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New AB Polyesters and a Polymethacrylate Containing Dipolar *p*-Phenyleneazo Groups

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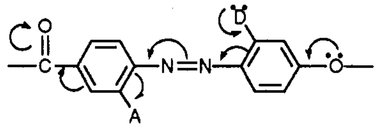
ABSTRACT: The AB monomers 4-[(4-hydroxy-2-methoxyphenyl)azo]benzoic acid (1), 4-[[4-[(4-hydroxy-2-methoxyphenyl)azo]-2-methoxyphenyl]azo]benzoic acid (2), and 4-[(4-hydroxy-2-methoxyphenyl)azo]-3-nitrobenzoic acid (3) containing dipolar *p*-phenyleneazo groups were synthesized and subsequently polymerized. The monomers were polymerized by recently developed direct polycondensation techniques. The polyester synthesized from 1 forms a red, transparent film. Monomer 2 did not polymerize, while 3 gave a powdered polymer. A comblike polymethacrylate 9 containing dipolar *p*-phenyleneazo groups in the side chains was also prepared by the free radical polymerization of 1-[3-methoxy-4-[(*p*-nitrophenyl)azo]phenoxy]hexyl methacrylate (8). Polymer 9 showed a t_g at 88 °C followed by decomposition at 255 °C; liquid-crystalline behavior was observed in this temperature range. All the polymers were found to have little or no absorption at the wavelengths of telecommunication interest. They may be useful as nonlinear optical materials.

Introduction

Polymers that possess high nonlinear optical activities have seen a recent growth in interest.[1,2] We have recently synthesized AB polyesters that contain highly dipolar quinodimethane units[3] or *p*-oxy-α-cyanocinnamate units[4] in the polymer main chain. These dipolar polyesters have been shown to possess a high nonlinear optical effect.[5] We have also previously synthesized polyesters containing multiple *p*-phenyleneazo groups, which have strongly delocalized π electrons.[6] The introduction of donor and acceptor substituents in a push-pull arrangement to these polymers through the diphenylazo group as shown below would make them highly attractive as polymeric nonlinear optical substrates.



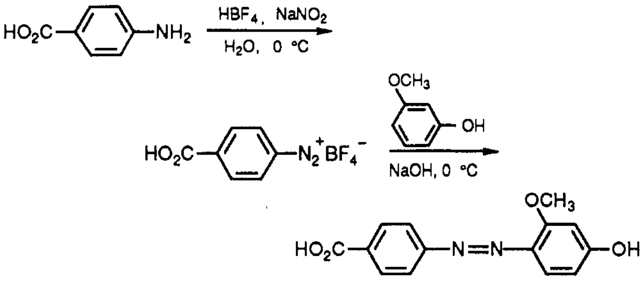
Similarly, these dipolar units shown above in the main chain can also be incorporated into the side chains of comblike polymethacrylates. Methacrylate or acrylate polymers containing dipolar azo groups in the side chains have recently been demonstrated to have a large third-order[7] or second-order[8] nonlinear optical effect.

Results and Discussion

We have now synthesized two types of polymers containing dipolar *p*-phenyleneazo groups.

Polyesters Containing Dipolar *p*-Phenyleneazo Units in the Main Chain. AB monomers containing methoxy or nitro substituents on the *p*-phenyleneazo groups were prepared by diazotization and coupling. These monomers were polymerized by recent direct polycondensation techniques.

Synthesis of the Monomers. Monomer 1, 4-[(4-hydroxy-2-methoxyphenyl)azo]benzoic acid, was prepared by diazotization of *p*-aminobenzoic acid, followed by coupling with *m*-methoxyphenol.



