Synthesis of Methacrylic Monomers Bearing Stilbenoid Chromophore and Their Free-Radical Polymerization To Give Luminescent Polymers

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ABSTRACT: In the present paper, we report the synthesis of two new methacrylates and their efficient free-radical polymerization to luminescent polymers. They dissolved in common organic solvents such as THF, dichloromethane, chloroform, and toluene and had relatively low T_g values (52−87 °C). In addition, they showed a satisfactory thermal stability, being stable up to 278−325 °C in N_2 or air and afforded anaerobic char yields of 47−73% at 800 °C. The optical properties of polymers were investigated both in solution and in thin film, utilizing the UV−vis, the PL excitation, and PL spectroscopy. The polymers behaved as violet-blue and violet-greenish emitting materials. Their PL spectra displayed maxima in solution at 397 or 457 nm and in thin film at 413 or 507 nm. The low-temperature PL spectra in solution were red-shifted by 7−15 nm in comparison with the respective room-temperature spectra, and for one polymer, they displayed a new peak due to the reduced rotation. The PL quantum yields in solution were up to 0.30. The influence of the polymer concentration in solution as well as of the solvent polarity on the PL curves was investigated. It was shown that the PL curves were progressively red-shifted with increasing the solvent polarity.

Introduction

Stilbenes are certainly one of the most thoroughly studied classes of compounds from the standpoint of mechanistic and preparative photochemistry. Considerable attention is devoted to stilbenes in textbooks on photochemistry and they have been covered in numerous reviews.[1−3] The connection between stilbenoid compounds and light is a field that has implications for many potential applications. More particularly, stilbenoid compounds exhibit interesting photochemical and photophysical properties and are suitable for various applications in material science.[3] Apart from their commercial use as optical brighteners and laser dyes, their applications in light-emitting diodes (LEDs), photoresists, photoconductive devices, imaging and optical switching techniques, and materials for nonlinear optics (NLO) are being investigated on this molecular basis.[4−7]

Recently, π-conjugated electroluminescent polymers have attracted much attention as the best candidate for a flat panel display application. Poly(*p*-phenylenevinylene) (PPV) and derivatives are among the most studied conjugated materials for fabrication of LEDs.[8] The structure of PPV was modified both to improve the processability and tune the wavelength of the emitted light. Thus, PPV-type segments were isolated within the polymer backbone or were attached as side groups along the main chain. A possibility for preparing polymers of this type is the functionalization of a polystyrene derivative precursor.[9,10] Another approach was the homopolymerization of a monomer carrying a chromophore and a polymerizable double bond such as of the acrylate[11,12] or the vinyl derivatives.[13]

The present work deals with the synthesis of two acrylic monomers bearing an emissive stilbenoid chromophore. More particularly, two methacrylates carrying a stilbenoid chromophore of different chemical structure were synthesized and characterized. The objective of the applied synthetic route was the synthesis of two alcohols that carried a stilbene-based chromophore. They were reacted subsequently with methacryloyl chloride to afford the desired methacrylates. The latter were homopolymerized by radical polymerization using azobis(isobutyronitrile), (AIBN), as initiator. Thus, two homopolymers were obtained, the backbone of which consisted of poly(methacrylate) (PMMA), and they contained pendant stilbenoid chromophores. The presence of the stilbene or the styryl units in the side chains of the polymers gives rise for efficient fluorescence, which makes the materials potential candidates for light emissions. Such polymers additionally exhibit superior processability because of their flexible backbones and possible amorphous character. The optical properties of the polymers were investigated both in solution and solid state. It is well-known that a good photoluminescent material may not necessarily be a good electroluminescent material.

The present luminescent poly(methacrylate)s differ from other related polymers[9−13] that have been previously prepared because their side chains contain more than one stilbene or styryl moieties which have an almost dendrimer quality. To the best of our knowledge the attachment of multiple stilbene or styryl moieties to a methacrylic unit and the free-radical polymerization of the latter to luminescent polymers have not been described previously. The parent monomers were synthesized by a convenient synthetic route utilizing inexpensive starting materials. In particular, one of the monomers was synthesized through a pyrylium salt via a method that has been used recently in our laboratory for preparation of photonic polymers.[14,15]

Experimental Section

Characterization Methods. IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. ^1H NMR (400 MHz) spectra were obtained using a Bruker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV−

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vis spectra were recorded on a Beckman DU-640 spectrometer with spectrograde THF. The PL spectra were obtained with a Perkin-Elmer LS45 luminescence spectrometer. GPC analysis was conducted with a Waters Breeze 1515 series liquid chromatograph equipped with a differential refractometer (Waters 2410) as detector using polystyrene as standard and THF as eluent. DSC and TGA were performed on a DuPont 990 thermal analyzer system. Ground polymer samples of about 10 mg each were examined by TGA, and weight loss comparisons were made between comparable specimens. The DSC thermograms were obtained at a heating rate of 10 °C/min in N_2 atmosphere at a flow rate of 60 cm^3/min. Dynamic TGA measurements were made at a heating rate of 20 °C/min in atmospheres of N_2 or air at a flow rate of 60 cm^3/min. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA using a loaded penetration probe at a scan rate of 10 °C/min in N_2 with a flow rate of 60 cm^3/min. The TMA experiments were conducted at least in duplicate to ensure the accuracy of the results. The TMA specimens were pellets of 8 mm diameter and 2 mm thickness prepared by pressing powder of polymer for 3 min under 5−7 kpsi at ambient temperature. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer.

To measure the PL quantum yields (Φ_f) a degassed solution of polymer in THF was prepared. The concentration was adjusted so that the absorbance of the solution would be lower than 0.1. The excitation was performed at the corresponding $\lambda_{ex,max}$, and a solution in 1 N H_2SO_4 of quinine sulfate, which has a Φ_f of 0.546 ($\lambda_{ex} = 350$ nm), was used.

