

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Synthesis and Characterization of Polymers Containing Azobenzene Chromophoric Group by ATRP

Wenjian Xu^a; Xiulin Zhu^a; Zhenping Cheng^a; Jian Zhu^a

^a School of Chemistry and Chemical Engineering, Suzhou University, Suzhou, P.R. China

To cite this Article Xu, Wenjian , Zhu, Xiulin , Cheng, Zhenping and Zhu, Jian(2006) 'Synthesis and Characterization of Polymers Containing Azobenzene Chromophoric Group by ATRP', Journal of Macromolecular Science, Part A, 43: 2, 393 – 403

To link to this Article: DOI: 10.1080/10601320500437318

URL: <http://dx.doi.org/10.1080/10601320500437318>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis and Characterization of Polymers Containing Azobenzene Chromophoric Group by ATRP

WENJIAN XU, XIULIN ZHU, ZHENPING CHENG,
AND JIAN ZHU

School of Chemistry and Chemical Engineering, Suzhou University, Suzhou,
P. R. China

*The 4-(4-phenylazo-phenylazo)-phenyl 2-bromopropionate (PPBP) was used as an initiator for atom transfer radical polymerization of methyl methacrylate (MMA) and styrene (St) in the presence of CuCl/N,N,N,N,N''-pentamethyldiethylenetriamine (PMDETA) at 90°C. The results showed that the polymerizations of MMA in different solvents were well controlled with a linear increase of molecular weights with conversion and relatively low polydispersities. However, the polymerization rate of St was much slower and polydispersity was relatively greater than that of MMA. Azobenzene end-capped polymers with predetermined molecular weights and low polydispersities (PDI < 1.3) were obtained and characterized by ¹H NMR and UV-Vis spectroscopy. In addition, copolymer of PMMA-*b*-PSt functionalized with azobenzene chromophoric group at the chain end of polymer was prepared via a chain-extension process.*

Keywords azobenzene, UV-Vis, ATRP

Introduction

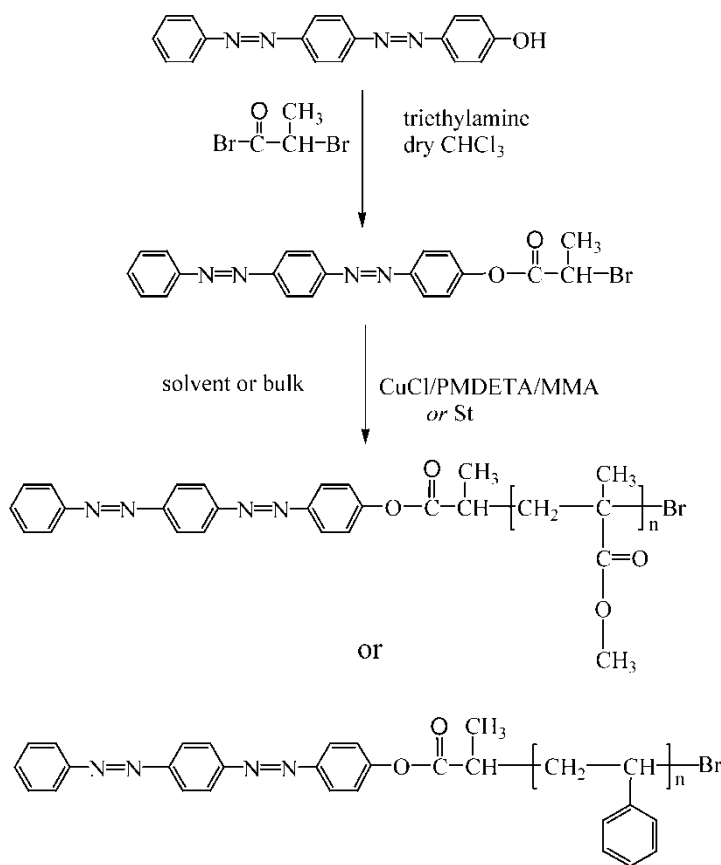
Polymers containing the appropriate chromophoric group have been prepared and investigated by many authors due to their potential use as photoresist material, semiconductors and fluorescent probes (1–4). Various methods have been used to attach the chromophoric group to polymers. Conventional free radical polymerization is usually used for the synthesis of polymer since it is easy to perform, but the structures of polymers obtained in this way are ill-defined. Anionic polymerization has been used to synthesize well-defined end-functional polymers with predetermined molecular weights and low polydispersities. However, very stringent reaction conditions are needed and the choice of monomers is quite limited. Living/controlled free radical polymerizations, such as nitroxide-mediated polymerization (NMP) (5, 6), atom transfer radical polymerization (ATRP) (7, 8), and reversible addition fragmentation chain transfer (RAFT) (9, 10), have recently attracted considerable attention as very useful methods for the synthesis of

Received December 2004; Accepted June 2005.

