Synthesis and Photoinduced Surface-Relief Grating of Well-Defined Azo-Containing Polymethacrylates via Atom Transfer Radical Polymerization

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ABSTRACT: A well-defined photoresponsive polymethacrylate containing azo chromophores, poly[6-(4-phenylazophenoxy)hexylmethacrylate] [Poly(PPHM)], was prepared with azo-based monofunctional and difunctional initiators via atom transfer radical polymerization in the presence of CuCl/1,1,4,7,10,10-hexamethyltriethylenetetramine. The polymerizations with first-order kinetics were well controlled with theoretical expected molecular weight and narrow molecular weight distributions in two initiation systems. The UV absorption intensities of the poly (PPHM)s increased with increasing molecular weight of the poly(PPHM)s in all cases. The 80-nm surface-relief gratings with 2.7% efficient diffraction formed on the poly (PPHM) film surface were obtained with a linearly polarized krypton laser with 10 min of irradiation at a recording beam intensity of 188 mW/cm^2 with a wavelength of 413.1 nm. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1234–1242, 2007

Key words: atom transfer radical polymerization (ATRP); azo polymers; initiators; irradiation

INTRODUCTION

In recent years, polymers containing azobenzene chromophores have attracted a great deal of attention because of their interesting properties related to the reversible photoisomerization between the trans and cis isomers of the chromophore.[1] Azobenzene polymers include amorphous polymers,[1–3] liquid-crystalline polymers,[4–9] block copolymers,[10,11] and dendrimers.[12–15] They have been used in diversified applications, including new optical switches,[16,17] novel azo-containing pH-sensitive hydrogels,[18,19] optical polyelectrolytes,[20] nonlinear optical materials,[21–23] and the preparation of holographic graftings.[3,24,25]

Atom transfer radical polymerization (ATRP),[26] one of the systems developed for controlled/living radical polymerization, has been used as a powerful tool for designing well-defined complex polymer structures in the past decades. The ATRP process has good tolerance for a wide range of functional monomers and requires less stringent experimental conditions.[26] ATRP or a combination of ATRP and other methods have been used to synthesize azobenzene-containing polymers and copolymers.[5,6,10,27–31] Zhao and coworkers[10,27,28] reported the preparation of a series of liquid-crystalline diblock or triblock copolymers with an azobenzene moiety in the side chain. Branched or hyperbranched azobenzene liquid-crystalline copolymers were prepared through a self-condensing ATRP copolymerization technique.[6,29] Xi et al.[30] reported the copolymerization of 4-[*N*-ethyl-(2-methacryloyloxyethylamino)-4′-nitro-azobenzene] and methyl methacrylate with poly (*p*-chloromethyl styrene) as a multicenter initiator by ATRP. Photoresponsive polymethacrylates containing bisazo chromophores were also prepared with ATRP by Lu et al.[31] The irradiation of these polymer films with a linearly polarized laser induced birefringence because of the reorientation of the biazo chromophores through trans–cis–trans isomerization cycles of double azo bonds. Iyoda et al.[5] synthesized well-defined poly{11-[4-(4-butylphenylazo)phenoxy]-undecyl methacrylate} containing an azobenzene mesogen via ATRP with 2-bromoisobutyrate as an

initiator and CuCl/1,1,4,7,10,10-hexamethyltriethyl-enetetramine (HMTETA) as the catalyst with a high initiation efficiency (>80%). In a previous article,[32] we reported the ATRP of methyl methacrylate with various initiators with monofunctional or difunctional azobenzenes. The structural effect of different ester-type initiators on the controllability of polymerization and the ultraviolet–visible (UV–vis) spectra of the obtained polymers were investigated. In recent years, most studies have been performed on donor–acceptor-substituted azobenzene, typically amino–nitro substituted azobenzene. It is well-known that the electronic spectrums of such groups have a strong absorption in the visible region. The π–π* and n-π* bands are practically superimposed; the light for photoactivation of the cis–trans isomerization will also photoactivate the trans–cis isomerization, which will significantly speed up the whole process. For simple azobenzene-containing polymers, less attention has been paid because the thermal cis–trans isomerization is relatively slow and because of the maximum absorbance shift toward higher energy (shorter wavelength) for the trans isomer. To our knowledge, no study on the surface-relief grating (SRG) properties of well-defined azo polymers without substituents on the azo group has been reported. This article presents the synthesis of polymers containing azobenzene groups without electron-donor and electron-acceptor substituents with monofunctional or difunctional azobenzene-based initiators. The azobenzene-based initiators afforded a well-controlled polymerization of the azobenzene monomer, [6-(4-phenylazo)phenoxy]hexylmethacrylate (PPHM). An efficient diffraction grating was inscribed on these novel polymer film surfaces under the irradiation of a linearly polarized Kr$^+$ laser beam (413.1 nm, 188 mW/cm^2) for the first time.