Reagents and Solvents. 4-Bromobenzaldehyde, 4′-bromoacetophenone, and phthalic anhydride were recrystallized from methanol, ethanol, and chloroform, respectively. 4-Methoxyphenylacetic acid sodium salt was prepared by reacting equimolar amounts of 4-methoxyphenylacetic acid with aqueous sodium hydroxide and subsequent fusing. Triethylamine was distilled over KOH. *N*,*N*-Dimethylacetamide (DMAc), 1,2-dichloroethane, and chloroform were dried by distillation over CaH_2. Ethanolamine, styrene, methacryloyl chloride, boron trifluoride etherate, acetic anhydride, 47−49% hydrobromic acid, $Pd(OAc)_2$, and tri-*o*-tolylphosphine were used as supplied.

Preparation of Monomers and Polymers. 2,4,6-Tri(4-bromophenyl)pyrylium Tetrafluoroborate (1). A flask was charged with a solution of 4-bromobenzaldehyde (1.00 g, 5.40 mmol), and 4′-bromoacetophenone (2.15 g, 10.8 mmol) in 1,2-dichloroethane (15 mL). Boron trifluoride etherate (1.7 mL, 13.5 mmol) was added to the solution. The mixture was stirred and refluxed for 4 h. It was subsequently concentrated under reduced pressure, and ether was added to the concentrate. The resulting yellow precipitate was filtered, washed with ether, and dried to afford **1**. It was recrystallized from acetonitrile/diethyl ether (1.10 g, yield 32%, mp >300 °C).

IR (KBr, cm^{-1}): 1622, 1582, 1488 (aromatic and pyrylium structure); 494 (C−Br).

^1H NMR (DMSO-d_6), δ: 8.67 (m, 2H, aromatic meta to O); 7.57−7.42 (m, 12H, other aromatic).

4-Methoxy-4″-bromo-2′,6′-di(4-bromophenyl)-*p*-terphenyl (2). A mixture of **1** (1.01 g, 1.59 mmol), 4-methoxyphenylacetic acid sodium salt (0.60 g, 3.18 mmol), and acetic anhydride (4 mL) was stirred and refluxed for 3 h. It was subsequently cooled in a refrigerator overnight, and the resulting precipitate was filtered, washed with methanol, and dried to afford **2** as a white solid. It was recrystallized from THF/petroleum ether (0.75 g, yield 73%, mp 145−147 °C).

IR (KBr, cm^{-1}): 1608, 1584, 1514, 1488, 1450 (aromatic); 1246, 1196, 1178 (ether bond); 530, 514 (C−Br).

^1H NMR ($CDCl_3$), δ: 7.55−7.40 (m, 16H, aromatic except those ortho to OCH_3); 6.97 (m, 2H, aromatic ortho to OCH_3); 3.83 (s, 3H, OCH_3).

4-Hydroxy-4″-bromo-2′,6′-di(4-bromophenyl)-*p*-terphenyl (3). Compound **2** (0.67 g, 1.03 mmol) was dissolved in glacial acetic acid (40 mL) by heating at boiling temperature. Hydrobromic acid (4 mL) was added in portions over a period of 50 h. Refluxing was continued for additional 10 h. The hot mixture was filtered, and the filtrate was concentrated under reduced pressure. Water was added to the concentrate, and the resulting pale brown precipitate was filtered, washed with water, and dried to afford **3**. It was recrystallized from ethanol/water (0.56 g, yield 85%, mp 131−133 °C).

IR (KBr, cm^{-1}): 3507, 3404 (OH stretching); 1608, 1584, 1516, 1488, 1446 (aromatic); 1260, 1216, 1170 (C−OH stretching and OH deformation).

^1H NMR ($CDCl_3$), δ: 7.56−7.41 (m, 16H, aromatic except those ortho to OH); 6.90 (m, 2H, aromatic ortho to OH); 4.81 (br, 1H, OH).

4-Hydroxy-4″-styryl-2′,6′-di(*p*-styrylbenzene)-*p*-terphenyl (4). To a solution of **3** (0.4900 g, 0.77 mmol) and styrene (0.3200 g, 3.08 mmol) in DMAc (5 mL) were added $Pd(OAc)_2$ (0.0170 g, 0.08 mmol), tri-*o*-tolylphosphine (0.0470 g, 0.16 mmol), and triethylamine (3 mL). The mixture was thoroughly degassed with N_2. It was stirred and heated at 100 °C for 60 h. The hot mixture was subsequently filtered to remove the inorganic catalyst. Methanol was added to the filtrate, and the resulting yellow-brown precipitate was filtered, washed with methanol, and dried to afford **4**. It was recrystallized from dioxane/water (0.52 g, yield 96%, mp 136−138 °C).

IR (KBr, cm^{-1}): 3510, 3444 (OH stretching); 1596, 1512, 1446 (aromatic); 1246, 1217, 1168 (C−OH and OH deformation); 960 (HC═CH trans).

^1H NMR (DMSO-d_6), δ: 9.35 (br, 1H, OH); 7.51−7.25 (m, 31H, aromatic except those ortho to OH); 7.10 (m, 6H, HC═CH); 6.89 (m, 2H, aromatic ortho to OH).

Anal. Calcd for $C_{54}H_{40}O$: C, 92.01; H, 5.72. Found: C, 91.76; H, 5.63.

4-[4″-Styryl-2′,6′-di(*p*-styrylbenzene)-*p*-terphenyl]-methacrylate (5). Compound **4** (0.55 g, 0.78 mmol) was dissolved in DMAc (5 mL) by heating at about 60 °C. Triethylamine (2 mL) was added to the solution. Soon after, at about 50 °C, methacryloyl chloride (1 mL diluted with 2 mL of DMAc) was added dropwise to the stirred solution. The mixture was stirred and heated at 50 °C for 24 h under N_2. At the end, the reaction mixture was poured into ice water. The resulting pale orange precipitate was filtered, washed thoroughly with methanol, and dried into a vacuum oven at about 40 °C to afford **5.** It was recrystallized from THF/petroleum ether (0.52 g, yield 87%, mp 128−130 °C).

