

Photoresponses and pH Responses of Hydrogels Composed of Acrylamido Azobenzene and Acrylic Acid

Li Chen, Shi-Geng Li, Yi-Ping Zhao, Yu-Cui Wang, Qing-Wen Wang

Key Laboratory of Hollow Fiber Membrane Materials and Membrane Processes (Ministry of Education), School of Materials Science and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China

Received 9 July 2004; accepted 30 September 2004

DOI 10.1002/app.21675

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

ABSTRACT: A monomer with a side-chain azobenzide, acrylamido azobenzene (AAAB), was synthesized, and a series of poly(acrylic acid-co-acrylamido azobenzene) polymers and gels were prepared through the copolymerization of this AAAB monomer with acrylic acid. Their responses to pH and ultraviolet light were studied. These copolymers and gels showed good pH responses and photoresponses; these responses were caused by the ionization of carboxyl and the cis-trans isomerism of azobenzide, respectively. The

molecular structures of the copolymers and gels were also studied with X-ray diffraction, and the results showed that the copolymers with a certain amount of AAAB could form crystalline structures. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2163–2167, 2005

Key words: copolymerization; hydrogels; stimuli-sensitive polymers

INTRODUCTION

Phase transitions and critical phenomena in polymer gels have been attracted much attention because of their scientific interest and technological importance. Polymer gels undergo a discrete and reversible volume phase transition upon changes in their environmental conditions, including the temperature, solvent composition, pH, and electric field.^{1–6} These findings have already opened up a wide variety of possible applications of gels as sensors, actuators, switches, display units, artificial muscles, and controlled delivery systems. However, the kinetics of these volume phase transitions induced by the temperature, the pH, or an electric field are usually limited by thermal diffusion or ion diffusion. In contrast to these variables, the imposition of light can be performed instantly. Therefore, it is clearly desirable for the phase transition of a gel to be controllable with light.

Azobenzene and its derivatives are interesting because of their environment stability, easy processability, and photosensitive behavior.^{7–11} Azobenzene-containing polymers, which are macromolecules with azobenzene groups in the main or side chain, can be

applied to optical switches, optical data recording, and optical information storage.

In this study, copolymers and hydrogels were synthesized through the copolymerization of acrylamido azobenzene (AAAB), which contained a photoreactive azobenzene chromophore as a photosensitive material, with the soluble monomer acrylic acid (AA), and the pH-responsive and photoresponsive behaviors and the molecular structures were investigated.

EXPERIMENTAL

Materials

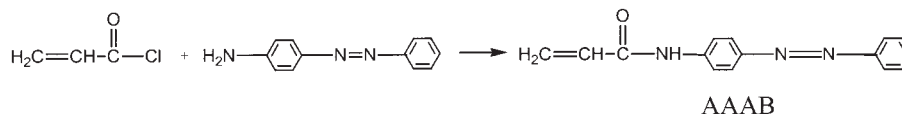
AA (Tianjin Chemical Reagents Co., Tianjin, China) was distilled *in vacuo* before it was used. α,α' -Azobisisobutyronitrile (AIBN; Shanghai Shisihewei Chemical Co., Ltd., Shanghai, China), used as a radical initiator, and *N,N'*-methylenebisacrylamide (MBAA; Tianjin Chemical Reagents), used as a crosslinking agent, were recrystallized from ethanol. All other reagents, including acryloyl chloride, *p*-aminoazobenzene, triethylamine, benzene, hydroquinone, and tetrahydrofuran (THF), were analytical-grade and were made in China; they were used as received without further purification.

Measurements

IR spectra were recorded on a Bruker microsampling IR spectrometer (Bruker, Germany) from 4000 to 500 cm^{-1} . The samples were mixed with KBr and pressed to produce films. ¹H-NMR measurements were con-

Correspondence to: L. Chen (chen_s62@hotmail.com).

Contract grant sponsor: National Natural Science Foundation of China (through the research project "Intelligent Hydrogel-Based Micromachine and Its Applications in Bio-separation").



Scheme 1

ducted at room temperature with dimethyl sulfoxide (DMSO- d_6) as a solvent (Unity Plus 400 NMR, Varian, United States).

Differential scanning calorimetry (DSC7, Perkin-Elmer) was performed at a scanning ratio of 10 K \cdot min $^{-1}$ from 20 to 300°C in nitrogen.