Address correspondence to Xiulin Zhu, School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, P. R. China. Tel.: 86-512-65111258; Fax: 86-512-65112796; E-mail: xlzhu@suda.edu.cn

chain-end functional polymers with smaller polydispersity and controlled molecular structure. Hawker and Zhu et al. (11–13) introduced chromophore units into the structure of alkoxyamine-based unimolecular initiator or TEMPO-based derivatives for NMP, but their results showed that it was difficult to achieve high end-group purity. Pekcan and Yagci (14) used 1-pyrenylmethyl 2-bromopropanoate as an initiator for ATRP to synthesize well-defined pyrene end-capped polystyrene. Winnik (15) also reported the synthesis of polyisoprene-polystyrene block copolymers containing a fluorescent dye molecule at the junction via ATRP and anionic polymerization. Similar work was also reported by Zhang (3).

Percec (16) first reported the ATRP initiated with sulfonyl chloride bearing an azobenzene group, satisfactory results were obtained when MMA was initiated by it in the presence of CuCl/bpy, with smaller polydispersity and controlled molecular weights. Recently, our group has reported different structural azobenzene initiator of ATRP (17), in this work, an azobenzene chromophoric group was introduced into 4-(4-phenylazo-phenylazo)-phenyl 2-bromopropionate (PPBP) as an initiator for the ATRP of methyl methacrylate and styrene in the presence of CuCl/PMDETA. Better results were found when PPBP was used as an initiator for ATRP of MMA, smaller polydispersities (most values were less than 1.2) and faster polymerization rate were achieved. The polymers end-capped by an azobenzene structure (Scheme 1) were obtained.



Scheme 1. Synthetic routes for azobenzene-ended polymers from 4-(4-phenylazo-phenylazo)-phenol.

Experimental

Materials

Styrene and methyl methacrylate (CP, Shanghai Chemical Reagent Co., Ltd.) were purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with deionized water and dried with sodium sulfate anhydrous overnight, then finally distilled under vacuum prior to polymerization. N, N-dimethylformamide (AR, Shanghai Chemical Reagent Co., LTD.) was distilled under vacuum. CuCl (CP, Shanghai Chemical Reagent Co., LTD.) was dissolved in hydrochloric acid, precipitated into a large amount of water, and then dried under vacuum.

N,N,N',N''-pentamethyldiethylenetriamine (PMDETA) (CP, Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4Å molecular sieve and distilled under vacuum. 4-(4-phenylazo-phenylazo)-phenol was commercially available and refined by recrystallization from alcohol twice prior to use. 2-bromo-propionyl bromide (purity > 98%) was commercially available without any purification. All other reagents used in this study were of analytic reagents.

Synthesis of PPBP

A solution of 4-(4-phenylazo-phenylazo)-phenol (5 g, 0.02 mol) and triethylamine (2.5 ml) in dry CHCl₃ (200 ml) was dropped in a solution of 2-bromo-propionyl bromide (4 g, 0.0185 mol) in dry CHCl₃ (25 ml) at 0°C. The resulting solution was allowed to stir overnight. The reaction mixture was transferred to a round flask and most of the solvent was removed by rotary evaporation. The residual solid was refined by recrystallization from ethanol twice. A yellow solid was obtained with a yield of 62.9%, 5.5 g. ¹H-NMR (CDCl₃, 400 MHz): δ 1.98–2.00 (t, 3H, CH₃), 4.61–4.67 (dd, 1H, CH-CH₃), 7.2–8.1 (m, 13H H-Ar). Anal. Calcd: %: C, 57.67; H, 3.89; N, 12.81; Found %: C, 57.81; H, 3.98; N, 12.96.

General Procedure of Polymerization

A series of polymerizations of styrene and MMA using PPBP as an initiator in conjunction with CuCl/PMDETA were performed. A typical polymerization procedure was as follows: MMA (3 ml, 282 mmol) was added to a dry tube containing the mixture of CuCl (14 mg, 0.14 mmol) and PMDETA (88 mg, 0.42 mmol), and then PPBP (56 mg, 0.14 mmol) was added. It was degassed under vacuum and charged with nitrogen three times, and sealed under vacuum, and then placed in an oil bath held by a thermostat at the desired temperature for polymerization. After a desired period of time, the tube was cooled with cold water to stop the polymerization. Afterwards, the tube was opened and the contents were dissolved in THF, which were precipitated in a large amount of methanol. The obtained polymer was dried at 50°C until constant weight. The monomer conversion of the polymerization was determined gravimetrically.