IR (KBr, cm^{-1}): 1736 (ester C═O); 1598, 1510, 1488 (aromatic); 1202, 1166, 1124 (C−O−C stretching); 962 (HC═CH trans).

^1H NMR ($CDCl_3$), δ: 7.50−7.24 (m, 31H, aromatic except those ortho to O); 7.08 (m, 6H, HC═CH); 6.80 (m, 2H, aromatic ortho to O); 6.33 and 5.75 (s, 2H, olefinic); 2.01 (s, 3H, CH_3).

Anal. Calcd for $C_{58}H_{44}O_2$: C, 90.12; H, 5.74. Found: C, 89.74; H, 5.65.

Polymer P1. A flask was charged with a solution of the monomer **5** (0.38 g, 0.49 mmol) in DMAc (5 mL). AIBN (0.0040 g, 0.02 mmol) was added to the solution. The radical polymerization was carried out by stirring and heating of the mixture at 110 °C for 48 h under N_2. Then, the mixture was filtered and methanol was added to the filtrate. The resulting yellow-brown precipitate was filtered, washed with methanol, and dried to afford **P1** (0.26 g, yield 68%).

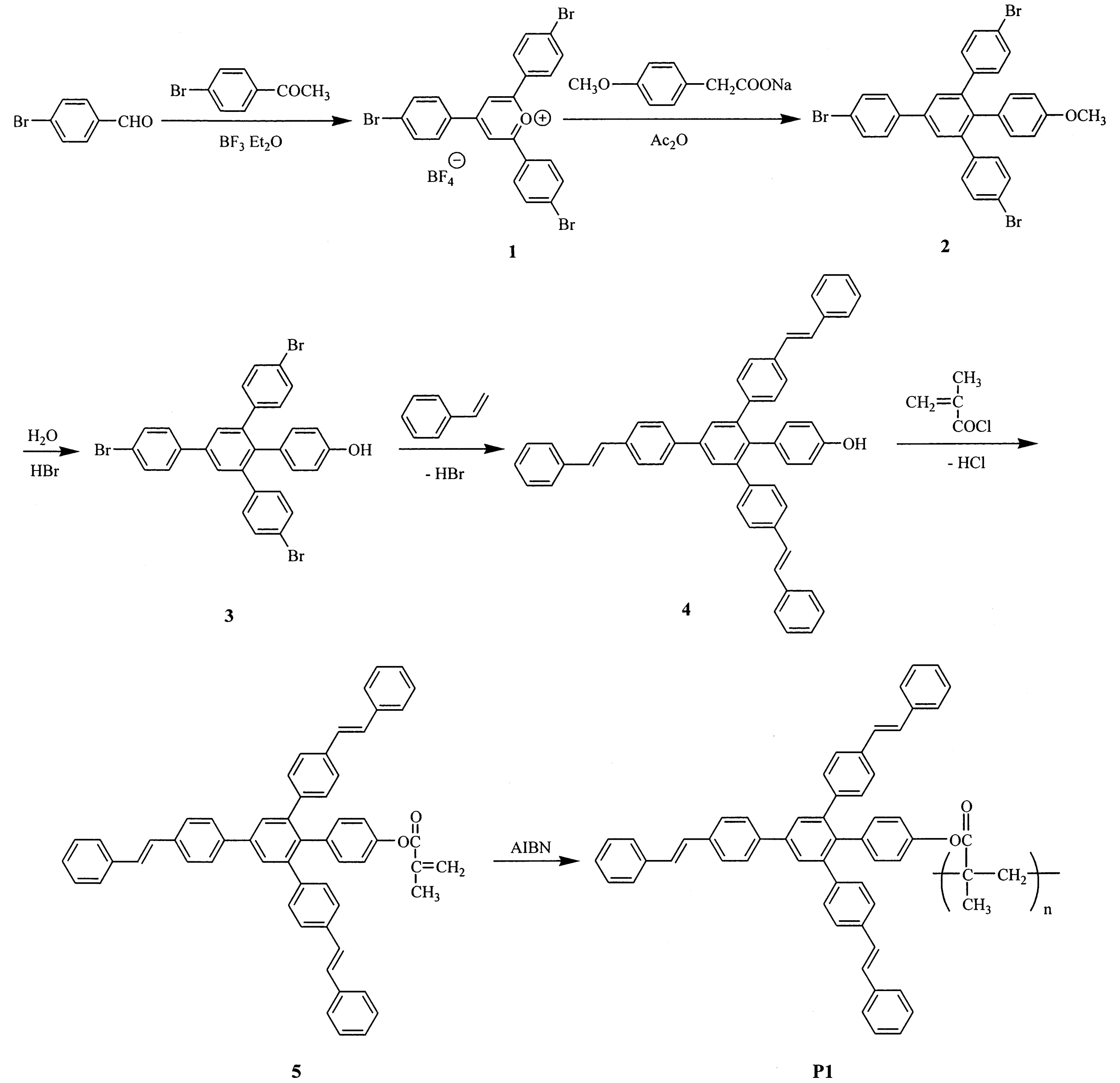
Anal. Calcd for $(C_{58}H_{44}O_2)_n$: C, 90.12; H, 5.74. Found: C, 89.70; H, 5.63.

Tetraiodophthalic Anhydride (6). Compound **6** was synthesized according to a reported method.[16]

***N*-(2-Hydroxyethyl)tetraiodophthalimide (7).** A flask was charged with a solution of tetraiodophthalic anhydride (5.58 g, 8.56 mmol) in DMAc (20 mL). Ethanolamine (0.52 g, 8.56 mmol) was added dropwise to the stirred solution, and a moderately exothermic reaction was observed. The mixture was subsequently stirred and heated at about 130 °C for 7 h under N_2. Then, it was concentrated under reduced pressure and water was added to concentrate. The resulting yellow-brown precipitate was filtered, washed with water, and dried to afford **7**. It was recrystallized from dioxane/water (5.36 g, yield 92%, mp 183−185 °C).