1

Monomer 2, 4-[[4-(4-hydroxy-2-methoxyphenyl)-2-methoxyphenyl]azo]benzoic acid, containing two azo units was also synthesized by diazotization and coupling as shown in the following reaction sequence. The sequence

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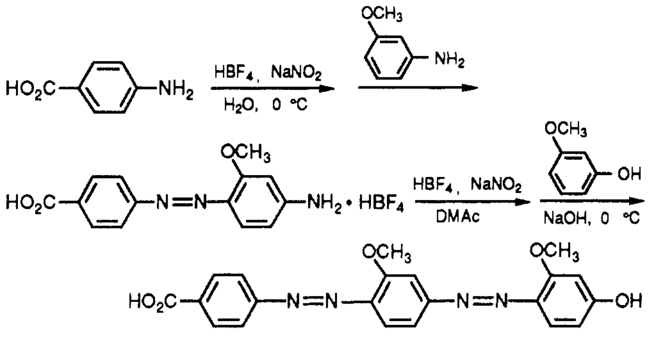
was repeated twice to produce the desired structure.



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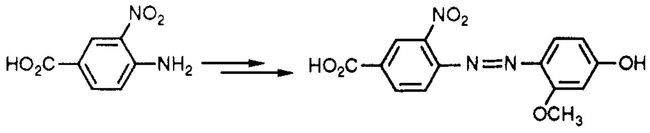
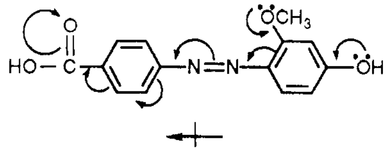
Monomer 3, 4-[(4-hydroxy-2-methoxyphenyl)azo]-3-nitrobenzoic acid, was synthesized similarly by diazotization of 4-amino-3-nitrobenzoic acid, followed by coupling with *m*-methoxyphenol. The diazotization reaction was carried out in *N,N*-dimethylacetamide (DMAc) because of the limited solubility of 4-amino-3-nitrobenzoic acid in aqueous solution.



3

An electron-donating methoxy group was incorporated into the ortho position relative to the azo linkage. The azo group, itself an acceptor,[9] is para to the carbonyl of the acid group which can also be considered to be an electron-withdrawing group of the monomer. The dipolar character of monomer 1 is shown below with arrows indicating the electron donation from both the hydroxy and methoxy groups while the carboxyl group is the electron acceptor.

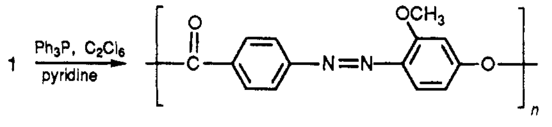


In this case, the azo linkage acts more like a conduit than an acceptor. This is evident in the IR spectra, which shows the shift of carbonyl group to lower frequency at 1680 cm^{-1}, indicating that the electrons are delocalized into the carboxylic acid group. It appears reasonable that the polarity of the monomer could be increased by introducing more methoxy and azo groups. Thus, we synthesized monomer 2 to extend the conjugation.

An electron-withdrawing nitro group was incorporated into monomer 3 by using 4-amino-3-nitrobenzoic acid in the diazo coupling reaction. The nitro group was introduced at a position in the molecule where it can act as an electron acceptor. The observation that the IR spectrum shows the carbonyl group absorption of monomer 3 at higher frequency (1694 cm^{-1}) than that of monomer 1 suggests that the electrons are delocalized largely into the nitro group instead of the carbonyl group.

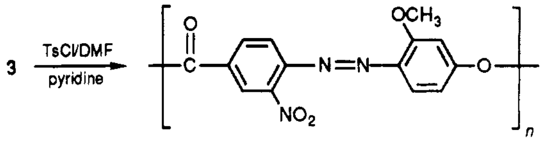
Polymerization of Monomers 1, 2, and 3. Monomer 1 was polymerized by direct polycondensation in the presence of triphenylphosphine and hexachloroethane in pyridine according to Ogata's method.[10,11]

Polymer 4 was initially produced as a red-brown powder. DSC showed the polymer to have t_g at 141 °C followed by decomposition at 322 °C. The polymer was soluble in strong acid solvents such as trifluoroacetic acid, sulfuric acid, and methanesulfonic acid. The inherent viscosity was determined to be 0.18 in methanesulfonic acid (0.5 g/dL, 30 °C) as the solvent. Red, transparent films can be cast by dissolving the powder in trifluroacetic acid, followed by evaporation of the solvent at room temperature.