EXPERIMENTAL

Materials

Copper(I) chloride (CuCl; analytical reagent, Shanghai Zhenxin Chemical Reagent Factory, Shanghai, China) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with absolute ethanol, and dried *in vacuo*. 4-Hydroxyazobenzene (HZO) and 4,4'-dihydroxyzaobenzene (HZO$_2$) were synthesized according to the literature.[33,34] The analytic results follow:

HZO: Yield = 80%. Anal.: Calcd: C, 72.71%; H, 5.08%; N, 14.14%. Found: C, 72.39%; H, 5.18%; N, 14.00%. ^{1}H-NMR (CDCl$_3$, δ): 7.88 (d, 4H), 7.48 (m, 3H), 6.95 (d, 2H).

HZO$_2$: Yield = 20%. ^{1}H-NMR (DMSO-d$_6$, δ): 10.09 (br, 2H), 7.72 (d, 2H), 7.70 (d, 2H), 6.92 (d, 2H), 6.89 (d, 2H). ^{13}C-NMR (δ): 159.93d (2s), 145.25 (2s), 115.73 (4d).

Tetrahydrofuran (THF; analytically pure, Changshu Yangyuan Chemical Reagent Co., Ltd., Jiangsu Province, China) was dried over sodium 1 week before use. HMTETA (97%, Aldrich, Beijing, China), 4-phenylazo-phenylamine (chemically pure, from Shanghai Chemical Reagent Co., Ltd., Shanghai, China), 1-chloro-6-hydroxyhexane (95%, Acros, Beijing, China), and other reagents were used as received without further purification.

Synthesis of PPHM

The azobenzene monomer, PPHM, was synthesized according to a procedure that was similar to a published method.[35]

Yield = 66% Anal.: Calcd: C, 72.11%; H, 7.15%; N, 7.64%. Found: C, 72.22%; H, 7.17%; N, 7.61%. ^{1}H-NMR (CDCl$_3$, δ): 7.93–7.89 (m, 2H); 7.89–7.87 (d, 2H); 7.52–7.49 (m, 3H); 7.01–6.94 (m, 2H); 6.11 (s, 1H); 5.56 (s, 1H); 4.19–4.13 (m, 2H); 3.94, 3.93 (d, 2H); 1.96 (s, 1H); 1.78–1.25 (m, 8H). UV–vis [chloroform, maximum absorption wavelength (λ_{max}) (nm)]: 340 nm.

Synthesis of 2-bromo-2-methyl-propionic acid 6-(4-phenylazo-phenoxy)-hexyl ester (BPAHE)

5-(4-Phenylazo-phenoxy)-hexan-1-ol was synthesized with a procedure that was similar to that reported in the literature (yield = 85%).[36] The crude products were purified by recrystallization from ethanol and were then used to further reaction. Triethylamine (5.3 mL, 37.9 mmol) was added to a solution of 5-(4-phenylazo-phenoxy)-hexan-1-ol (7.5 g, 25.2 mmol) in dry THF (250 mL). The solution was stirred in a cryohydrate bath ($-10°$C), and 2-bromo-isobutyryl bromide (6.2 mL, 37.8 mmol) in dry THF (20 mL) was added dropwise over a period of 0.5 h under an argon atmosphere; the solution was then stirred at room temperature overnight. The solution was filtered, and the filtrate was washed with deionized water three times and then dried with anhydrous magnesium sulfate overnight. Finally, the solvent was removed *in vacuo*. The obtained crude product was purified by recrystallization three times from ethanol to give a pale yellow power (7.3 g).

Yield = 65%. Anal.: Calcd: C, 59.06%; H, 6.08%; N, 6.26%. Found: C, 60.3%; H, 6.27%; N, 6.4%. ^{1}H-NMR (CDCl$_3$, δ): 7.89–7.87 (d, 2H), 7.52–7.42 (m, 3H), 7.26–6.99 (m, 2H), 4.22–4.19 (m, 2H), 4.07–4.04 (m, 2H), 1.94 (s, 6H), 1.83–1.82 (m, 2H), 1.78–1.72 (m, 2H), 1.55–1.50 (m, 4H). UV–vis [chloroform, λ_{max} (nm)] = 325 nm.

Synthesis of 2-bromo-2-methyl-propionic acid 4-[4-(2-bromo-2-methyl-propionyloxy)-phenylazo]-phenyl ester (BPPAPE)