IR (KBr, cm^{-1}): 3500−3356 (OH stretching); 2936, 2850 (C−H of the aliphatic segments); 1762, 1706 (imide C═O);

Scheme 1



1390, 1356, 1290, 1024 (C−OH stretching and OH deformation); 630, 610 (C−I).

^{1}H NMR (DMSO-d_6), δ: 8.17 (br, 1H, OH); 3.88 (m, 2H, NCH$_2$); 2.87 (m, 2H, *CH$_2$*OH).

***N*-(2-Hydroxyethyl)tetrastyrylphthalimide (8).** A flask was charged with a solution of **7** (2.5000 g, 3.67 mmol) and styrene (1.9100 g, 18.35 mmol) in DMAc (8 mL). To this solution were added Pd(OAc)$_2$ (0.0824 g, 0.37 mmol), tri-*o*-tolylphosphine (0.2234 g, 0.73 mmol), and triethylamine (6 mL). The mixture was stirred and heated at 100 °C for 60 h under N$_2$. It was subsequently filtered, and the filtrate was concentrated under reduced pressure. Methanol was added to the concentrate. The resulting yellow-brown precipitate was filtered, washed with methanol, and dried to afford **8**. It was recrystallized from THF/petroleum ether (2.12 g, yield 96%, mp 125−127 °C).

IR (KBr, cm^{-1}): 3422 (OH stretching); 2924 (C−H of the aliphatic segments); 1756, 1700 (imide C=O); 1396, 1358, 1026 (C−OH stretching and OH deformation); 966 (HC=CH trans).

^{1}H NMR (DMSO-d_6), δ: 8.20 (br, 1H, OH); 7.56−7.25 (m, 20H, aromatic); 7.11 (m, 8H, HC=CH); 4.06 (m, 2H, NCH$_2$); 2.80 (m, 2H, *CH$_2$*OH).

Anal. Calcd for $C_{42}H_{33}NO_3$: C, 84.11.11; H, 5.55; N, 2.34. Found: C, 83.95; H, 5.42; N, 2.38.

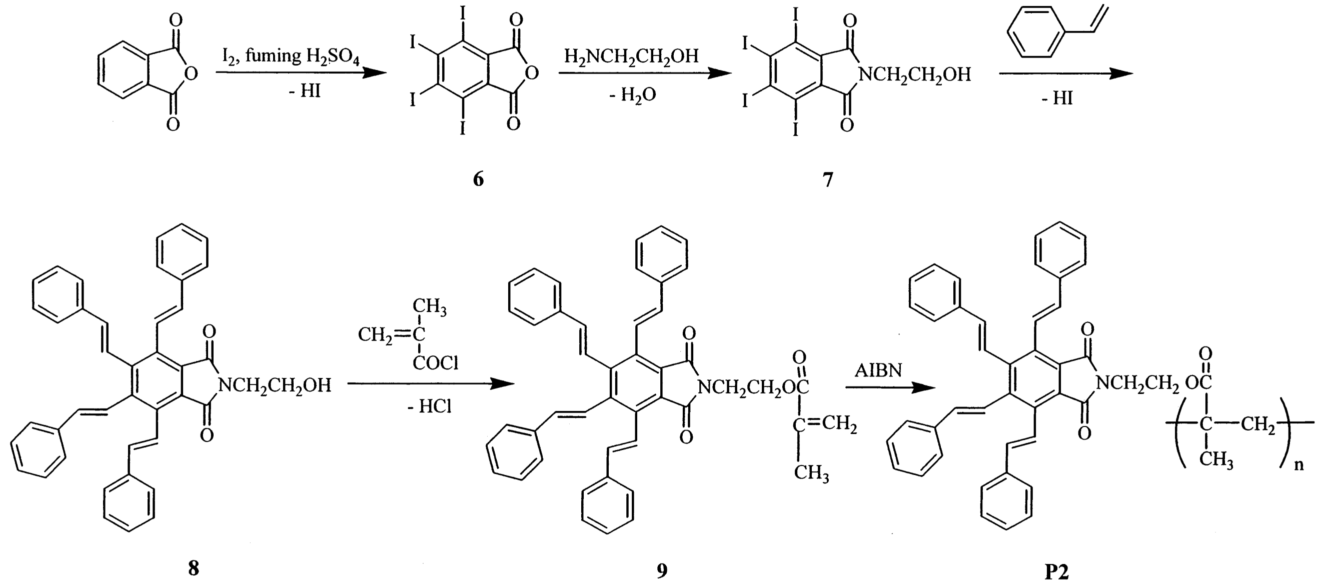
2-(*N*-Tetrastyrylphthalimido)ethyl Methacrylate (9). Compound **8** (0.66 g, 1.10 mmol) was dissolved in freshly dried chloroform (8 mL). Triethylamine (3 mL) was added to the solution. Methacryloyl chloride (2 mL diluted with 3 mL of chloroform) was added dropwise to the stirred solution. The mixture was stirred and refluxed for 48 h under N$_2$. It was subsequently concentrated under reduced pressure, and methanol was added to the concentrate. The resulting pale brown precipitate was filtered, washed with methanol, and dried into a vacuum oven at about 40 °C to afford **9**. It was recrystallized from THF/*n*-hexane (0.31 g, yield 43%, mp 119−121 °C).

IR (KBr, cm^{-1}): 2922 (C−H stretching of the aliphatic segments); 3026, 1600, 1452 (aromatic); 1634 (olefinic C=C stretching); 1758, 1706 (imide C=O); 1740 (ester C=O); 1158 (C−O−C stretching); 966 (HC=CH trans).

^{1}H NMR (CDCl$_3$), δ: 7.58−7.24 (m, 20H, aromatic); 7.10 (m, 8H, HC=CH); 6.08 and 5.53 (s, 2H, olefinic); 4.39 (s, 2H, CH$_2$O); 4.02 (s, 2H, NCH$_2$); 1.88 (s, 3H, CH$_3$).