Characterizations

The molecular weights and molecular weight distributions of the polymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with refractive index detector. HR 1, HR 3, and HR 4 column were used with molecular weight

ranging from 100–500,000, calibrated with poly(methyl methacrylate) or polystyrene standard samples. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30°C . $^1\text{H-NMR}$ spectra of the PMMA were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument using CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard.

Results and Discussion

ATRP of MMA and StU using PPBP as Initiator

First, the bulk and solution polymerizations of MMA initiated by PPBP in the presence of $\text{CuCl}/\text{PMDETA}$ were carried out. As can be seen from Figure 1, the results of polymerizations showed that PPBP was an effective initiator for the polymerizations of MMA, and the rate of polymerization in bulk was faster than that in solvent. Compared to anisole and toluene, DMF was a poor solvent for this process as a long induction period and a slower polymerization rate. Pascual and coworker (18) found that the DMF to monomer ratio had an important effect on polymerization, M_w/M_n was up to 1.77 when DMF (25% v/v) was used because of a possible competitive complexation or ligand exchange of the copper species by the DMF.

Figure 2 also showed that the molecular weights increased with monomer conversion linearly, and the polydispersities of polymer were significantly lower (below 1.2) even when the monomer conversion was more than 90% in bulk and solution polymerization except for that in DMF. In bulk, anisole and toluene, it was also found that the

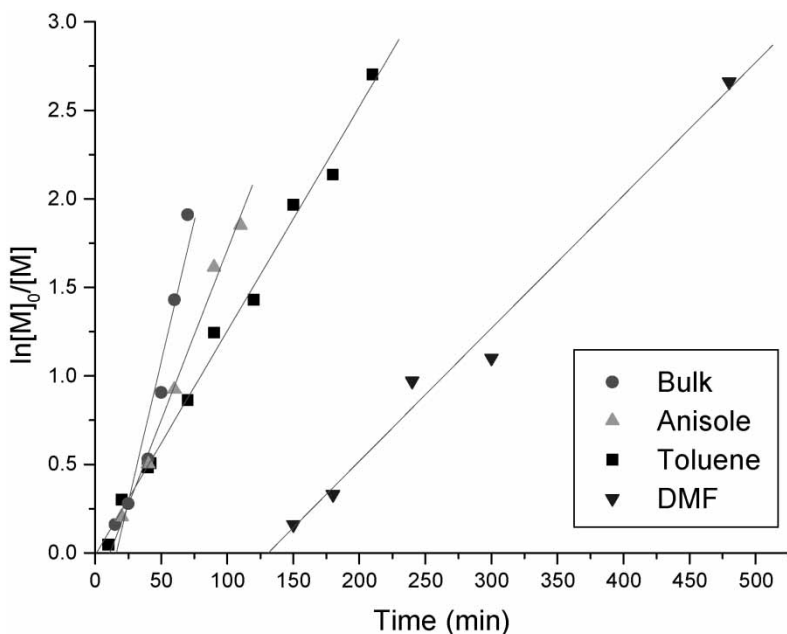


Figure 1. First-order kinetic plots for ATRP of MMA initiated by PPBP with $\text{CuCl}/\text{PMDETA}$ in bulk and various solvents at 90°C . $[\text{MMA}]_0: [\text{PPBP}]_0: [\text{CuCl}]_0: [\text{PMDETA}]_0 = 200:1:1:3$; $V_{(\text{MMA})}/V_{(\text{Solvent})} = 3/1$.