Triethylamine (5.9 mL, 42.1 mmol) was added to a solution of HZO$_2$ (3 g, 14 mmol) in dry THF
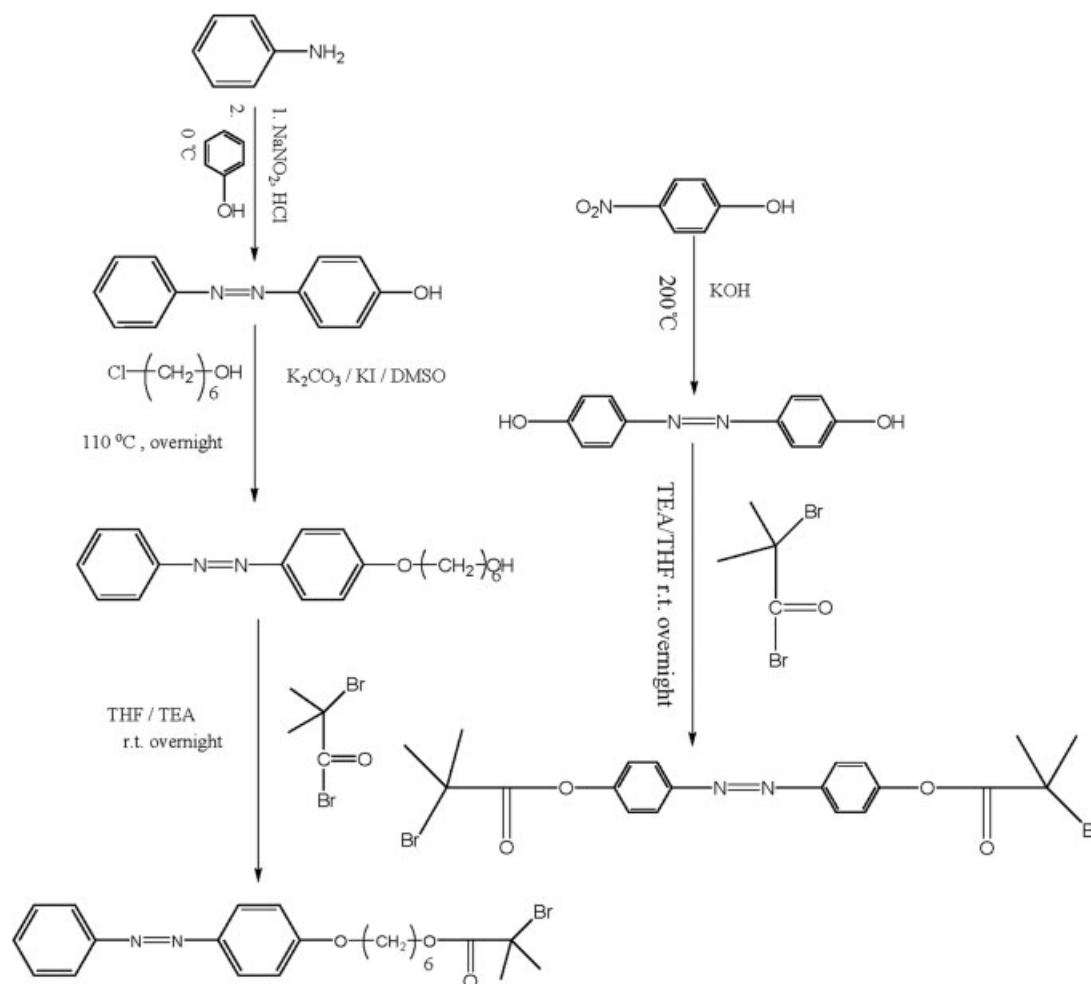
Scheme 1 Synthesis routes of the azo-based initiators.

(150 mL). The solution was stirred in a cryohydrate bath (−10°C), and 2-bromo-isobutyryl bromide (6.9 mL, 42.1 mmol) in dry THF (20 mL) was added dropwise over a period of 0.5 h under an argon atmosphere; the solution was then stirred at room temperature overnight. The solution was filtered, and the solvent was removed *in vacuo*. The crude product was dissolved in chloroform, washed with deionized water three times, and then dried with anhydrous magnesium sulfate overnight. Finally, the solvent was removed *in vacuo*. The obtained crude product was purified by recrystallization three times from ethyl acetate to give a pale yellow crystal.

Yield = 58%. Anal.: Calcd: C, 46.90%; H, 3.94%; N, 5.47%. Found: C, 46.94%; H, 4.35%; N, 5.60%. ^{1}H-NMR (CDCl$_3$, δ): 7.99–7.98 (d, 4H), 7.32–7.27 (m, 4H), 2.10–1.94 (m, 12H). UV–vis [chloroform, λ_{max} (nm)] = 345 nm.

General polymerization procedure

A dry glass tube was filled with CuCl (0.0067 g), HMTETA (18 μL), initiator (3.33 × 10^{-5} mol), anisole

(4 mL), and azo monomer (0.37 g). Then, it was degassed *in vacuo*, charged with argon (Ar) five times, sealed under Ar, and placed in an oil bath held by a thermostat at the desired temperature to polymerize. At timed intervals, the tube was immersed into cold water. Afterward, the tube was opened, and the contents were dissolved in THF. The solution was passed through a neutral Al$_2$O$_3$ column with THF as the eluent to remove the catalyst. Then, the solution was precipitated into a large amount of methanol. The reprecipitation process was carried out twice. Conversion of the monomer was determined by gravimetry.