4

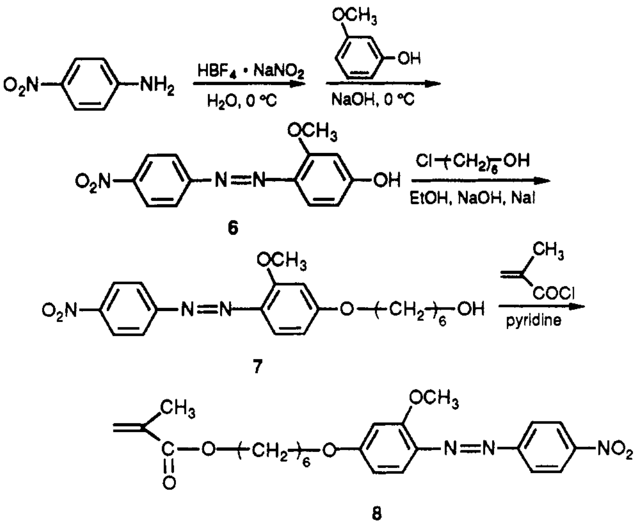
Monomer 3 did not polymerize by Ogata's method. Another direct polycondensation method using tosyl chloride (TsCl) and DMF as the catalysts with pyridine as the solvent was used.[12] A black powder corresponding to polymer 5 was obtained. DSC showed polymer decomposition at 24 °C. Like the previous polymer, it was soluble in trifluoroacetic acid, sulfuric acid, and methanesulfonic acid. The inherent viscosity was determined to be 0.13 in methanesulfonic acid (0.5 g/dL, 30 °C). Only a brittle film could be cast from trifluoroacetic acid.



5

We were unable to polymerize monomer 2 by either Ogata's method or the TsCl/DMF method. This may be due to the more rigid nature of the three-ring double-azo monomer molecules.

Comblike Polymethacrylate Containing Dipolar *p*-Phenyleneazo Units in the Side Chains: Liquid-Crystalline Properties. Synthesis of the Methacrylate Monomer. The methacrylate monomer 8, 1-[3-methoxy-4-[(*p*-nitrophenyl)azo]phenoxy]hexyl methacrylate, was prepared by a multistep synthesis according to the following scheme.



In the synthesis of this monomer, the second step was the most difficult one; the reaction was very slow, presumably due to stabilization of the phenoxide ion by resonance effect:

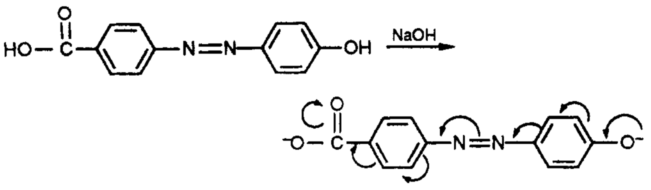


Table I
Thermotransition Temperatures of the Compounds Containing Dipolar *p*-Phenyleneazo Group by DSC

compd	transition temp,[a] °C		
7	t_m 146	t_{n-i} 212	(lc)
8	t_m 73	t_{n-i} 152	(lc)

[a] t_m, transition from the solid to the mesophase; t_{n-i}, transition from the mesophase to the isotropic phase.

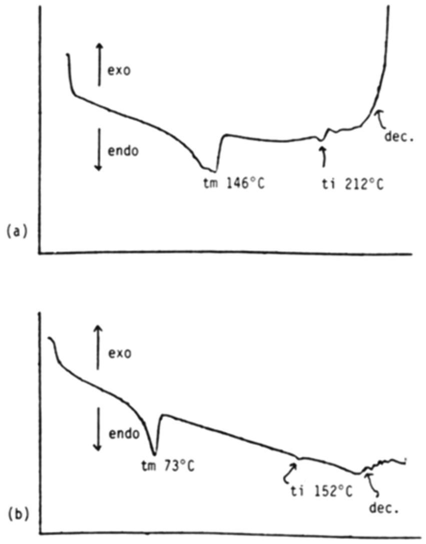
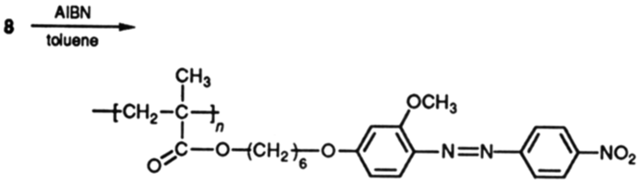


Figure 1. DSC thermograms of (a) 7 and (b) 8.