Electronic spectra were obtained with a model 2401PC ultraviolet-visible spectrophotometer (Shimadzu, Kyoto, Japan). Ultraviolet irradiation was performed with a 60-W ultraviolet lamp with a wavelength of approximately 254 nm at room temperature. The distance between the ultraviolet lamp and the sample cell was 15 cm. The absorption spectra were recorded in solutions of the monomer and copolymers before and after irradiation.

Wide-angle X-ray diffraction (WAXD) patterns were taken with an imaging plate with a flat-plate camera mounted on a Shimadzu XD-610 X-ray generator (Rigaku, Japan) emitting Ni-filtered Cu K α radiation (40 kV and 40 mA) in transmission geometry. Small-angle X-ray diffraction (SAXD) patterns were recorded on a Rigaku RINT-2000 X-ray diffractometer (Rigaku, Japan) (40 kV and 200 mA) in transmission geometry.

Synthesis of AAAB

An acrylate monomer containing azobenzene groups (AAAB) was synthesized by a method described elsewhere.¹² In brief, *p*-aminodiphenylazobenzene (10%, g/mL), triethylamine (7%, mL/mL), and a little hydroquinone were dissolved in benzene, and a small amount of acryloyl chloride was then added to the mixture solution. The reaction mixture was stirred for 3 h at 60°C. After that, the solution was cooled, the precipitate was collected by filtration and drying, and then the products were recrystallized from ethanol. The yield was 77.8%, and the melting point was 125°C. The synthesis of AAAB is shown in Scheme 1.

The structure of AAAB was determined by $^1\text{H-NMR}$ and IR. The $^1\text{H-NMR}$ (DMSO- d_6 , ppm, δ) signals [6.4–6.8 (3H, CH $_2$ =CH) and 7.4–8.0 (9H, C $_6$ H $_5$, C $_6$ H $_4$)] and IR (KBr, cm $^{-1}$) signals (3382.6 and 1758.3 cm $^{-1}$) were indicative of the NH $_2$ group and COCl group, respectively. These two bands disappeared, and a strong new CONH band at 1630–1680 cm $^{-1}$ appeared in the IR spectra of the products; this suggested the structure of the AAAB monomer.

Preparation of the copolymers and gels

A series of poly(acrylic acid-*co*-acrylamido azobenzene) (PAA-AAAB) copolymers with various AAAB

concentrations (f) were prepared by the free-radical copolymerization of AA and AAAB in THF with AIBN as the initiator. The total monomer concentration was kept at 2.0 mol/L. The polymerization was carried out at 70°C for 24 h under nitrogen. The obtained solution was added dropwise into petroleum ether with stirring. The precipitate was collected by filtration and washed with petroleum ether twice.

PAA-AAAB gels were prepared by the same method as the linear copolymer in the presence of MBAA in ethanol. The obtained gel was immersed in a large amount of ethanol for 3 days and then in water for 1 week for the removal of unreacted substances. The degree of swelling of the gel was calculated as a weight ratio of the water-swollen gel to its dry state.

RESULTS AND DISCUSSION

Characterization of the copolymers and hydrogels

Copolymers with azobenzene group AAAB and AA moieties, that is, PAA-AAAB with f values of 0.01, 0.05, and 0.10, were prepared by radical copolymerization. They were pale or dark orange powders. They were soluble in THF and dissolved partly in water. IR spectra showed a band around 3000 cm $^{-1}$ from the AA group and a band around 1680 cm $^{-1}$ from the AAAB group. The absorptions of C=C at 1600 cm $^{-1}$ disappeared in comparison with the spectrum of the AAAB monomer. For the $^1\text{H-NMR}$ measurement (DMSO- d_6), the peak at 12.3 ppm could be assigned to OH from AA, the peaks at 7.8 and 7.5 ppm were assigned to C $_6$ H $_5$ and C $_6$ H $_4$ from AAAB, and the integrated signals of CH $_2$ =CH from AA and AAAB disappeared.

PAA-AAAB gels with f values of 0.05 and 0.1 were also prepared by radical copolymerization with MBAA as a crosslinking agent. The obtained gels were dark red and swelled in water. The PAA-AAAB gels showed relatively high equilibrated degrees of swelling of 54 and 43 for a degree of crosslinkage (the molar ratio of the crosslinking agent to the polymer) of 10 mol % with $f = 0.05$ and $f = 0.1$, respectively. These gels exhibited viscoelastic behavior, like most hydrogels, and the shear modulus of the gels was approximately 10 6 Pa.