Azo-homopolymer thin-film preparation

Suitable amounts of the polymer samples were dissolved in THF to obtain solutions with concentrations of about 0.1 g/mL. Thin-film samples of the homopolymers were prepared by spin-coating of the polymer solution in THF onto glass slides at 1500 rpm. The thickness of the film was controlled to be about 200 nm. After it was dried *in vacuo* for 24 h,
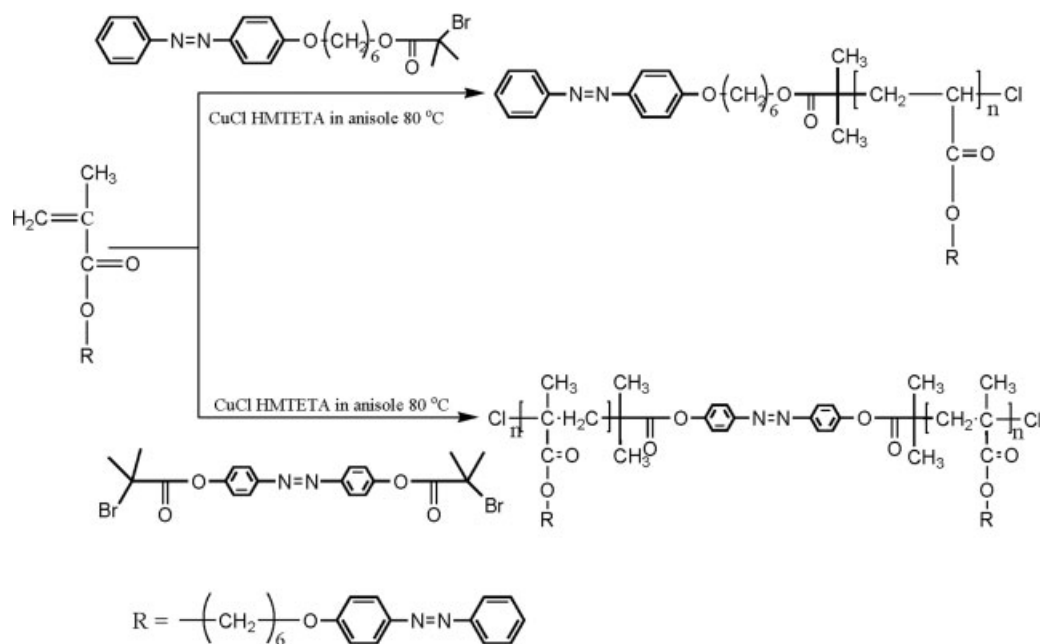
Scheme 2 Synthesis of linear poly(PPHM)s by ATRP with BPAHE and BPPAPE as initiators.

the films were stored in a desiccator for further study.

Characterization

Elemental analyses of C, H, and N, were measured by an EA1110 CHNO—S instrument (Carlo-Erba, Italy). The molecular weights and molecular weight distributions of the polymers were determined with a Waters 1515 gel permeation chromatograph (Milford, MA) equipped with a refractive-index detector with HR 1, HR 3, and HR 4 columns with a molecular weight range of 100–500,000 calibrated with poly (methyl methacrylate) standard samples. THF was used as the eluent at a flow rate of 1.0 mL/min operated at 30°C. ^{1}H-NMR and ^{13}C-NMR spectra of the polymers were recorded on a Varian 400-MHz NMR instrument (Palo Alto, CA) with CDCl$_3$ as a solvent and tetramethylsilane as the internal standard. The UV–vis absorption spectra of the polymers and initiator in chloroform solutions were determined on a Shimadzu RF540 spectrophotometer (Pekin, Japan). The experimental setup for SRG fabrication was similar to those reported before.[37] A linearly polarized Kr$^+$ laser beam (413.1 nm, 188 mW/cm^2) was used as the light source. SRGs were optically inscribed on the polymer films with p-polarized interfering laser beams. The surface images of the SRGs were probed by atomic force microscopy (NT-MDT SOLVER P47-PRO) (Hitachi, Japan). The diffraction efficiency of the gratings was monitored by measurement of the first-order diffracted-beam intensity of an unpolarized low-power diode laser beam (650 nm) in transmission mode.

RESULTS AND DISCUSSION

Two azobenzene-based initiators were synthesized by the condensation of phenols, alcohols with 2-bromo-isobutyryl bromide. The structure of the initiators and the synthetic procedures used in the preparation of the initiators are described in Schemes 1 and 2.

BPAHE and BPPAPE showed λ_{max} values at 320 and 350 nm, respectively, which was due to different conjugating lengths. PPHM was polymerized in anisole at 80°C with monofunctional and difunctional azo-based initiators along with CuCl/HMTETA. A
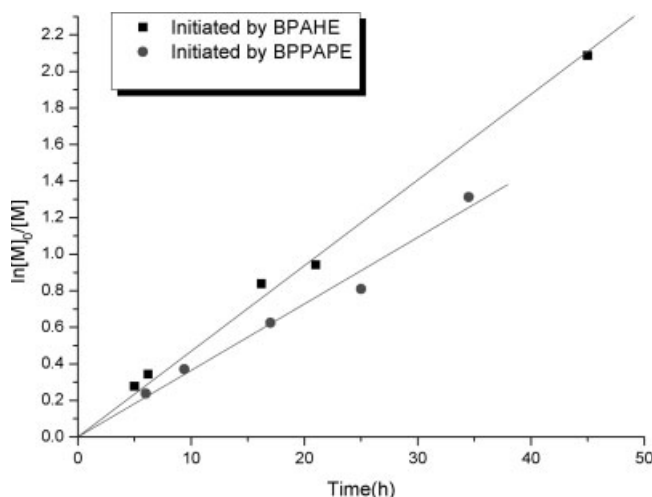