The phenyleneazo unit was prepared in a manner similar to the main-chain monomers. A six-carbon spacer was used between the rigid polarizable group and the methacrylate unit. The monomer was polymerized by free radical polymerization using AIBN as the initiator.



9

Liquid-Crystalline Properties of the Small Molecules. The intermediate 7 and the monomer 8 showed liquid-crystal behavior as illustrated in Table I.

Differential scanning calorimetry clearly showed two peaks, indicating melting and clearing temperatures. The DSC thermograms of 7 and 8 are shown in Figure 1. By polarizing light microscopy, the liquid-crystalline (LC) phase exhibits a schlieren texture typical of a nematic phase both on melting from the crystal into the liquid-crstal phase and on cooling from the isotropic liquid to the liquid-crystal phase. Figure 2 is a photomicrograph of 7 at 175 °C with a magnification of 94.5 times. Notice the loop disclination (arrow) indicating the schlieren texture is from a nematic phase and not a smectic C phase, which does not show disclination loops.

Polymer 9 was only slightly soluble in most of the solvents and due to the low solubility, good films could not be cast. A number of solvents were tried and all gave poor films. DSC shows a T_g at 88 °C followed by decomposition at 255 °C. No peak was clearly evident in the DSC for an isotropic to liquid-crystal phase transition. However, liquid-crystal behavior was observed on a hot-stage polarizing microscope. The reason for the DSC not clearly showing a transition from the isotropic to LC phase is evident when the sample is observed under the polarizing microscope. One can see different areas of the polymer film undergoing the phase transition at different temperatures. Since the enthalpy involved with a liquid crystal to isotropic liquid phase transition typically is small, it cannot be detected when it occurs over a broad range of temperatures. This phenomenon often will occur with LC polymers that have a very broad molecular weight distribution.

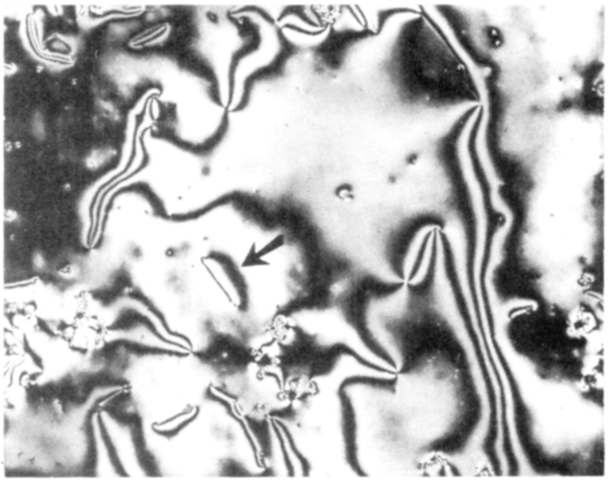


Figure 2. Photomicrograph of 7 at 175 °C with a magnification of ×94.5.

Ultraviolet and Visible Spectroscopy of the Monomers and Polymers. All spectra were taken on a Varian Lambda 9 UV/vis/near-IR spectrophotometer from 350 to 2000 nm (2 μm) with trifluoroacetic acid (TFA) as the solvent. The use of only one solvent for the studies eliminates complications that may arise due to solvatochromism.[13]

For nonlinear optics, the wavelengths of importance are the two laser diode frequencies 1.3 μm and 830 nm. Many telecommunication applications use these two frequencies. The other wavelengths of importance are 1.91, 1.34, and 1.06 μm. These wavelengths are all available to the laboratory scientist from a neodymium laser as the fundamental or after Raman shifting. It is also important for the compounds to have little or no absorption at the second or third harmonics of these frequencies in order to evaluate the second- and third-order response of the compounds.