Photoresponses of the copolymers

The absorption spectra were recorded before and after ultraviolet irradiation for 5, 10, and 20 min. The results

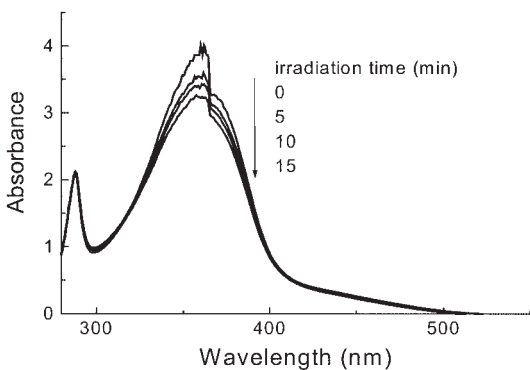


Figure 1 Electronic spectra of an AAAB solution in THF after irradiation (monomer concentration = 1×10^{-4} mol/L, temperature = 25°C).

are shown in Figure 1. AAAB showed one absorption peak at $\lambda_{\text{max}} = 350$ nm, which was assigned to be a very intensive $\pi-\pi^*$ transition of the azobenzene chromophore. Similar spectral peaks were observed when they were exposed to 254-nm light. However, with the irradiation time, the intensity of the absorption began to decrease, and this suggested that the azobenzene chromophore underwent trans (*E*) to cis (*Z*) photoisomerization and that the trans units had greater absorbance than the cis one.

Furthermore, we studied the photoresponsiveness of the PAA-AAAB copolymers. As shown in Figure 2, all the copolymers showed an absorption peak at $\lambda_{\text{max}} = 350$ nm, just as the AAAB monomer did, and the intensity of the absorption decreased with increasing irradiation time. The peak increased at 350 nm with increasing *f*. This result suggested that these copolymers showed photoresponses similar to those of the AAAB monomer because of a trans-cis photoisomerization of the azobenzene chromophore, and *f* played an important role in the photoresponses of the PAA-AAAB copolymers.

pH responses of the copolymers

Aqueous solutions of PAA-AAAB (pHs 3, 5, 7, 9, and 12) were prepared. The 0.1M NaCl solution was used in all cases to keep the ionic strength of all the solutions constant. Figure 3 shows electronic absorption spectra of the PAA-AAAB copolymers with various *f* values in various pH solutions. All the copolymers showed two absorption peaks at $\lambda_{\text{max}} = 350$ nm and $\lambda_{\text{max}} = 430$ nm in various pH regions, and these could be attributed to the $\pi-\pi^*$ and $n-\pi^*$ transitions of the AAAB group, respectively. The intensity of the absorption peaks increased and a redshift of the absorption maximum was observed for every polymer when the pH increased. This redshift was ascribed to an enhanced effective electronic conjugation length of the polymer main chain associated with a conformational change from the aggregated state to the extended state due to the electrostatic repulsion of the ionized carboxylates in the high-pH regions.

Volume phase transitions of the gels

Volume phase transitions of PAA-AAAB gels with *f* values of 0.05 and 0.1 were investigated in response to the pH and light. When PAA-AAAB gels ($5 \times 5 \times 3$ mm) were immersed in aqueous solutions of various pHs, they swelled in high-pH solutions and contracted in low-pH solutions (a 0.1M NaCl solution was used in all cases). Figure 4 shows the pH dependence of the degree of swelling for PAA-AAAB gels with *f* values of 0.05 and 0.1 in pH solutions. The degree of swelling abruptly increased in the pH region of 4–8 and then became saturated for all the gels. The pH-induced increase in the degree of swelling was due to a conformational transition from the aggregated state to an extended state by electrostatic repulsion among the dissociated carboxylic groups in the network due to the presence of AA groups. The minimum pH value at