Figure 1 Kinetic plots for the polymerizations of PPHM with BPAHE and BPPAPE as initiators in anisole solution at 80°C: $[PPHM]_0/[Initiator]_0/[CuCl]_0/[HMTETA]_0 = 50:1:2:2$.
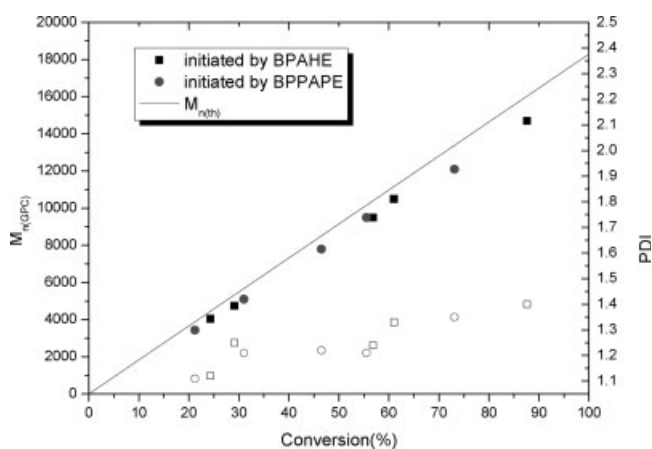
Figure 2 Evolution of $M_{n,GPC}$ and PDI with conversion for the polymerizations of PPHM with the azobenzene-based initiators BPAHE and BPPAPE in anisole solution at 80°C: $[PPHM]_0/[Initiator]_0/[CuCl]_0/[HMTETA]_0 = 50:1:2:2$.

Figure 3 GPC traces for poly(PPHM) obtained in anisole: $[PPHM]_0/[BPAHE]_0/[CuCl]_0/[HMTETA]_0 = 50:1:2:2$; reaction temperature = 80°C.

mixed-halogen (R—Br/CuCl)[38] catalytic system was used to improve the control level of the polymerization. The kinetic plots of $\ln([M]_0/[M])$ (where $[M]_0$ is the initial monomer concentration and $[M]$ is the monomer concentration at a given time) versus time are shown in Figure 1. The straight line through the original point indicated that the concentration of propagating radicals remained constant during the polymerization. The rate of polymerization initiated by BPPAPE was slightly slower than that initiated by BPAHE. The apparent polymerization rate constants determined from the slope of first-order kinetics plot were 1.3×10^{-5} s^{-1} for the BPAHE/CuCl/HMTETA system and 1.0×10^{-5} s^{-1} for the BPPAPE/CuCl/HMTETA system. In both of these two polymerization systems, the molecular weight of the polymer increased linearly with monomer conversion (Fig. 2), and the number-average molecular weight measured by gel permeation chromatography ($M_{n,GPC}$) matched the theoretical number-average molecular weight ($M_{n,th}$):

$$M_{n,th} = \text{Conversion} \times M_{AZOM} \times [AZOM]_0/[Initiator]_0 + MW_{initiator}$$

(1)

where $[AZOM]_0$ and $[Initiator]_0$ are the initial concentrations of the azo monomer and initiator, respectively, and M_{AZOM} and $MW_{initiator}$ are the molecular weights of the azo monomer and the initiator, respectively. This indicated that the polymerizations were well controlled in the cases of both azo-based initiators. Figure 2 also shows that the polydispersities (PDIs) of the polymer increased with increasing conversion and the PDIs were in the range
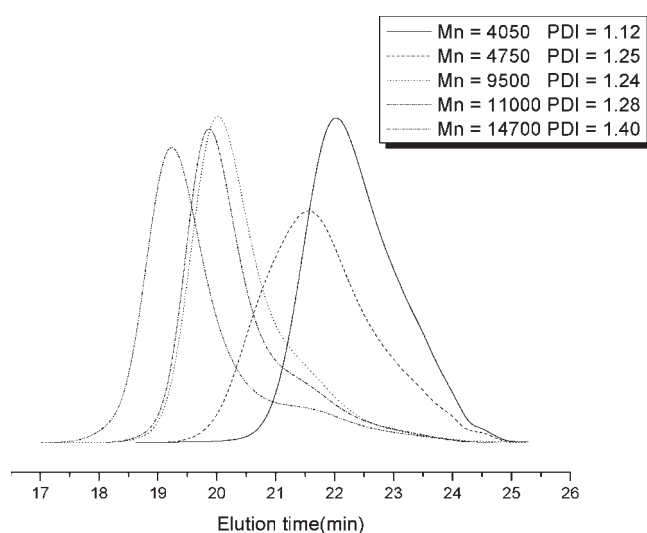
1.11–1.40. From the gel permeation chromatography (GPC) traces depicted in Figures 3 and 4, it is clear that the entire distribution shifted toward a higher molecular weight with increasing monomer conversion in both polymerization systems, which indicated that the polymerization was well-controlled with living characteristics. However, some GPC curves showed some tailing toward low molecular weight with increasing monomer conversion. Such a trend, accompanied by the increase in PDI with molecular weight, suggested that some termination reaction occurred at higher conversion.
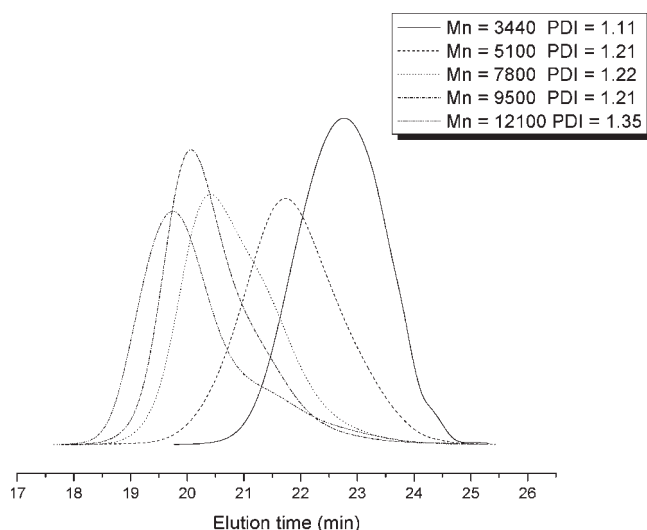