Figure 3 shows the spectra of monomer 1 (λ_{max} 455 nm, ϵ 5.7 × 10^4), polymer 4 (λ_{max} 504 nm, ϵ 4.4 × 10^4, shoulder 485 nm), and a thin film cast from TFA. The ϵ of the polymer was calculated based on a unit mer weight. It is not unreasonable to expect λ_{max} for the polymer to shift slightly toward longer wavelengths coupled with a broadening of the absorption peak. This may be due to either the close proximity of the chromophore that is forced upon them when polymerized or a very slight amount of cross conjugation at the ester linkages.

This bathochromic shift with broadening is also seen for the main-chain polymers 5 (λ_{max} 497 nm, shoulder 440 nm) when compared to the corresponding monomer 3 (λ_{max} 466 nm). What is interesting is the appearance of a shoulder at wavelengths shorter than that of the main peak in both the polymers. At this time, the authors can offer no clear reason for this behavior.

The extended conjugation of monomer 2 (λ_{max} 568.5) is clearly evident from its absorption spectrum. By the addition of the second methoxyazo group into the monomer unit, the maximum absorption peak has shifted over 100 nm to the red when compared to the single methoxyazo monomer compound 1. It is known from theoretical considerations[14] and experimental considerations[13] that extended conjugation of the push–pull chromophore en-

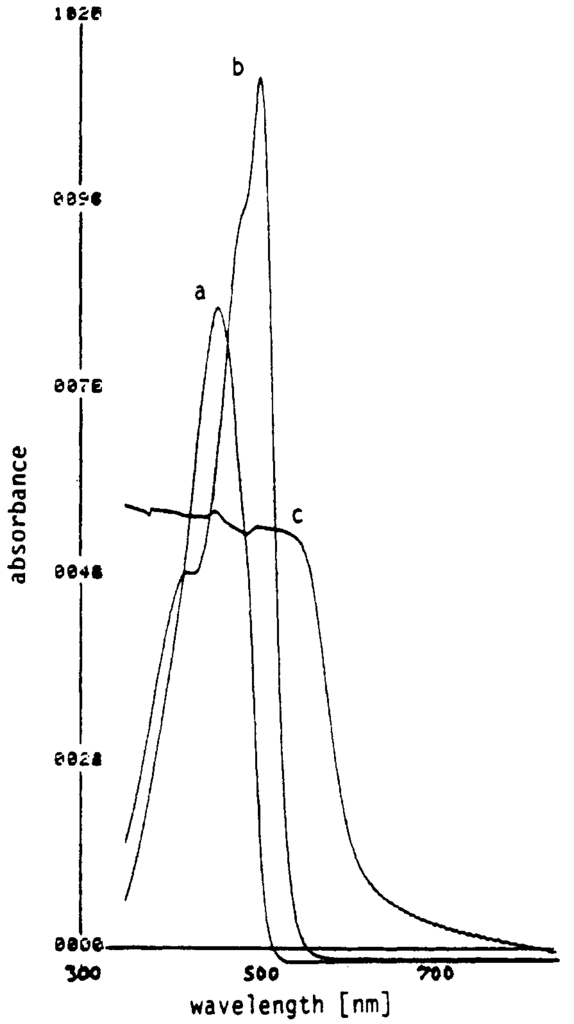


Figure 3. Absorption spectra of (a) monomer 1, (b) polymer 4, and (c) film of polymer 4.

hances the nonlinear optical (NLO) properties. However, by adding conjugating units to the chromophore in order to further separate the donor and acceptor, one often creates complications such as insolubility, instability, or the inability to process the polymer. In this case, it was found that the monomer could not be polymerized by any of the techniques attempted.