Anal. Calcd for $C_{46}H_{37}NO_4$: C, 82.74; H, 5.58; N, 2.10. Found: C, 81.92; H, 5.40; N, 2.36.

Scheme 2



Polymer P2. A flask was charged with a solution of the monomer **9** (0.29 g, 0.44 mmol) in xylene (5 mL). A catalytic amount of AIBN (0.0033 g, 0.02 mmol) was added to the solution. The mixture was degassed with N_2. It was stirred and heated at 110 °C for 48 h. After cooling, the solution was poured into methanol. The resulting yellow-brown precipitate was filtered, washed with methanol, and dried to afford polymer **P2** (0.18 g, yield 62%).

Anal. Calcd for $(C_{46}H_{37}NO_4)_n$: C, 82.74; H, 5.58; N, 2.10. Found: C, 81.90; H, 5.47; N, 2.36.

Results and Discussion

Synthesis and Characterization of Monomers and Polymers. Two new methacrylates bearing stilbenoid chromophore were synthesized and polymerized according to the procedure summarized in Schemes 1 and 2. The first methacrylate was synthesized through pyrylium salt. In particular, 4-bromobenzaldehyde was reacted with 4′-bromoacetophenone in the presence of boron trifluoride etherate to afford the pyrylium salt **1**.[17,18] It was reacted subsequently with 4-methoxyphenylacetic acid sodium salt in acetic anhydride to yield compound **2**.[19] The methoxy group of the latter was hydrolyzed by aqueous hydrobromic acid solution to the corresponding phenol **3**. Aryl methyl ethers can be cleaved to phenols with hydrogen bromide in glacial acetic acid or by concentrated hydrobromic acid.[20] The Heck coupling[21] of **3** with styrene yielded the tristyryl derivative **4**. It was reacted with methacryloyl chloride in the presence of triethylamine to yield the methacrylate **5**. Finally, the radical polymerization of **5,** using AIBN as initiator, afforded polymer **P1**.

The second methacrylate was synthesized via the following step-by-step route: Phthalic anhydride was halogenated with iodine in fuming sulfuric acid to yield the tetraiodophthalic anhydride **6**.[16] The latter was subsequently condensed with ethanolamine to the corresponding imide **7**. The Heck coupling of the latter with styrene afforded the tetrastyryl compound **8**. It was reacted with methacryloyl chloride to yield the methacrylate **9**. Finally, it was polymerized in the presence of AIBN as initiator to afford polymer **P2**.

The polymers were obtained in 62–68% yields. Since they were soluble in THF, their number-average molecular weights (M_n) were determined by GPC to be 16 000 for **P1** with a polydispersity index of 2.4 and 21 000 for **P2** with a polydispersity index of 2.6. However, it is well established that classical GPC, using polystyrene as calibration standard, misrepresents the M_n values of rigid or semirigid polymers and leads to underestimated values.[22] Thin films of polymers could be readily obtained from the polymer solution by a spin-casting technique.

No optimization of the polymerization conditions was made. G. Hadziioannou and co-workers have polymerized a PPV trimer, 4-*tert*-butyl-4′-(4-vinylstyryl)-*trans*-stilbene, by using two routes: a classical radical polymerization with AIBN as initiator, and the TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxy)dibenzoyl peroxide initiated method. The second polymerization method afforded a polymer of higher molecular weight and of lower polydispersity than the first one.[13]

The structures of the polymers were confirmed by IR and NMR spectroscopy. Figure 1 presents the FT-IR

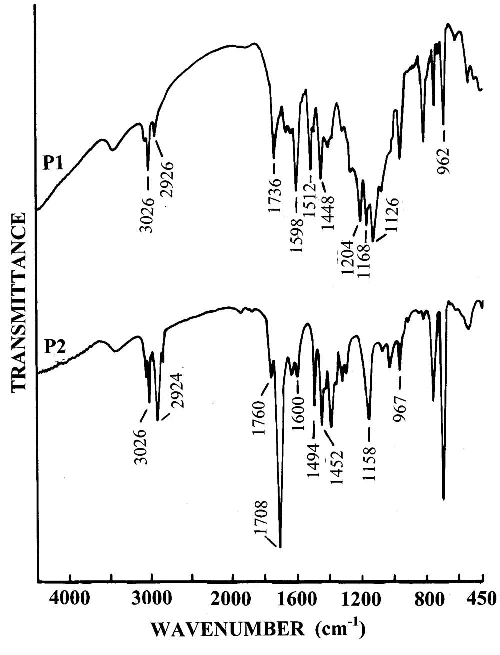


Figure 1. FT-IR spectra of polymers **P1** (top) and **P2** (bottom).

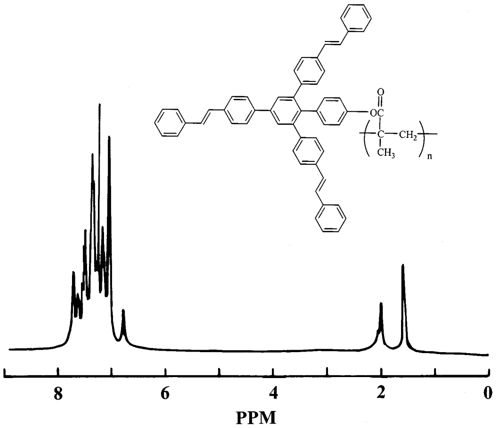


Figure 2. ^{1}H NMR spectrum of polymer **P1** in $CDCl_3$ solution.