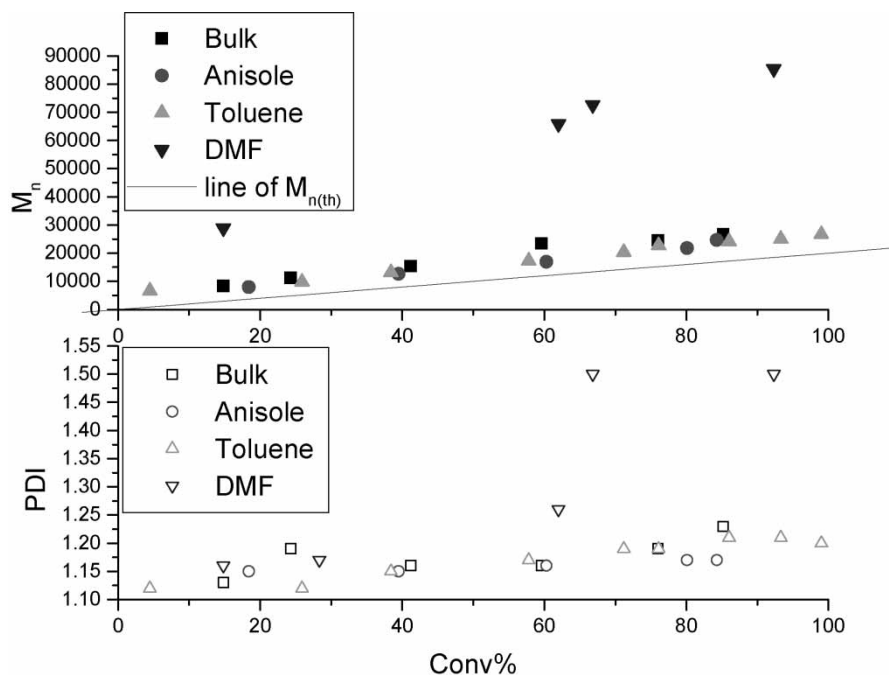


Figure 2. Dependence of M_n and PDI on conversion for ATRP of MMA initiated by PPBP with CuCl/PMDETA in bulk and various solvents at 90°C. $[MMA]_0 : [PPBP]_0 : [CuCl]_0 : [PMDETA]_0 = 200 : 1 : 1$; $V_{(MMA)}/V_{(Solvent)} = 3/1$.

$M_n S_{(GPC)}$ slightly deviated from the theoretic values determined by $M_{n-th} = ([M]_0/[RX]_0)M_{RX}$, which indicated that PPBP in such a process had a low initiation efficiency (initiation efficiency calculated by M_{n-th}/M_{n-GPC}) about 0.7, where $[M]_0$ and $[RX]_0$ are the initial concentrations of monomer and initiator, respectively. M_M and M_{RX} are molecular weights of the monomer and initiator, respectively, and $Conv$ is the monomer conversion. As shown in Figure 3, the GPC traces are uni-modal and narrow, indicating that no side reactions occurred. Moreover, dual detection by refractive index and UV measurement provides clear evidence for the complete functionalization, GPC traces of PMMA ended by azobenzene group measured by UV ($\lambda = 254\text{ nm}$) and refractive index appear at the same elution volume. Furthermore, PPBP was also used to initiate styrene in conjunction with CuCl/PMDETA. The results in Table 1 showed that the molecular weights of polymers increased with the increase of conversion and PDI remained at relatively high values (1.35–1.57), but the polymerization rate was slower than that of MMA.

Analysis of UV-Vis Spectrum and Chain-end by $^1\text{H-NMR}$

According to the mechanism of ATRP, there will be a fragment from the initiator at the chain end. Here, $^1\text{H-NMR}$ and UV-Vis spectrum were used to confirm the structure of polymer obtained by ATRP. As shown in Figure 4, the benzene protons that resulted from PPBP are seen at 7.526–8.082 ppm, signals of a, b, and c correspond to a different H of benzene ring. Signal e at 3.739–3.819 ppm corresponds to methyl ester

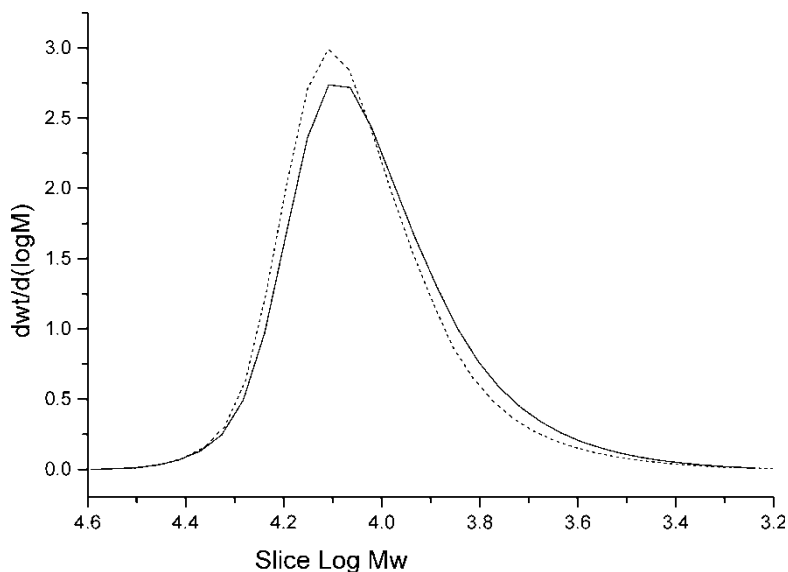


Figure 3. GPC traces of PMMA obtained via ATRP of MMA with PPBP/CuCl/PMDETA as an initiating system: refractive index signal (.....) and UV signal at $\lambda = 254$ nm (—).