The side-chain methacrylate polymer was not soluble in TFA and its absorption spectra was not recorded. A different solvent was not used due to the possibility of solvatochromic shifts, which would not allow us to draw any conclusions. The methacrylate monomer 8 (λ_{max} 523) shows a shift to longer wavelengths when compared to monomer 1. This is easily explained by the fact that the nitro group in monomer 8 is a better electron acceptor than the carboxylate group of monomer 1 and one would expect a red shift. The parent alcohol 7 of monomer 8 was found to have a slightly shorter absorption maximum (λ_{max} 518) than the corresponding monomer.

All the compounds were found to have little or no absorption at the wavelengths of telecommunications interest. All except the film of polymer 4 had very little tailing past 700 nm. The tailing of polymer 4's absorption dissipates around 900 nm. These materials may all be of interest for NLO applications at diode laser wavelengths.

Conclusion

In conclusion, we have successfully incorporated dipolar diphenylazo groups into the polymer main chain or polymer side chains. These new AB polyesters and polymethacrylate were found to be of interest for nonlinear optical applications as evidenced by the UV-visible absorption spectra.

Experimental Section

^{1}H NMR spectra were taken on a 60-MHz Varian EM 360L or 250-MHz Bruker WM 250 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Inherent viscosities were determined by using a Ostwald-type viscometer in a constant-temperature bath. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Characterization of Liquid-Crystalline Compounds. All the thermal transition temperatures were recorded on a Perkin-Elmer DSC 4 at a heating rate of 20 °C/min under a nitrogen atmosphere. The optical textures were observed on a Leitz Laborlux 12 Pol polarizing microscope fitted with long working length objectives and a Mettler FP 80/82 controller microfurnace assembly.

Synthesis of Monomers. 4-[(4-Hydroxy-2-methoxyphenyl)azo]benzoic Acid (1). To a stirred solution of 2.74 g (0.02 mol) of 4-aminobenzoic acid in the minimum amount of water needed to dissolve it, 8.8 g (0.05 mol, 49% in water) of fluoboric acid was slowly added. The mixture was then cooled in an ice bath and a solution of 1.45 g (0.0202 mol) of sodium nitrite was added. The mixture was tested for the presence of free nitrous acid with potassium iodide–starch paper after 15 min. The above mixture was added to a stirred solution of 4.96 g (0.04 mol) of *m*-methoxyphenol and 2.0 g (0.05 mol) of sodium hydroxide in ice–water over a period of 30 min. The reaction mixture was then stirred for an additional hour. The resulting yellow suspension was acidified with dilute HCl and cooled. The yellow precipitate was collected on a funnel, dried, and recrystallized from 70% ethanol to give 5.3 g (97%) of 1: yellow; dec 264 °C; IR (KBr) 3300, 2820, 1680, 1600, 1523, 1260, 1161, 1104, 835, 770 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 3.9 (s, 3 H), 6.3–8.5 (m, 7 H). Anal. Calcd for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.41; N, 10.29. Found: C, 61.46; H, 4.30; N, 10.05.

4-[[4-[(4-Hydroxy-2-methoxyphenyl)azo]-2-methoxyphenyl]azo]benzoic Acid (2). 2.74 g (0.02 mol) of 4-aminobenzoic acid was diazotized and coupled with *m*-anisidine as described previously. The resulting crude 4-(4-amino-2-methoxyphenylazo)benzoic acid hydrofluoroborate 1.35 g (3.8 mmol), was dissolved in *N*,*N*-dimethylacetamide; the solution was then diazotized and subsequently coupled with *m*-methoxyphenol in aqueous sodium hydroxide. The resulting mixture was acidified as above, the precipitate was isolated and recystallized from 80% of ethanol twice to yield 0.98 g (64%) of 2: red-brown; dec 268–270 °C; IR (KBr) 3390, 1694, 1599, 1504, 1272, 1146, 1100, 865, 837, 775 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 3.9 (s, 3 H), 4.05 (s, 3 H), 6.3–8.3 (m, 10 H). Anal. Calcd for $C_{21}H_{18}N_4O_5$: C, 62.07; H, 4.43; N, 13.79. Found: C, 61.14; H, 4.46; N, 13.33.