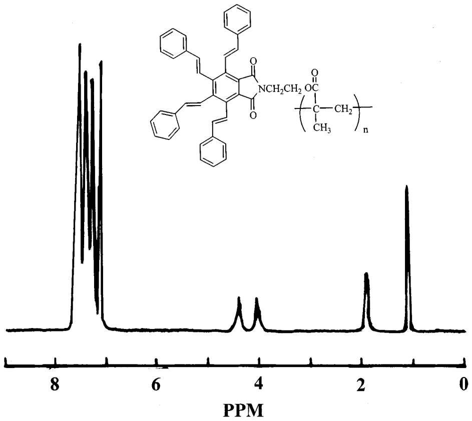


Figure 3. ^{1}H NMR spectrum of polymer **P2** in $CDCl_3$ solution.

spectra of polymers. **P1** showed characteristic absorptions at 3026, 1598, 1512, 1448 (aromatic); 2926 (C−H stretching of the aliphatic segments); 1736 (ester C=O); 1204, 1168, 1126 (C−O−C stretching); and 962 cm^{-1} (HC=CH trans). The most characteristic absorptions for **P2** emerged at 3026, 1600, 1494, 1452 (aromatic); 2924 (C−H stretching of the aliphatic segments); 1760, 1708 (symmetric and asymmetric imide C=O, respectively); 1158 (C−O−C stretching); and 967 cm^{-1} (HC=CH trans). In the case of **P2,** the absorption of the ester carbonyl was overlapped with the strong absorption band of the imide carbonyls. However, the absorption of C−O−C stretching gave evidence for the ester formation. The absorption near 2926 cm^{-1} associated with the aliphatic segments was much stronger in **P2** than **P1**, because **P2** additionally contained the ethanolamine segment.

The ^{1}H NMR spectra of polymers exhibited broad resonance peaks typical of polymers (Figures 2 and 3). They did not show peaks in the region of the resonance of vinylic hydrogens. Specifically, the ^{1}H NMR spectrum of **P1** in $CDCl_3$ solution displayed peaks as follows: 7.70−7.26 (m, 31H, aromatic except those ortho to O); 7.10 (m, 6H, HC=CH); 6.80 (m, 2H, aromatic ortho to O); 2.03 (m, 2H, CH_2); 1.57 (s, 3H, CH_3). The ^{1}H NMR spectrum of **P2** in $CDCl_3$ solution exhibited peaks at 7.50−7.21 (m, 20H, aromatic); 7.14 (m, 8H, HC=CH); 4.42 (m, 2H, CH_2O); 4.03 (m, 2H, NCH_2); 1.88 (m, 2H, CH_2); 1.24 (s, 3H, CH_3).

The polymers showed an excellent solubility, being readily soluble at room temperature in THF, dichloromethane, chloroform, 1,2-dichloroethane, 1,2-dichlorobenzene, toluene, xylene, and acetonitrile. Polymer **P2** seemed to be more soluble than **P1** due to the incorporation of the ethanolamine moiety into the side group.

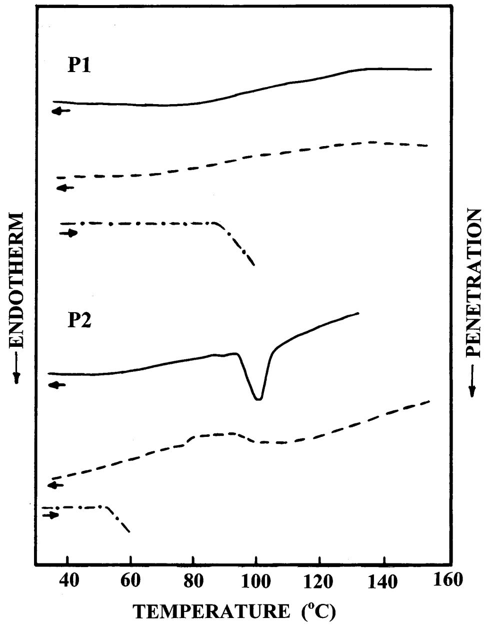


Figure 4. DSC thermograms (—, first heating; – – , second heating) of polymers **P1**(top) and **P2** (bottom) as well as TMA thermograms (– • –) of these polymers.

Table 1. TMA and TGA Data of Polymers

		TGA				
	TMA	in N_2			in air	
polymer	T_g[a] (°C)	T_1[b] (°C)	T_{10}[b] (°C)	Y_c[c] (%)	T_1[b] (°C)	T_{10}[b] (°C)
P1	87	325	503	73	285	397
P2	52	321	377	47	278	344

[a] T_g: Glass transition temperature. [b] T_1, T_{10}: Temperatures at which weight losses of 1 and 10%, respectively, were observed. [c] Y_c: Char yield at 800 °C.

Thermal and thermomechanical characterization of polymers was accomplished by DSC, TMA, and TGA. Figure 4 presents the DSC curves (first heating and second heating) as well as the TMA curves (second heating) for both polymers. The DSC traces of **P1** did not show any transition even during repeated scans. No melting endotherm was observed, thus supporting the amorphous nature of this polymer. In contrast, the DSC trace of **P2** displayed, during the first heating, a strong endotherm at 101 °C (onset temperature 94 °C) associated with melting. The determination of the T_g's by DSC was impossible for both polymers. The T_g's were determined by the TMA method utilizing a loaded penetration probe (Table 1). The T_g is assigned by the first inflection point in the TMA curve, and it was obtained from the onset temperature of this transition during the second heating. **P1** showed higher T_g (87 °C) than **P2** (52 °C). The aliphatic segment of the ethanolamine that was incorporated into the side groups of **P2** should be responsible for this behavior. Generally, these polymers exhibited relatively low T_g's because of their flexible backbone.

The thermal stability of the polymers was ascertained by TGA, and the data obtained are summarized in Table 1. The polymers were stable up to 278−325 °C in N_2 or air and afforded char yield of 47−73% at 800 °C in N_2. All thermal characteristics of **P1** were higher than those of **P2**, indicating the superior thermal stability of the former due to its lower content in aliphatic moieties.