protons in the PMMA-end having a ω -halogen group. Typical UV-Vis spectrum of azobenzene-labeled PMMA in THF is shown in Figure 5. The UV-Vis spectra of the azobenzene-labeled PMMAs in THF are identical with that of PPBP in both the shape and peak position (360 nm), indicating that azobenzene units are definitely present in the polymers. By assuming that the molar extinction coefficient of the polymer-attached azobenzene unit is the same as that of PPBP and there is only one azobenzene group per polymer chain, the number average molecular weights of the polymers can be calculated by comparing the UV-Vis absorbance of the polymer solutions with that of PPBP.

The calibration curve was obtained by plotting absorbance vs. concentration for solutions of PPBP in THF. With these values, we could either assess the degree of azobenzene incorporation or, assuming complete incorporation, calculate M_{n-UV} (number average molecular weights determined by UV-Vis method) for the samples. Herein, as shown in Figure 6, PPBP was used to make a standard curve for the concentration arranging

Table 1
ATRP polymerization of styrene with CuCl in bulk at 90°C

| Entry | Time (h) | Conv.% | M_{n-GPC} | PDI | M_{n-th} |
|-------|----------|--------|-------------|------|------------|
| 1 | 10 | 23.2 | 5970 | 1.35 | 4826 |
| 2 | 17 | 33.5 | 8960 | 1.42 | 6989 |
| 3 | 26 | 54.4 | 16110 | 1.47 | 11315 |
| 4 | 32 | 63.6 | 16210 | 1.57 | 13223 |

$$[\text{Styrene}]_0/[\text{PPBP}]_0/[\text{CuCl}]_0/[\text{PMDETA}]_0 = 200/1/1/3.$$

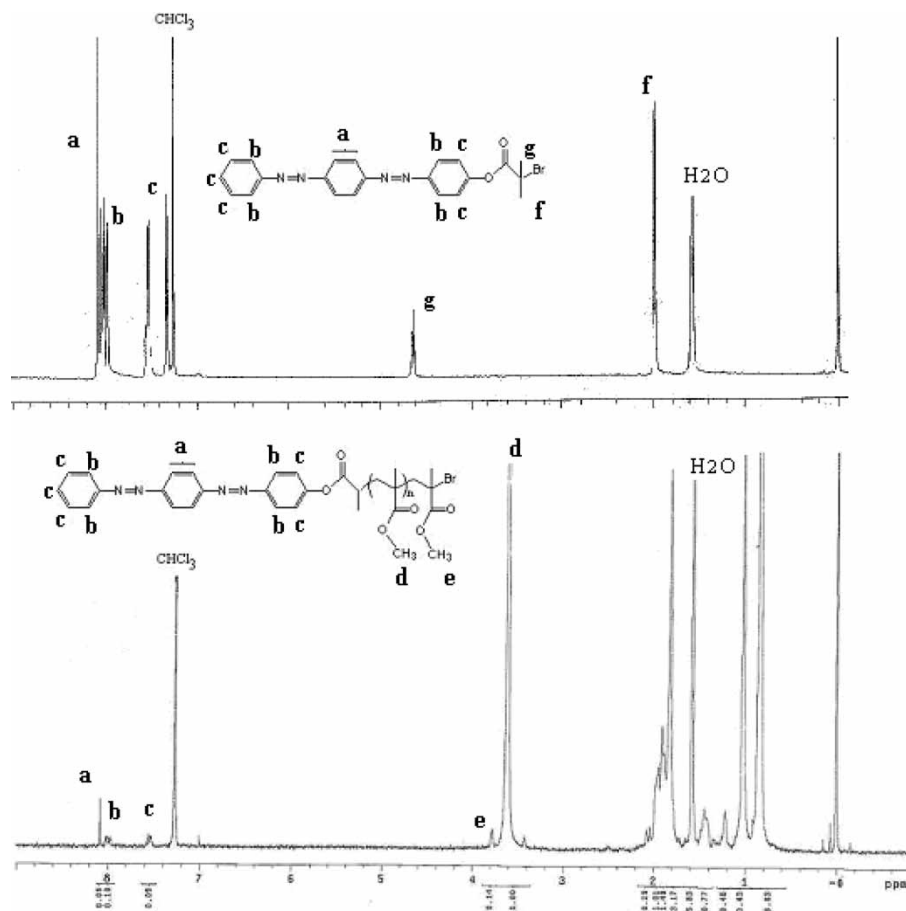


Figure 4. ¹H-NMR spectra of PPBP and polymer synthesized via ATRP of MMA with PPBP as an initiator. Sample: $M_{n,GPC} = 8890$, $M_w/M_n = 1.21$.