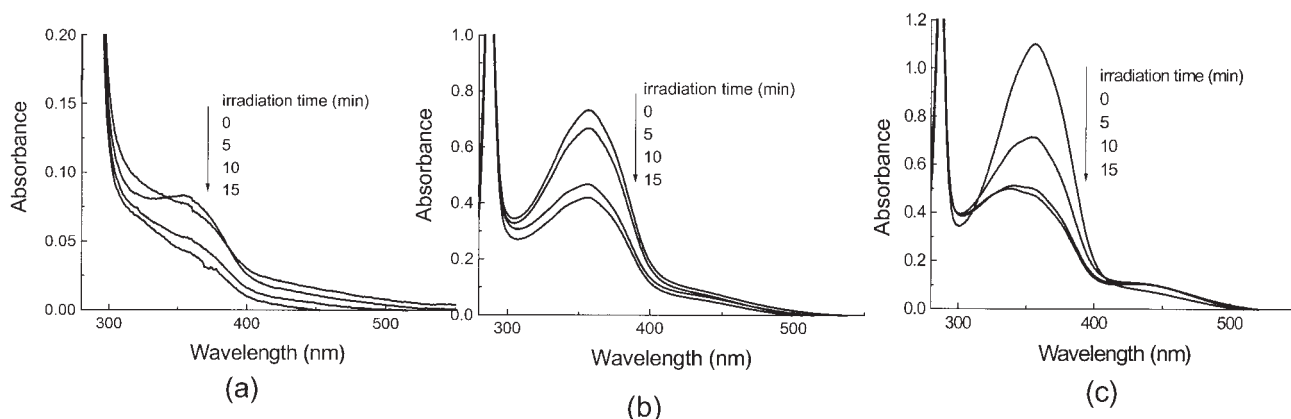


Figure 2 Electronic spectra of 1×10^{-4} mol/L PAA-AAAB copolymers in THF after irradiation (temperature = 25°C): (a) *f* = 0.01, (b) *f* = 0.05, and (c) *f* = 0.10.

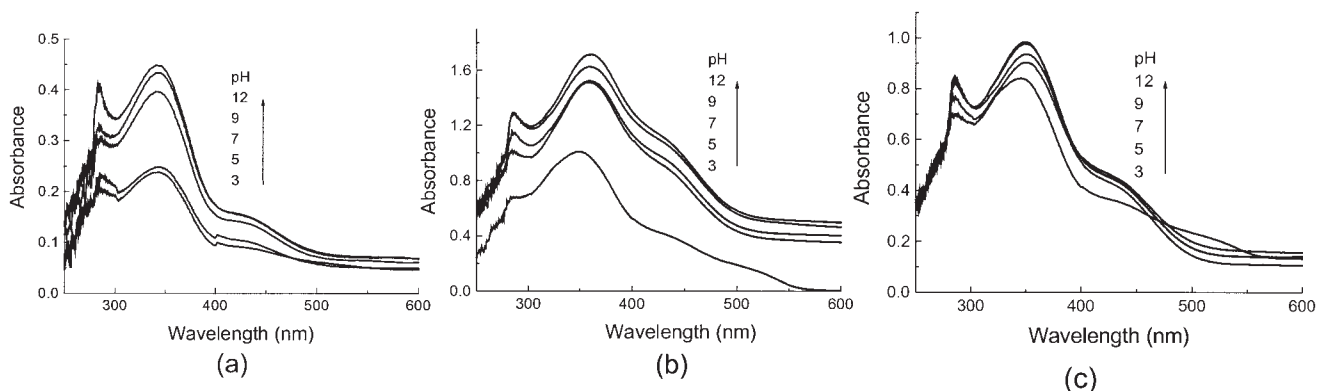


Figure 3 Electronic spectra of 8×10^{-3} mol/L PAA-AAAB solutions with changes in the pH (temperature = 25°C): (a) $f = 0.01$, (b) $f = 0.05$, and (c) $f = 0.10$.

which the swelling started increased when f increased. This indicated that the dissociations of the PAA-AAAB gels were suppressed, presumably by the incorporation of the hydrophobic AAAB unit in the low-pH region.

The PAA-AAAB gels shrank when they were exposed to ultraviolet irradiation. The volume changes in the gels were measured as a function of the ultraviolet irradiation time. The contraction ratio of the gel was defined as the ratio of the volume of the gel after irradiation to its volume before irradiation. Figure 5 shows the relationship between the contraction ratio and the irradiation time. There was a large contraction of the gels as the irradiation time increased, and as expected, the greater the AAAB concentration was, the faster the gel contraction was. The reduction of the contraction ratio was due to a conformational transition from trans isomerization of the azobenzene units to cis isomerization. This phenomenon demonstrated that the PAA-AAAB gels had a sensitive response to ultraviolet light. Because such light is readily available, safe, and clean and is easily manipulated for changing the gel volume in contrast to other parameters, photosensitive gels are technologically important

for developing various applications, not only in engineering but also in biochemical fields.