Table 2. UV−Vis, PLE, and PL Data of Polymers

polymer	$\lambda_{a,max}{}^{a}$ in solution (nm)	$E_g{}^{b}$ (eV)	$\lambda_{ex,max}{}^{c}$ in solution (nm)	$\lambda_{f,max}{}^{d}$ in solution at RT (nm)	$\lambda_{f,max}{}^{d}$ in solution at ca. −50 °C (nm)	$\Phi_f{}^{e}$ in solution	$\lambda_{ex,max}{}^{c}$ in thin film (nm)	$\lambda_{f,max}{}^{d}$ in thin film (nm)
P1	330	3.20	359	397	*404*,[f] 421	0.30	357	413
P2	290, *325*	2.94	357, *383*	457	472	0.11	397	507

[a] $\lambda_{a,max}$: The absorption maxima from the UV−vis spectra in THF solution. [b] E_g: The optical energy gaps calculated from the UV−vis spectra in THF solution. [c] $\lambda_{ex,max}$: The PL excitation maxima in THF solution or in thin film. [d] $\lambda_{f,max}$: The PL maxima in THF solution or in thin film. [e] Φ_f: PL quantum yields. [f] Italicized numerical values denote absolute maxima.

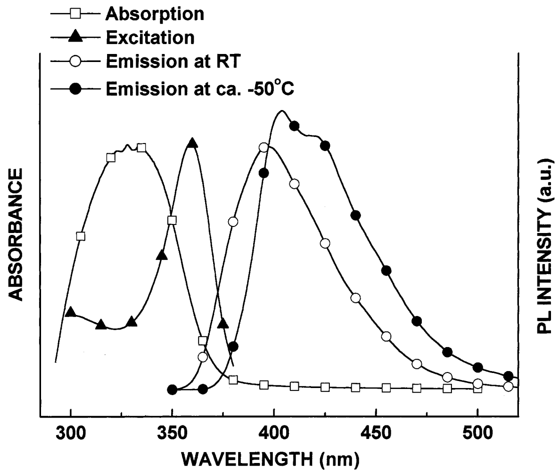


Figure 5. Absorption and PL excitation spectra as well as PL spectra at room temperature and at low temperature (ca. −50 °C) of polymer **P1** in THF solution.

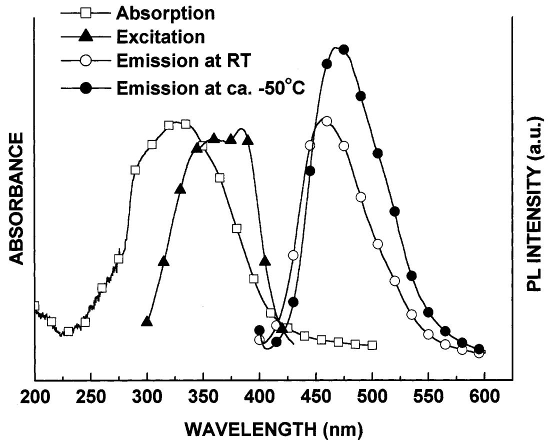


Figure 6. Absorption and PL excitation spectra as well as PL spectra at room temperature and at low temperature (ca. −50 °C) of polymer **P2** in THF solution.

Optical Properties of Polymers. The spectroscopic data of polymers that were acquired from their UV−vis, the PL excitation (PLE), and the photoluminescence (PL) spectra both in THF solution and in thin film are summarized in Table 2. Figures 5 and 6 present these spectra for polymers **P1** and **P2**, respectively, in THF solution.

The UV−vis spectra of polymers in THF showed absorption maxima around 330 nm which was assigned to the $\pi-\pi^*$ transitions of the conjugated segment that consisted of the stilbenoid segment. Moreover, **P2** displayed a shoulder near 290 nm, attributable to the $n-\pi^*$ transition of the imide carbonyls. The optical energy gaps (E_g) were calculated from the onset wavelength of these spectra, and they were 3.20 and 2.94 eV for **P1** and **P2**, respectively.

The PLE spectra of polymers in THF were red-shifted in comparison to the respective absorption spectra. Polymer **P1** exhibited a maximum ($\lambda_{ex,max}$) at 359 nm, whereas **P2** had maxima at 357 and 383 nm. The two exciting sites of **P2** gave the same PL maximum ($\lambda_{f,max}$) at 457 nm, but of different intensities.

Polymers **P1** and **P2** behaved as violet-blue and blue-greenish emitting materials in THF solution and their $\lambda_{f,max}$ appeared at 397 and 457 nm, respectively, by exciting at the corresponding $\lambda_{ex,max}$. Although both polymers had comparable chemical structures with stilbenoid segments, **P2** showed an emission at longer wavelength region due to the imide carbonyls.

The temperature effect on the emission characteristics of polymers was examined. For this purpose, the THF solutions of polymers were cooled by gradually pouring liquid nitrogen on the sample solutions and their PL spectra were recorded at low temperature (ca. −50 °C). As shown in Figures 5 and 6, the emission intensity of both polymers was increased at low temperature. The PL maximum of **P1** was red-shifted by 7 nm. In addition, a new shoulder of **P1** appeared at 421 nm obviously due to the reduced rotation between the adjacent phenyls at low temperature. This behavior conforms with certain literature data.[23] Polymer **P2** did not show a new peak at low temperature, but its maximum was red-shifted by 15 nm.

The PL quantum yields (Φ_f) of polymers in THF were determined[24] using quinine sulfate ($\Phi_f = 0.546$) as standard. Interestingly, **P1** displayed a higher Φ_f value (0.30) than **P2** (0.11). The presence of the imide carbonyls contributed to the lower PL efficiency of the latter. A luminescence quenching can take place in polyimides by an energy transfer mechanism.[25] The Φ_f values of the parent methacrylates were also determined for comparative purposes. Specifically, compounds **5** and **9** had Φ_f values in THF solution of 0.33 and 0.13, respectively, which are comparable with those of the corresponding polymers **P1** and **P2**.