Figure 4 GPC traces for poly(PPHM) obtained in anisole: $[PPHM]_0/[BPPAPE]_0/[CuCl]_0/[HMTETA]_0 = 50:1:2:2$; reaction temperature = 80°C.
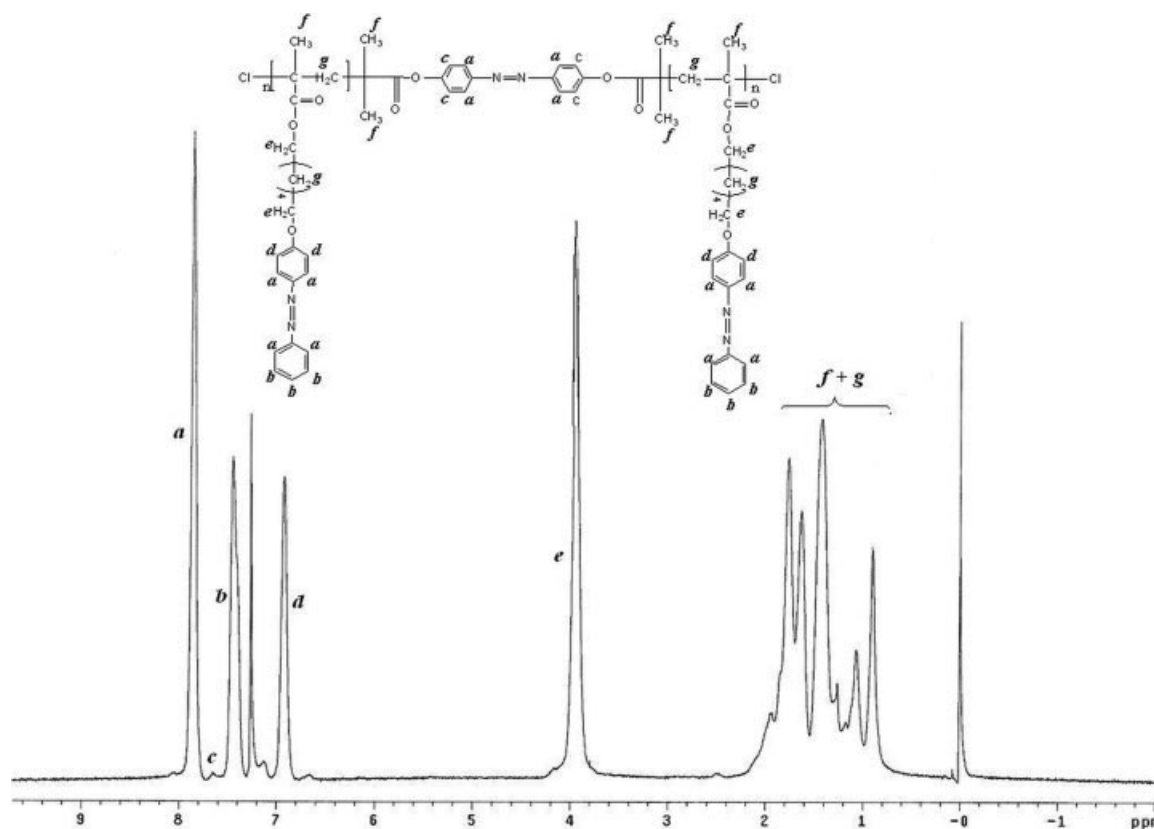
Figure 5 ^{1}H-NMR spectrum of a typical azobenzene-containing homopolymer in CDCl$_3$ solvent.

Figure 5 shows the typical ^{1}H-NMR spectrum of the polymers. The characteristic signals corresponding to the phenyl protons of the azo group were observed at 7.85 and 6.93 ppm [Fig. 5(a–d)]; the signal at 3.79 ppm was assigned to the methylene group of those —CH$_2$— adjacent to oxygen atoms in the side chain [Fig. 5(e)]. The peaks from 0.90–1.94 were attributed to the methyl group and methylene group in the main chain and methylene in the side groups except for those adjacent to oxygen atoms [Fig. 5(f + g)]. The ^{1}H-NMR analyses supported the successful incorporation of azobenzene chromophores in both the main chain and side chains of the polymer. Figures 6 and 7 show the UV–vis spectra of the monomer and corresponding polymer. As shown in Figures 6 and 7, both the monomer and corresponding polymer exhibited two strong absorption peaks. The first peak appeared in the shorter wavelength region (ca. 240–250 nm), which corresponded to the absorption by the biphenyl moiety,[39] and the second peak appeared the azobenzene characteristic intense π–π* transition in 340 nm. In addition, a much weaker n-π* transition was observed at 440 nm. The azo-containing polymers obtained by both monofunctional and difunctional azo-based initiators had the same λ$_{max}$. In addition, the intensity of UV absorptions of the polymers were stronger than those of the corresponding monomer in chloroform and increased with increasing molecular weights of polymers in all cases, which was due to the increasing content of the azo chromophores attached to polymeric side chains with the increasing molecular weights of the polymers.

