 10^4 in high yields. In addition to the solubility and thin film formability, high T_g values and good thermal stability, polymers **Ie** also showed excellent electrochromic stability with 98 and 96% reversibility at the first and second oxidation state, respectively. Besides, the photochemical reaction and photochromic phenomenon of the resulted TPA-containing polymers in chloroform solution under irradiation

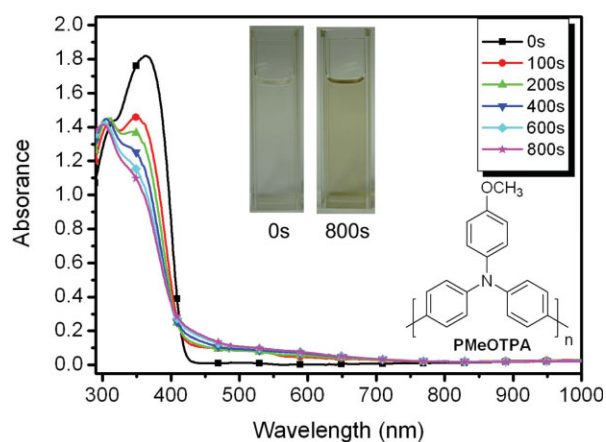
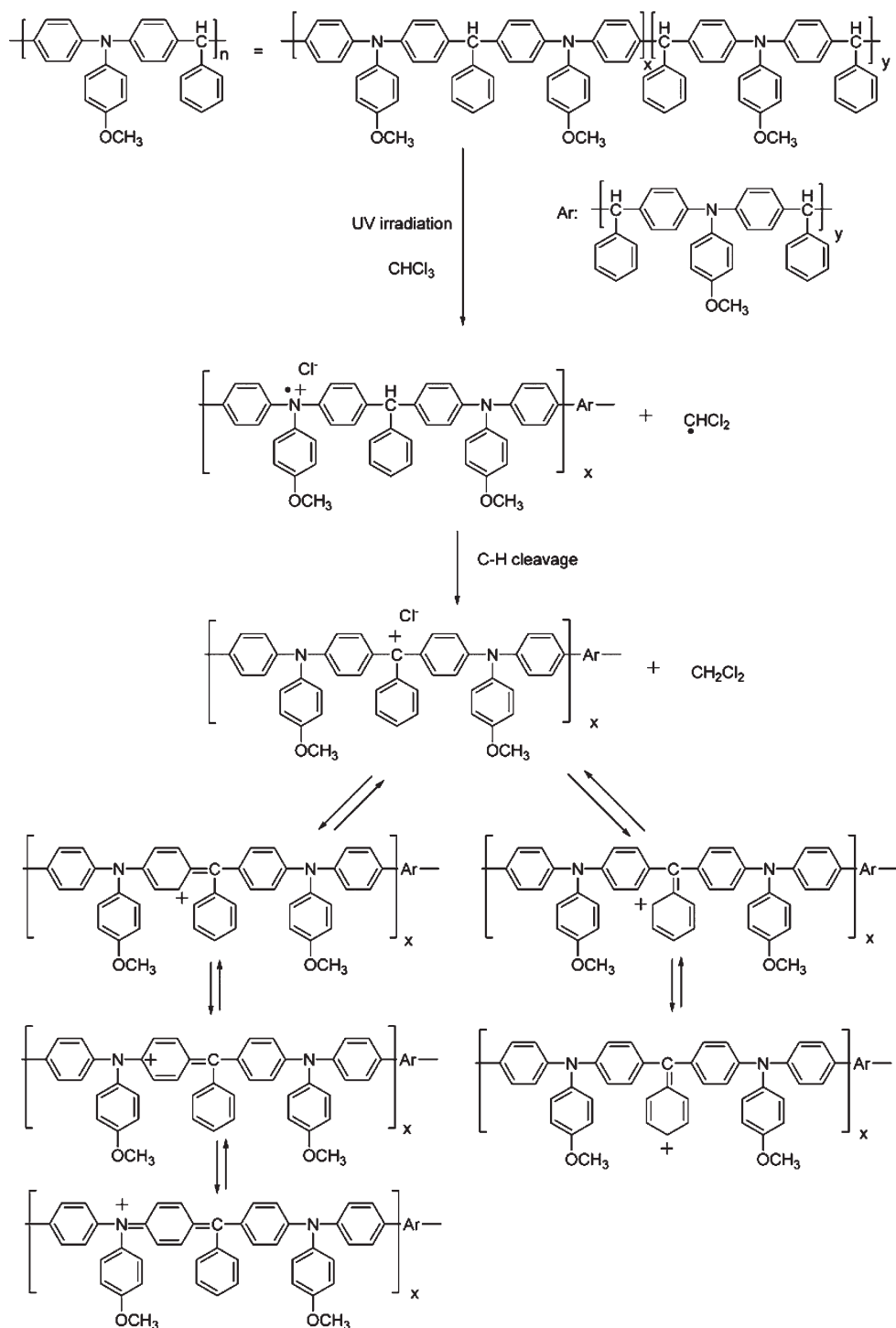