from 10^{-6} to 10^{-5} M. Equation (1) was obtained according to the line.

$$\text{Absorbance} = 0.02267 + 0.0437[\text{PPBP}] \times 10^6 \quad (1)$$

The absorbance of azobenzene—labeled PMMA was introduced to Equation (1) to calculate the concentration of the azobenzene group. The result is shown in Table 2. It was found that $M_{n,UV}$ is close to $M_{n,GPC}$ for a polymer with low molecular weight, which indicated that azobenzene moiety has proven to be incorporated into the polymers quantitatively.

*Synthesis of PMMA-*b*-PSt Polymer using PMMA as Macroinitiator*

ATRP, as a robust process in the controlled polymerization of styrenes and (meth)acrylates, has been extensively applied to prepare well-defined copolymers. In particular, this approach enables control over functionality, composition, and molecular weight. Here, poly(methyl methacrylate) with an azobenzene chromophoric group at the chain

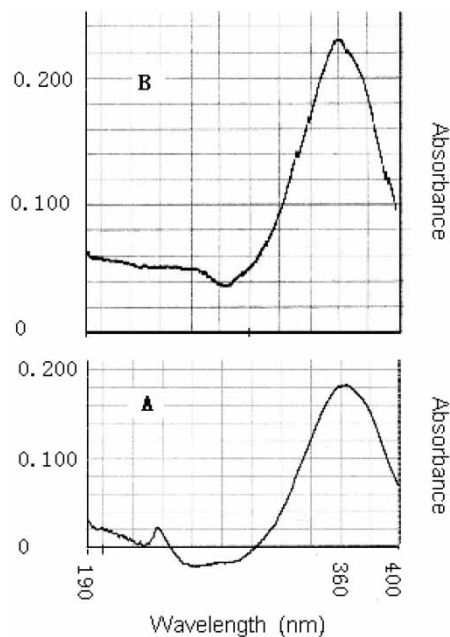


Figure 5. Typical UV-Vis spectra of PPBP (B) and azobenzene—capped PMMA (A) in THF, respectively.

end was used as the macroinitiator for the polymerization of St. As shown in Figure 7, molecular weight of the resulting polymer increased from 10400 to 40900. The greater polydispersity of copolymer with low initiator efficiency for styrene in this case may be due to the PMMA macroinitiator end-capped by a mixed halogen (19–21), the initiator efficiency was about 0.3.

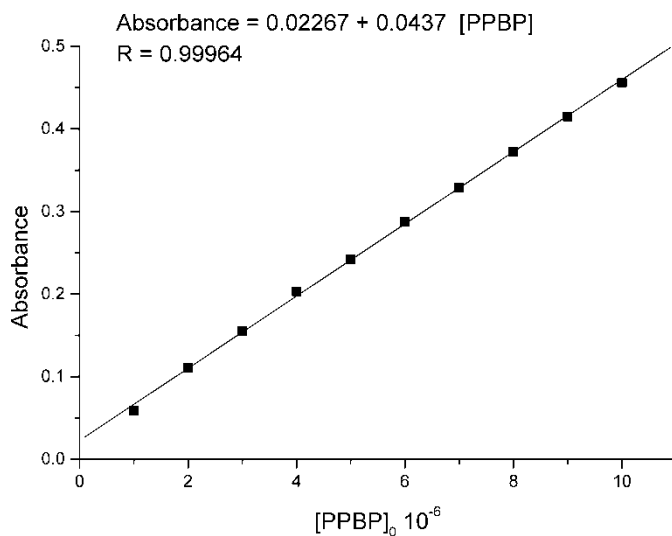


Figure 6. Dependence of absorbance on concentration of PPBP in THF.

Table 2
Comparison of number average molecular weights determined by GPC and UV-Vis of azobenzene-labeled PMMA

| Entry | Absorbance | [PPBP] $\times 10^{-6}$ M ^b | M_{n-GPC} | M_{n-UV}^c |
|----------------|------------|--|-------------|--------------|
| 1 ^a | 0.203 | 4.13 | 8300 | 10100 |
| 2 ^a | 0.178 | 3.46 | 11200 | 16100 |
| 3 ^a | 0.153 | 2.98 | 26700 | 43600 |

^aPolymers 1,2, and 3 were prepared via the ATRP of MMA using PPBP as the initiator.

^bThe concentration of PPBP was calculated according to Equation (1).