Photoinduced SRGs

For azo polymers containing azo chromophores, the optical storage property is an important function that has been well studied.[1,3,25,40] To test the optical storage properties of this kind of polymer, the polymer film was used to prepare SRGs under the irradiation of a violet laser. As shown in Figure 8, a Kr$^+$ laser beam (413.1 nm) was split into two by means of a polarization beam splitter (PBS). With suitable wave plates, these two beams, which were orthogonally polarized, were two p-polarized or s-polarized beams and were used to produce the interference pattern on the polymer films. A relatively low light intensity (188 mW/cm^2) was used to write the gratings to prevent sample damage and other possible side effects caused by high-intensity laser irradiation. Although two circularly polarized interfering beams can produce SRGs more efficiently,[41] the p/p-polarization condition has also been frequently used to
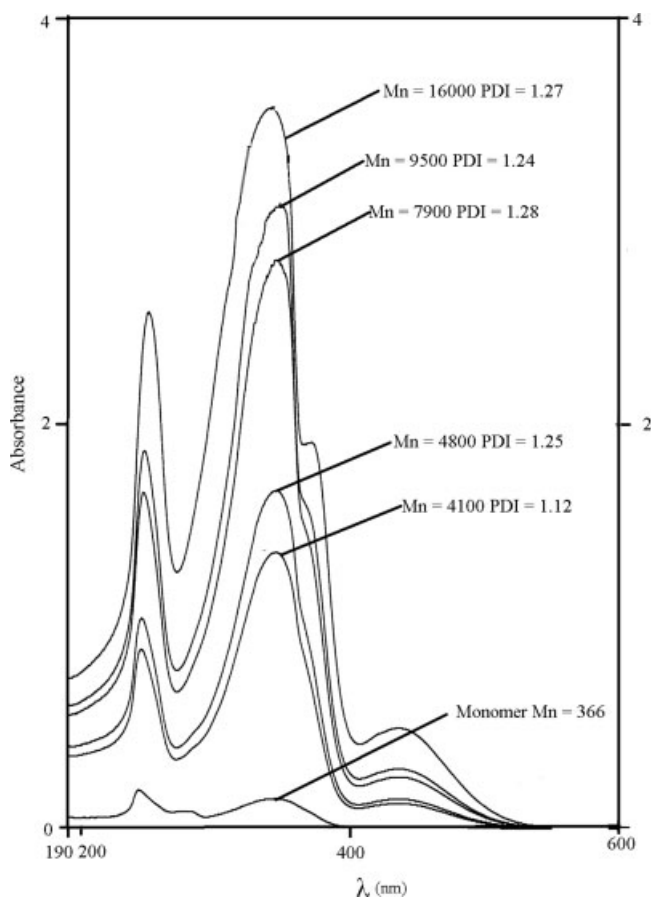
Figure 6 UV–vis spectra of the azo-containing polymers and corresponding azo monomer in chloroform solutions. The polymerization was initiated by BPAHE. The concentration for all solutions was 8×10^{-6} mol/L.
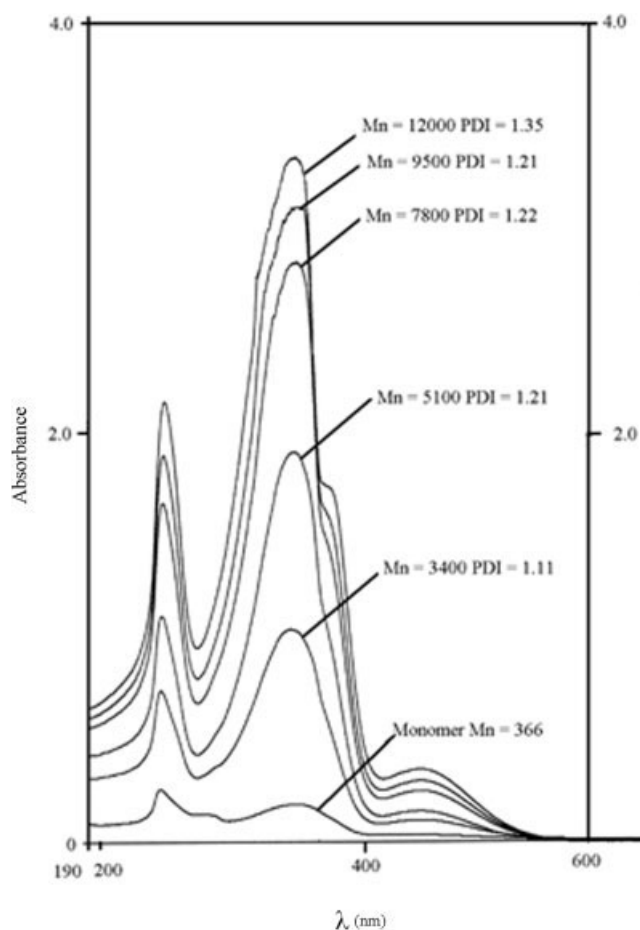