Figure 13. Photochromism of **PMeOTPA** in CHCl_3 solution (10^{-4} M) after UV irradiation (Excited 365 nm); irradiation time = 0 s (\blacksquare), 100 s (\bullet), 200 s (\blacktriangle), 400 s (\blacktriangledown), 600 s (\blacklozenge), 800 s (\blackstar). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 2. The halocarbon-sensitized photooxidation mechanism of **1c**.

with UV-light were also investigated. Thus, these polymers have good potential for use in electrochromic applications and also provide interesting photochemical results for further academia study.

REFERENCES AND NOTES

1. Mortimer, R. *J Chem Soc Rev* 1997, 26, 147–156.
2. Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism and Electrochromic Devices*;

- Cambridge University Press: Cambridge, UK, 2007.
- Gao, J.; Liu, D. G.; Sansinena, J. M.; Wang, H. L. *Adv Funct Mater* 2004, 14, 537–543.
 - Walczak, R. M.; Reynolds, J. R. *Adv Mater* 2006, 18, 1121–1131.
 - Groenendaal, L.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J. R. *Adv Mater* 2003, 15, 855–879.
 - Unur, E.; Jung, J.-H.; Mortimer, R. J.; Reynolds, J. R. *Chem Mater* 2008, 20, 2328–2334.
 - Sonmez, G.; Shen, C. K. F.; Rubin, Y.; Wudl, F. *Angew Chem Int Ed* 2004, 43, 1497–1502.
 - Argun, A. A.; Aubert, P.-H.; Thompson, B. C.; Schwendeman, I.; Gaupp, C. L.; Hwang, J.; Pinto, N. J.; Tanner, D. B.; MacDiarmid, A. G.; Reynolds, J. R. *Chem Mater* 2004, 16, 4401–4412.
 - Thelakkat, M. *Macromol Mater Eng* 2002, 287, 442–461.
 - Lee, C. C.; Yeh, K. M.; Chen, Y. *J Polym Sci Part A: Polym Chem* 2008, 46, 7960–7971.
 - Vellis, P. D.; Mikroyannidis, J. A.; Cho, M. J.; Choi, D. H. *J Polym Sci Part A: Polym Chem* 2008, 46, 5592–5603.
 - Shirota, Y. *J Mater Chem* 2005, 15, 75–93.
 - (a) Liou, G. S.; Lin, H. Y.; Hsieh, Y. L.; Yang, Y. L. *J Polym Sci Part A: Polym Chem* 2007, 45, 4921–4932; (b) Liou, G. S.; Yang, Y. L.; Chen, W. C.; Su, Y. O. *J Polym Sci Part A: Polym Chem* 2007, 45, 3292–3302.
 - Beaupre, S.; Dumas, J.; Leclerc, M. *Chem Mater* 2006, 18, 4011–4018.
 - Choi, K.; Yoo, S. J.; Sung, Y. E.; Zentel, R. *Chem Mater* 2006, 18, 5823–5825.
 - Otero, L.; Sereno, L.; Fungo, F.; Liao, Y. L.; Lin, C. Y.; Wong, K. T. *Chem Mater* 2006, 18, 3495–3502.