4-[(4-Hydroxy-2-methoxyphenyl)azo]-3-nitrobenzoic Acid (3). 4-Amino-3-nitrobenzoic acid, 9.1 g (0.05 mol), was diazotized in the mixed-solvent system *N*,*N*-dimethylacetamide/water and coupled with *m*-methoxyphenol according to the previous procedure. The resulting crude product was recrystallized twice from 80% ethanol to give 9.8 g (62%) of 3: yellow-brown; dec 279 °C; IR (KBr) 3223, 1694, 1614, 1486, 1219, 1178, 1159, 815, 751, 100 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 3.9 (s, 3 H), 6.3–8.5 (m, 6 H). Anal. Calcd for $C_{14}H_{11}N_3O_6$: C, 53.00; H, 3.47; N, 13.25. Found: C, 52.64; H, 3.52; N, 13.69.

Polymerization: 4. A 50-mL three-necked round-bottom flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen inlet was flushed with dry N_2 and charged with 10 mL of pyridine, 1.09 g (4 mmol) of 4-[(4-hydroxy-2-methoxyphenyl)-azo]benzoic acid (1), and 1.05 g (4 mmol) of triphenylphosphine. To this mixture was added 0.95 g (4 mmol) of hexachloroethane with stirring. The mixture was then refluxed for 10 h and subsequently poured into methanol. The resulting precipitate was isolated and dried under vacuum to afford 0.8 g (74%) of 4: red-brown; t_g 141 °C, dec 322 °C; η_{inh} 0.18; IR (KBr) 3439, 1730, 1600, 1486, 1240, 1151, 1059 cm^{-1}. Anal. Calcd for $C_{14}H_{10}N_2O_3$: C, 66.14; H 3.94; N, 11.02. Found: C, 65.80; H, 3.71; N, 10.88.

5. A pyridine (5 mL) solution of toluenesulfonyl chloride (6 mmol) was prepared and allowed to stand at room temperature for 30 min.

A solution of 0.63 g (2 mmol) of 4-[(4-hydroxy-2-methoxyphenyl)azo]-3-nitrobenzoic acid (**3**) in 6 mL of pyridine and 2.5 mL of *N,N*-dimethylformamide was preheated at 120 °C for 5 min. To this mixture was added dropwise the above TsCl/pyridine solution over a period of 30 min. The reaction mixture was then refluxed under a nitrogen atmosphere for 2 days and subsequently poured into water. The precipitate was filtered, extracted with ethanol in a Soxhlet extractor, and dried under vacuum to give 0.35 g (56%) of **5**: black; dec 249 °C; η_{inh} 0.13; IR (KBr) 3438, 1744, 1612, 1536, 1486, 1233, 1094 cm^{-1}. Anal. Calcd for $C_{14}H_9N_3I_5$: C, 56.19; H, 3.01; N, 14.05. Found: C, 57.68; H, 2.99; N, 14.84.

Synthesis of 1-[3-Methoxy-4-[(*p*-nitrophenyl)azo]phenoxy]hexyl Methacrylate: 3-Methoxy-4-[(*p*-nitrophenyl)azo]phenol (6). To a stirred solution of 1.86 g of (0.015 mol) of *m*-methoxyphenol and 1.00 g (0.025 mol) of sodium hydroxide in ice–water was added a solution of 2.37 g (0.01 mol) of *p*-nitrobenzenediazonium tetrafluoroborate in acetonitrile. The reaction mixture was then stirred for 2 h. The resulting dark red suspension was acidified with dilute HCl and cooled. The precipitate was isolated and recrystallized from 70% ethanol to give 2.5 g (93%) of **6**: red-brown; mp 174 °C; IR (KBr) 1591, 1516, 1336, 1259, 1206, 1161, 1105, 854 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 3.85 (d, 3 H), 6.3–8.5 (m, 7 H). Anal. Calcd for $C_{13}H_{11}N_3O_4$: C, 57.14; H, 4.03; N, 15.38,. Found: C, 56.98; H, 3.78; N, 16.15.