Figure 7 UV–vis spectra of the azo-containing polymers and corresponding azo monomer in chloroform solutions. The polymerization was initiated by BPPAPE. The concentration of all solutions was 8×10^{-6} mol/L. λ is the absorption wavelength.

fabricate good quality SRGs, and the result is more easily explained.[42] The SRGs formed on the poly[6-(4-phenylazophenoxy)hexylmethacrylate] [poly(PPHM)] film surface were probed with an atomic force microscope, as shown in Figures 9 and 10, which was written with a linearly polarized krypton laser for 10 min at a recording beam intensity of 188 mW/cm^2 at a wavelength of 413.1 nm. For this film, a typical grating spacing of 1000 nm and a depth of 80 nm were obtained with a linearly polarized krypton laser for 10 min of irradiation. The diffraction efficiency of the film was measured under two different polarization states of the writing beam. When the film was exposed to s-polarized beams for 1000 s, the diffraction efficiency was 0.02%, whereas a 2.7% diffraction efficiency was obtained within 10 min when the film was exposed to a p-polarized beam. The p-polarized light had no component of the electric field normal to the plane of the polymer film; therefore, it cycled more azo moieties through a trans–cis–trans cycle than the s-polarized light. A similar phenomena was also observed by Kim et al.[24]

In Figure 8, M is a mirror, and HWP is a half-wave plate. When the HWP was placed at position 1, the two recording beams were p-polarized; when it was placed at position 2, they were s-polarized. LD is a laser diode that emitted a 650-nm beam. D is a detector for the first-order diffracted beam intensity.
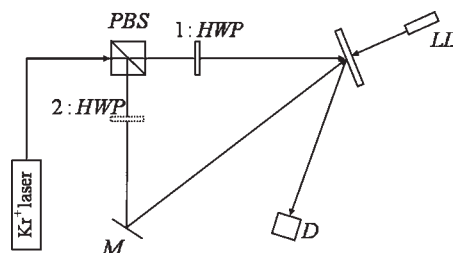

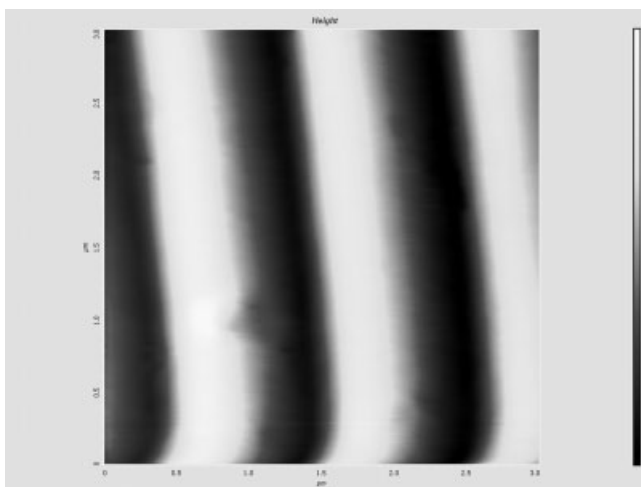**Figure 8** Experimental setup for the recording and detecting of SRGs.

Figure 9 Plane view of the SRGs formed on the poly (PPHM) film [number-average molecular weight (M_n) = 11,000, PDI = 1.27] inscribed on the polymer film with *p*-polarized light (413.1 nm).

CONCLUSIONS

Well-defined polymethacrylates containing azo chromophores were prepared via ATRP with monofunctional or difunctional azobenzene based initiators. The polymerizations with first-order kinetics were well controlled with the theoretical expected molecular weight and narrow molecular weight distributions in two initiation systems. The intensity of UV absorptions of the polymers were stronger than those of the corresponding monomer in chloroform and increased with increasing molecular weights of the polymers in all cases. SRGs with high efficient diffraction formed on the polymer film surface were obtained within 10 min of irradiation at a recording beam intensity of 188 mW/cm^2.
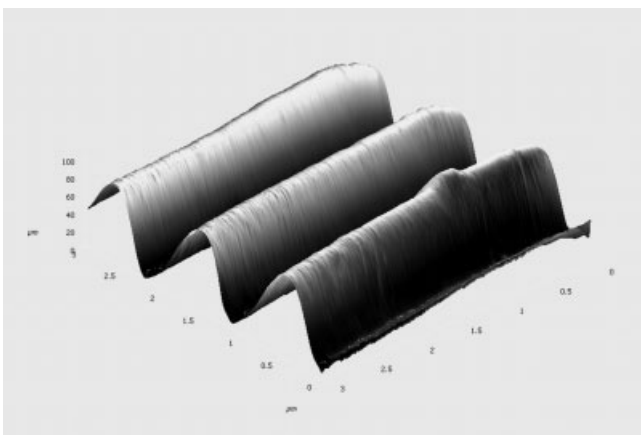

Figure 10 Atomic force microscopy images of the SRGs formed on the poly(PPHM) films.

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