^cThe M_{n-UV} was calculated to the concentration of PPBP calculated according to Equation (1).

Meanwhile, the ¹H-NMR of PMMA-*b*-PSt was conducted to confirm the copolymeric structure. As shown in Figure 8, it is obviously found that characteristic protons of St, benzene protons are shown at 6.44–7.08 ppm and CH_3O protons of MMA are at 3.58 ppm. The azobenzene protons are also found though the molecular weight is up to 40900.

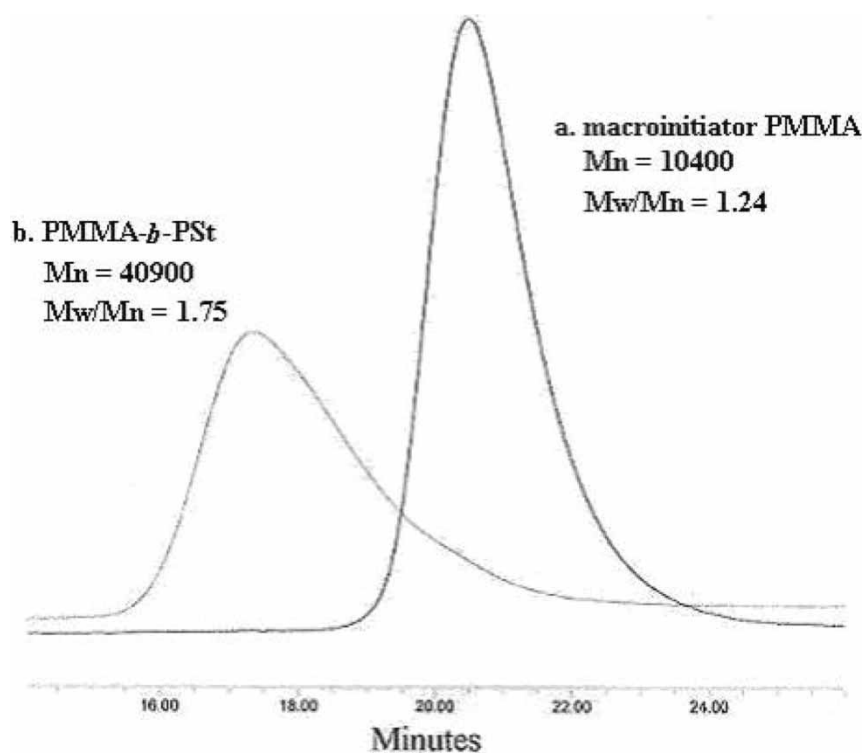


Figure 7. GPC curves of polymers: (a) macroinitiator obtained via ATRP of MMA with PPBP/CuCl/PMDETA as an initiating system and, (b) PMMA-*b*-PSt. $[St]_0 = 2.9$ M, $[macroinitiator]_0 = 0.014$ M, $[CuCl]_0 = 0.045$ M, $[PMDETA]_0 = 0.135$ M; $V_{toluene} = 2$ ml; temperature = 90°C; time = 16 h; conversion = 43%.

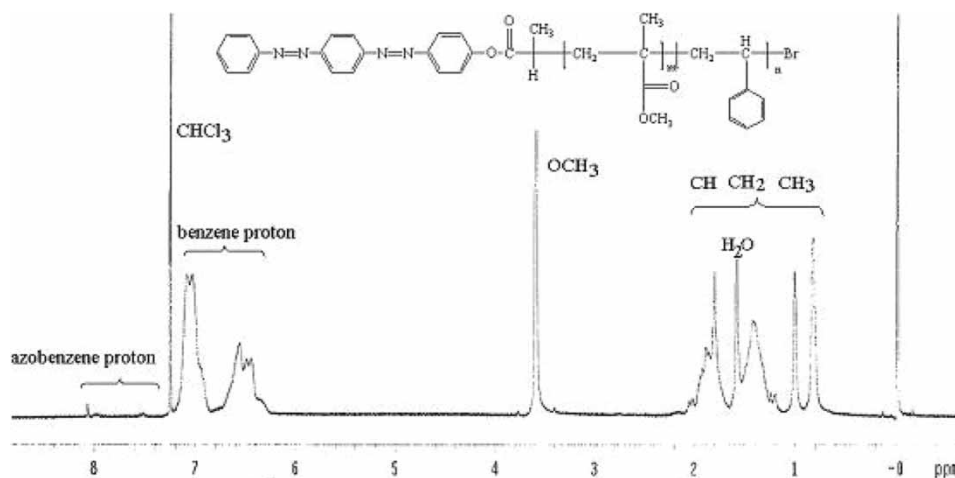


Figure 8. $^1\text{H-NMR}$ spectra of PMMA-*b*-PSt synthesized via ATRP of St with PMMA as a macroinitiator. Sample: $M_{n, \text{GPC}} = 40900$, $M_w/M_n = 1.75$. $[\text{St}]_0 = 2.9 \text{ M}$, $[\text{macroinitiator}]_0 = 0.014 \text{ M}$, $[\text{CuCl}]_0 = 0.045 \text{ M}$, $[\text{PMDETA}]_0 = 0.135 \text{ M}$; $V_{\text{toluene}} = 2 \text{ ml}$; temperature = 90°C ; time = 16 h; conversion = 43%.