Molecular structure

To study the molecular structure of PAA-AAAB samples with various f values, we performed a WAXD study. Figure 6(a) shows the WAXD pattern of the AAAB monomer. There are several diffraction rings, which show the good crystalline structure of the AAAB monomer. The WAXD patterns of the copolymers with $f = 0.1$ and $f = 0.05$ also show clear crystalline peaks with a d -spacing of 0.49 nm, as shown in Figure 6(b,c). This diffraction can be attributed to the side-by-side stacking of azobenzene aligned perpendicularly to the main chain. This result suggests that the copolymers with f values of 0.05 and 0.1 formed the side-by-side stacking of azobenzene pendant groups with a d -spacing of 0.49 nm. The WAXD pattern of the copolymer with $f = 0.01$ shows only the halo ring, and this indicates that it was amorphous [Fig. 6(d)].

We also performed an SAXD analysis. The AAAB monomer and PAA-AAAB copolymers showed no

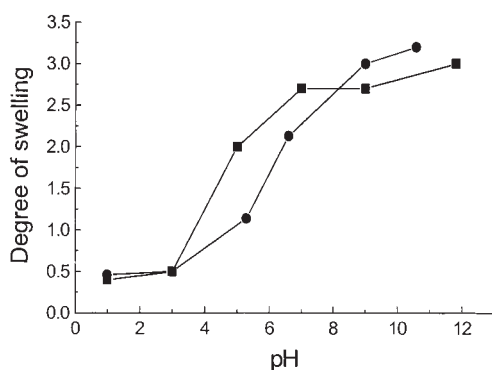


Figure 4 pH dependence of the degree of swelling for PAA-AAAB gels in pH solutions at 25°C: (■) $f = 0.05$ and (●) $f = 0.1$.

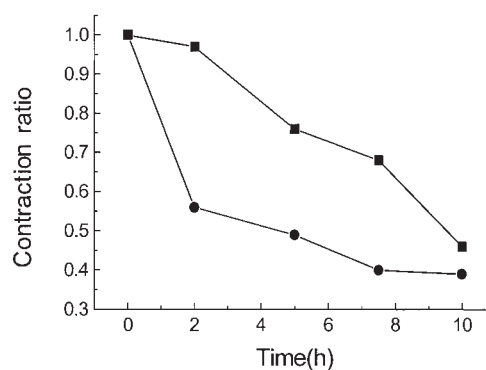


Figure 5 Relationship between the contraction ratio of PAA-AAAB gels and the irradiation time: (■) $f = 0.05$ and (●) $f = 0.1$. The gels were 10 mm \times 10 mm \times 3 mm.