6-[3-Methoxy-4-[(*p*-nitrophenyl)azo]phenoxy]-1-hexanol (7). To a stirred solution of 2.7 g (0.01 mol) of **6**, 100 mL of 95% ethanol, and 1.2 g (0.03 mol) of sodium hydroxide in a three-necked round-bottom flask equipped with a magnetic stirrer, a dropping funnel, and a reflux condenser was added 1.5 g (0.01 mol) of sodium iodide. The mixture was then heated at reflux temperature for 15 min, followed by the slow addition of 2.74 g (0.02 mol) of 6-chloro-1-hexanol. The reaction was stopped after refluxing for 3 days followed by removal of the solvent using a rotary evaporator. The residue was dissolved in dichloromethane and extracted repeatedly with 5% sodium hydroxide. The organic layers were combined and dried with sodium sulfate. The solvent was evaporated under vacuum and the crude product was recrystallized from ethanol/H_2O to give 2.3 g (62%) of **7**: red-brown; IR (KBr) 2931, 1597, 1494, 1455, 1291, 1251, 1204, 1168, 1029, 856, 808 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1–2 (m, 8 H), 3.4–4.3 (m, 7 H), 6.4–8.6 (m, 7 H). Anal. Calcd for $C_{19}H_{23}N_3O_5$: C, 61.13; H, 6.17; N, 11.26. Found: C, 62.34; H, 6.20; N, 11.64.

1-[3-Methoxy-4-[(*p*-nitrophenyl)azo]phenoxy]hexyl Methacrylate (8). To a stirred solution of 0.6 g (1.4 mmol) of **7** in 30 mL of pyridine in a round-bottom flask fitted with a condenser was added an excess of methacryloyl chloride. The reaction mixture was refluxed for 10 h, followed by the removal of the solvent by vacuum distillation. The residue was taken up in dichloromethane and extracted with water and the organic layer dried with sodium sulfate. The solvent was evaporated and the crude product was recrystallized from acetone/H_2O to give 0.63 g (89%) of **8**: red; IR (KBr) 2936, 1714, 1678, 1597, 1456, 1293, 1251, 1204, 1167, 1114, 1031, 858, 831, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1–2 (m, 11 H), 3.5–4.3 (m, 7 H), 6.4–8.6 (m, 9 H). Anal. Calcd for $C_{23}H_{27}N_3O_6$: C, 62.59; H, 6.12; N, 9.52. Found: C, 63.46; H, 6.06; N, 9.10.

Polymerization of 1-[3-Methoxy-4-[(*p*-nitrophenyl)azo]phenoxy]hexyl Methacrylate. To a stirred solution of 0.4 g (0.9 mmol) of **8** in 20 mL of dry toluene in a round-bottom flask equipped with a condenser and a nitrogen inlet was added a catalytic amount of AIBN. The reaction mixture was then refluxed under nitrogen atmosphere for 5 h and the resulting suspension poured into methanol. The precipitate was isolated, washed repeatedly with hot ethanol, and dried under vacuum to give 2.9 g (73%) of **9**: red; t_g 88 °C, dec 255 °C; IR (KBr) 2940, 1721, 1596, 1461, 1250, 1166, 1112, 804 cm^{-1}. Anal. Calcd for $C_{23}H_{27}N_3O_6$: C, 62.59; H, 6.12; N, 9.52. Found: C, 63.50; H, 6.09; N, 9.25.

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Registry No. **1**, 120743-28-4; **1** (homopolymer), 120743-38-6; **2**, 120743-29-5; **3**, 120743-30-8; **3** (homopolymer), 120743-39-7; **4**, 120743-36-4; **5**, 120743-37-5; **6**, 120743-34-2; **7**, 120743-35-3; **8**, 120743-31-9; **8** (homopolymer), 120743-40-0; $Cl(CH_2)_6OH$, 2009-83-8; $H_2C{=}C(CH_3)COCl$, 920-46-7; 4-nitroaniline, 100-01-6; 4-aminobenzoic acid, 150-13-0; *m*-methoxyphenol, 150-19-6; 4-[(4-amino-2-methoxyphenyl)azo]benzoic acid hydrofluoroborate, 120743-33-1; 4-amino-3-nitrobenzoic acid, 1588-83-6.

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