 - Natera, J.; Otero, L.; Sereno, L.; Fungo, F.; Wang, N. S.; Tsai, Y. M.; Hwu, T. Y.; Wong, K. T. *Macromolecules* 2007, 40, 4456–4463.
 - Liou, G. S.; Chang, C. W.; Huang, H. M.; Hsiao, S. H. *J Polym Sci Part A: Polym Chem* 2007, 45, 2004–2014.
 - Liou, G. S.; Chang, C. W. *Macromolecules* 2008, 41, 1667–1674.
 - Hsiao, S. H.; Liou, G. S.; Kung, Y. C.; Yen, H. J. *Macromolecules* 2008, 41, 2800–2808.
 - Liou, G. S.; Hsiao, S. H.; Su, T. H. *J Mater Chem* 2005, 15, 1812–1820.
 - Liou, G. S.; Hsiao, S. H.; Huang, N. K.; Yang, Y. L. *Macromolecules* 2006, 39, 5337–5346.
 - Liou, G. S.; Hsiao, S. H.; Chen, H. W. *J Mater Chem* 2006, 16, 1831–1842.
 - Cheng, S. H.; Hsiao, S. H.; Su, T. H.; Liou, G. S. *Macromolecules* 2005, 38, 307–316.
 - Chang, C. W.; Yen, H. J.; Huang, K. Y.; Yeh, J. M.; Liou, G. S. *J Polym Sci Part A: Polym Chem* 2008, 46, 7937–7949.
 - Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J Am Chem Soc* 1966, 88, 3498–3503.
 - Nelson, R. F.; Adams, R. N. *J Am Chem Soc* 1968, 90, 3925–3930.
 - Chiu, K. Y.; Su, T. X.; Li, J. H.; Lin, T. H.; Liou, G. S.; Cheng, S. H. *J Electroanal Chem* 2005, 575, 95–101.
 - Wienk, M. M.; Janssen, R. A. J. *J Am Chem Soc* 1997, 119, 4492–4501.
 - Yu, W. L.; Pei, J.; Huang, W.; Heeger, A. J. *Chem Commun* 2000, 8, 681–682.
 - Ohsawa, Y.; Ishikawa, M.; Miyamoto, T.; Murofushi, Y.; Kawai, M. *Synth Met* 1987, 18, 371–374.
 - Strzelec, K.; Tsukamoto, N.; Kook, H. J.; Sato, H. *Polym Int* 2001, 50, 1228–1233.
 - Son, J. M.; Mori, T.; Ogino, K.; Sato, H.; Ito, Y. *Macromolecules* 1999, 32, 4849–4854.
 - Shikatani, Y.; Kataoka, N.; Shimo, Y.; Kuroda, N.; Matsuura, K. U.S. Patent 5, 1991, 006, 633.
 - Nishikitani, Y.; Kobavashi, M.; Uchida, S.; Kubo, T. *Electrochim Acta* 2001, 46, 2035–2040.
 - Chiu, K. Y.; Su, T. H.; Huang, C. W.; Liou, G. S.; Cheng, S. H. *J Electroanal Chem* 2005, 578, 283–287.
 - Lewis, G. N.; Lipkin, D. *J Am Chem Soc* 1942, 64, 2801–2808.
 - Fitzgerald, E. A.; Wuelfing, J. P.; Richtol, H. H. *J Phys Chem* 1971, 75, 2737–2741.
 - Duxbury, D. F. *Chem Rev* 1993, 93, 381–433.
 - MacLachlan, A.; Riem, R. H. *J Org Chem* 1971, 36, 2275–2280.
 - MacLachlan, A. *J Phys Chem* 1967, 71, 718–722.
 - Wangwijit, T.; Sato, H.; Tantayanon, S. *Polym Adv Technol* 2002, 13, 25–32.