The influence of the polymer concentration in THF solutions on their PL curves was investigated for both polymers. Figure 7 presents their PL spectra with a wide concentration range in THF. It seems that for **P1** the intra- and intermolecular interactions were not significant since the $\lambda_{f,max}$ was red-shifted only by 4 nm with increasing polymer concentration. In contrast, **P2** displayed remarkable interactions because the $\lambda_{f,max}$ was red-shifted by 16 nm with increasing polymer concentration. It is apparent that, in concentrated solutions of **P2**, aggregates were formed, probably between the adjacent styryl groups that emitted at longer wavelengths.[10,26] The greater number of the styryl groups per each repeated unit of **P2** as well as the less rigid structure of this polymer as was shown from the T_g values should be responsible for its higher tendency for aggregate formation.

The effect of the solvent polarity on the PL curve was investigated. Figure 8 depicts the PL spectra of **P2** in

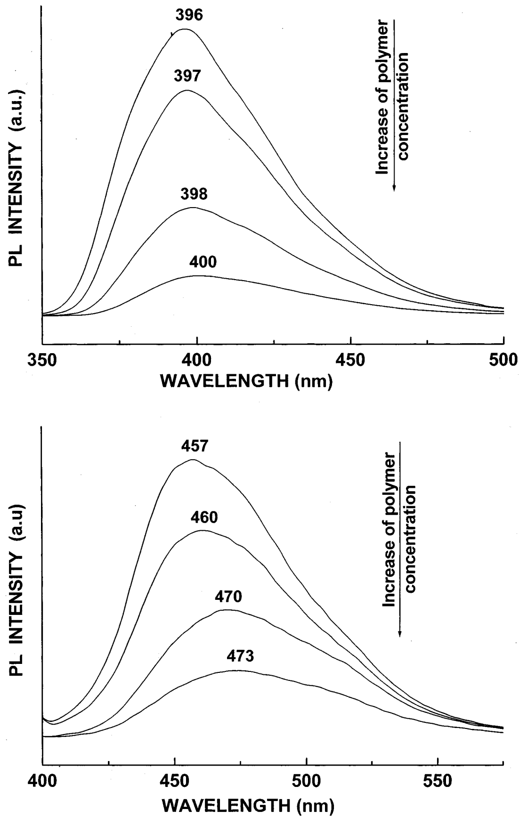


Figure 7. PL spectra of polymers **P1** (top) and **P2** (bottom) at various concentrations in THF solutions with excitation at the corresponding $\lambda_{ex,max}$.

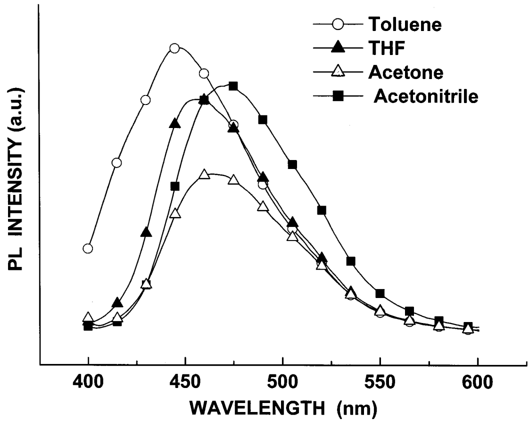


Figure 8. PL spectra of polymer **P2** in solvents of different polarity with excitation at 383 nm.

various solvents. More particular, the $\lambda_{f,max}$ of this polymer in toluene, THF, acetone, and acetonitrile appeared at 447, 456, 464, and 473 nm, respectively. It is well-known that the PL spectra are progressively red-shifted with increasing the solvent polarity.[27, 28]

Furthermore, the PLE and PL spectra of polymers were recorded in thin films (Figure 9). The thin films of polymers were obtained from their solutions in THF by spin casting on quartz substrates. By exciting at the $\lambda_{ex,max}$ (357 and 397 nm for **P1** and **P2**, respectively) the respective $\lambda_{f,max}$ emerged at 413 and 507 nm, thus indicating red shifts of 16 and 50 nm in comparison to the corresponding solutions. This feature is in agreement with the behavior observed in concentrated solutions of polymers, according to which **P2** presents a higher tendency than **P1** to form aggregates.

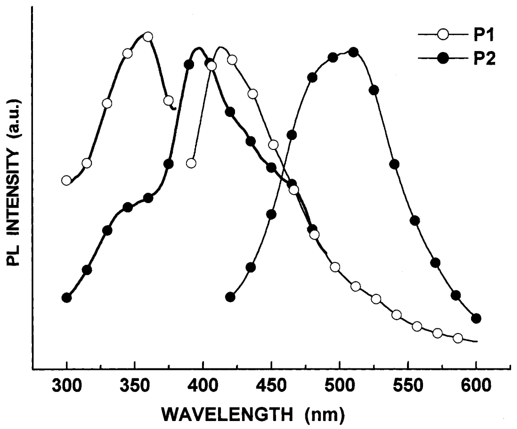


Figure 9. PL excitation spectra (bold line) and PL spectra (thin line) in thin films of polymers **P1** and **P2**.

Conclusions

Methacrylates **5** and **9** were synthesized and subjected to free-radical polymerization to afford the respective polymers **P1** and **P2** that carried side stilbenoid groups. They showed a satisfactory thermal stability and an enhanced solubility in common organic solvents and had T_g values of 52−87 °C. The polymers were violet-blue or blue-greenish emitting materials. The tuning factor of the emissive wavelength was the structure of the chromophore. Polymer **P1** showed a PL maximum in solution at 397 nm and in thin film at 413 nm. Polymer **P2,** which contained imide carbonyls, displayed PL maxima at longer wavelengths, to be precise in solution at 457 nm and in thin film at 507 nm. At low temperature, the PL maximum in solution was red-shifted by 7−15 nm in comparison with the room-temperature spectra, and **P1** showed also a new peak at 421 nm. The PL quantum yields in THF were for 0.30 **P1** and for 0.11 **P2**, which were comparable with those of the corresponding parent methacrylates. Polymer **P2** exhibited a higher tendency than **P1** to form aggregates both in concentrated solutions and in thin film. The PL maximum in solution was red-shifted with increasing solvent polarity.

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