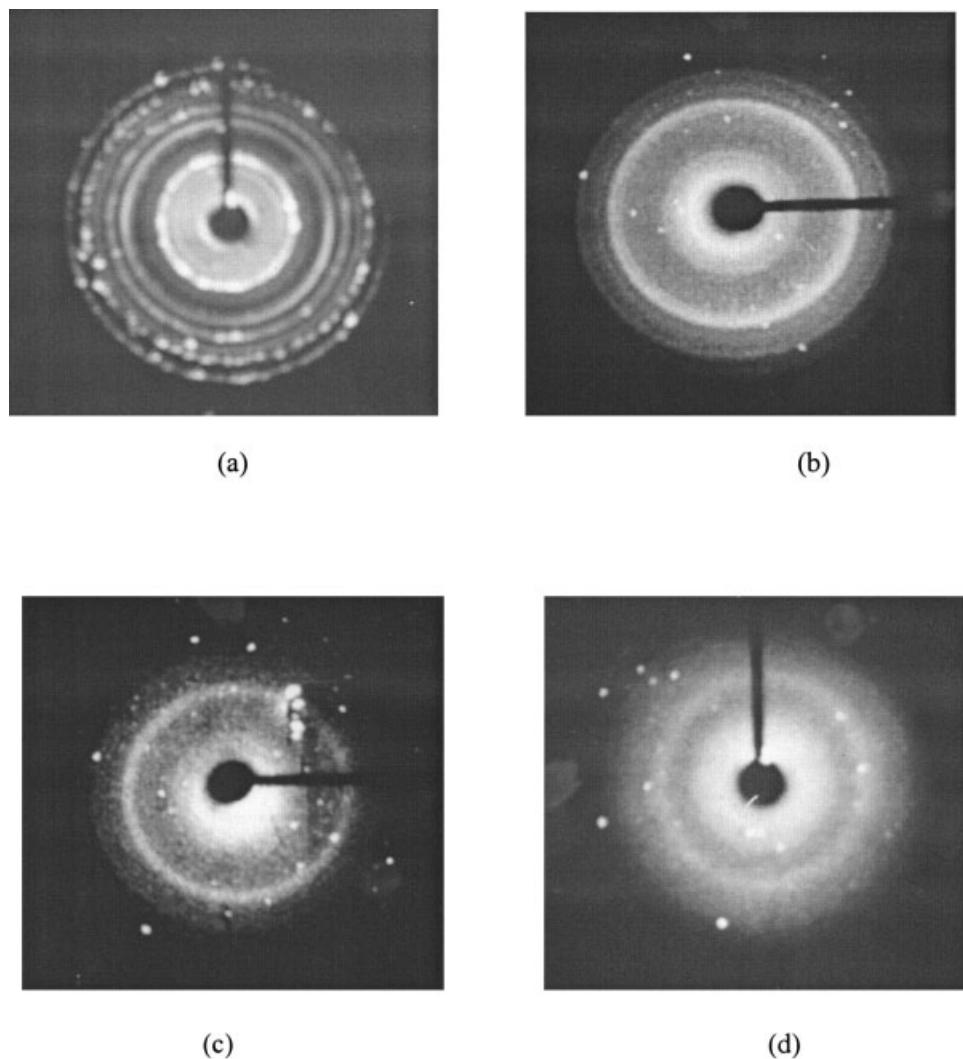


Figure 6 X-ray diffraction images of the AAAB monomer and PAA-AAAB copolymers: (a) AAAB monomer, (b) PAA-AAAB with $f = 0.1$, (c) PAA-AAAB with $f = 0.05$, and (d) PAA-AAAB with $f = 0.01$.

distinct diffraction patterns, regardless of f , and this indicated the absence of the particular structure with long-range periodicity.

The molecular structure of the PAA-AAAB gels was also studied with WAXD and SAXD analysis, and they showed neither short-range nor long-range order.

CONCLUSIONS

Water-soluble copolymers and their hydrogels containing a photoreactive azobenzene chromophore were synthesized.

The PAA-AAAB copolymers and gels showed good pH responsiveness and photore sponsiveness because of the ionization of carboxyl and the *cis*-*trans* isomerism of azobenzide, respectively. The PAA-AAAB gels shrank as the irradiation time increased.

This research was supported by the Research Project 'Intelligent Hydrogel Based Micromachine and its Applications in

Bioseparation' from the National Nature Science Foundation of China.

References

- Hirokawa, Y.; Tanaka, T. *J Chem Phys* 1984, 81, 6379.
- Siegel, R. A.; Firestone, B. A. *Macromolecules* 1988, 21, 3254.
- Osada, Y. *Adv Polym Sci* 1987, 82, 1.
- Osada, Y.; Gong, J. P. *Prog Polym Sci* 1993, 18, 187.
- Osada, Y.; Ross-Murphy, S. B. *Sci Am* 1993, 268, 82.
- Chen, L.; Kim, B. S.; Nishino, M.; Gong, J. P.; Osada, Y. *Macromolecules* 2000, 33, 1232.
- Ali, T.; Bernd, T. *Macromol Rapid Commun* 1998, 19, 591.
- Ali, P.; Bibi, F. M.; Ali, A. E.; Mohammad, J. Z.-M. *Eur Polym J* 2001, 37, 2111.
- Cheng, H.; Tuo, X. L.; Gao, W. W. *Acta Polym Sinica* 2002, 1, 96.
- Liu, X. H.; Wang, X. G.; Liu, D. S. *J Tsinghua Univ Sci Technol* 2002, 42, 622.
- Kurihara, S.; Sakamoto, A.; Yoneyama, D.; Nonaka, T. *Macromolecules* 1999, 32, 6493.
- Shi, X. Y.; Sun, C. M.; Wu, S. K. *Photograph Sci Photochem* 1999, 17, 38.