Conclusions

4-(4-phenylazo-phenylazo)-phenyl 2-bromopropionate was successfully used as an effective initiator in the atom transfer radical polymerization of MMA and styrene in the presence of CuCl/PMDETA, and well-defined UV-Vis chromophoric group end-capped polymers and copolymer of PMMA-*b*-PSt were obtained. $^1\text{H-NMR}$ of the resulting PMMA was performed to further confirm the “living”/controlled nature of the polymerization process.

Acknowledgements

This work was supported by Science and Technology Development Planning of Jiangsu Province (no. BG2004018) and Suzhou (no. SG0413).

References

1. Anufrieva, E.V. and Gotlib, Y.Y. (1981) *Adv. Polym. Sci.*, 40: 1–68.
2. Liu, R., Winnik, M.A., Di Stefano, F., and Vanketessan, J. (2001) *J. Polym. Sci., Part A: Polym. Chem.*, 39 (9): 1495–1504.
3. Zhang, H., Klumperman, B., and Linde, R. (2002) *Macromolecules*, 35: 2261–2267.
4. De Deus, J.F., Souza, G.P., Corradini, W.A., Atvars, T.D.Z., and Akcelrud, L. (2004) *Macromolecules*, 37 (18): 6938–6944.
5. Georges, M.K., Veregin, R.P.N., Kazmaier, P.M., and Hamer, G.K. (1995) *Macromolecules*, 28: 8441–8443.
6. Georges, M.K., Veregin, R.P.N., Kazmaier, P.M., and Hamer, G.K. (1993) *Macromolecules*, 26: 2987–2988.
7. Kato, M., Kamigaito, M., Sawamoto, M., and Higashimura, T. (1995) *Macromolecules*, 28 (5): 1721–1723.
8. Wang, J.S. and Matyjaszewski, K. (1995) *Macromolecules*, 28: 7901–7910.

9. Mayadunne, R.T.A., Rizzardo, E., Chiefari, J., Chong, Y.K., Moad, G., and Thang, S.H. (1999) *Macromolecules*, 32 (21): 6977–6980.
10. Chong, Y.K., Le, T.P.T., Moad, G., Rizzardo, E., and Thang, S.H. (1999) *Macromolecules*, 32 (6): 2071–2074.
11. Rodlert, M., Harth, E., Rees, I., and Hawker, C.J. (2000) *J. Polym. Sci., Part A: Polym. Chem.*, 38: 4749–4763.
12. Zhu, Y., Howell, B.A., and Priddy, D.B. (1997) *Preprints*, 38: 97–98.
13. Hawker, C.J. and Hedrick, J.L. (1995) *Macromolecules*, 28 (8): 2993–2995.
14. Erdogan, M., Hepuzer, Y., Cianga, I., Yagci, Y., and Pekcan, O. (2003) *J. Phys. Chem. A*, 107 (40): 8363–8370.
15. Tong, J.D., Ni, S., and Winnik, M.A. (2000) *Macromolecules*, 33 (5): 1482–1486.
16. Percec, V., Kim, H.J., and Barboiu, B. (1997) *Macromolecules*, 30: 8526–8528.
17. Wang, G., Zhu, X.L., Cheng, Z.P., and Zhu, J. (2005) *J. Polym. Sci., Part A: Polym. Chem.*, 43: 2358–2367.
18. Pascual, S., Coutin, B., Tardi, M., Polton, A., and Varion, J.-P. (1999) *Macromolecules*, 32: 1432–1437.
19. Matyjaszewski, K., Shipp, D.A., Wang, J.-L., Grimaud, T., and Patten, T.E. (1998) *Macromolecules*, 31 (20): 6836–6840.
20. Shipp, D.A., Wang, J.-L., and Matyjaszewski, K. (1998) *Macromolecules*, 31 (23): 8005–8008.
21. Matyjaszewski, K. and Xia, J.H. (2001) *Chem. Rev.*, 101 (9): 2921–2990.