Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 44 (2003) 7645–7649

polymer

www.elsevier.com/locate/polymer

Controlled grafting of *N*-isoproply acrylamide brushes onto self-standing isotactic polypropylene thin films: surface initiated atom transfer radical polymerization

Shrojal M. Desai, Shailendra S. Solanky, A.B. Mandale, K. Rathore, Raj Pal Singh*

Polymer Chemistry Division, National Chemical Laboratory, Pune 411008, India

Received 12 February 2003; received in revised form 26 August 2003; accepted 22 September 2003

Abstract

Surface initiated atom transfer radical polymerization (ATRP) technique using CuBr/$CuBr_2$/bpy complex is employed to graft *N*-isopropyl acrylamide (NIPAA) brushes onto 'self-standing' isotactic polypropylene (iPP) film surface via iPP-Br macro-initiator. The successful accomplishment of surface grafting is understood from the UV–Vis, ATR-FTIR, XPS, SEM analysis and contact angle measurements of the modified samples. The ability to control the degree of grafting of NIPAA brushes reaffirms the elegance of the surface initiated ATRP technique to develop tailor-made polymer surfaces. The LCST nature of the NIPAA brushes would introduce stimuli responsive character onto the surface of the iPP films used for various specialty applications, especially for biomedical purposes.

Keywords: ATRP; Polymer brushes; Surface initiated grafting

1. Introduction

Surface modification of polymers is an important area both for applied [1–3] as well as basic research [4,5]. A number of surface modification techniques such as plasma, corona discharge, Langmuir–Blodgett monolayer formation, chemical treatment and traditional free-radical grafting have been used to modify polymer surfaces, of which, the latter two are of particular interest since they can lead to the direct introduction of desired functional moieties onto the substrate surface. However, for surface modification using traditional free-radical grafting technique, control over the chain length and chain length distribution has always remained a limitation. The grafted polymer layers have higher resistance towards the wet chemical etchant than the patterned monolayer from which they are grown. Amongst all the polymerizations for the synthesis of polymer brushes, living polymerization is the most convenient technique due to its ease to control the length and composition of polymer brushes [6]. Covalent attachment of polymer chains to solid substrates by surface-initiated atom transfer radical polymerization (ATRP) is an effective method for tailoring surface properties such as wetting, adhesion and biocompatibility with greater uniformity and control over the chain length. Several research groups have recently reported the use of controlled/living polymerization techniques [7–15] to grow polymer chains onto the surfaces of silicon wafers, gold-coated plates, porous glass filters and ceramics in a well-defined manner for different applications [16,17]. However, surface modification of 'self-standing' thin polymer films using this technique, to our knowledge, has yet not been reported.

In our sole attempt, we have extended the technique of surface-initiated ATRP for the controlled free-radical surface grafting of functional monomers onto self-standing polymer thin films. Attempts have been made herewith, to graft *N*-isopropyl acrylamide (NIPAA) and hence prepare polymer brushes/layers onto the surface of isotactic polypropylene (iPP) films (~100 μm) via two-step mechanism involving surface bromination of iPP film by free radical gas phase photochemical reaction (which generated allyl/alkyl bromide onto the surface of the iPP films), followed by grafting of *N*-isopropyl acrylamide (NIPAA) through surface-initiated ATRP. Thus, to modify polyolefin surfaces, we have selected bromination of iPP as a first step.

---

* Corresponding author. Tel./fax: +91-20-5893234.
E-mail address: singh@poly.ncl.res.in (R.P. Singh).

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.09.060

Bromination is well known to offer better regioselectivity compared to other halides [18]. The resultant dangling polymer brushes are analyzed by gravimetric and contact angle measurements, UV–Vis, ATR-FTIR and XPS spectroscopies.

2. Experimental

2.1. Materials

Isotactic polypropylene (iPP) pellets obtained from IPCL, Baroda, India, after purification (additive free) were used for the preparation of thin iPP films (~100 μm) by compression molding at 176.6 °C, 725 kg/cm^2 for 1 min in a laboratory Carver press. The films of 4.5 × 1.5 cm^2 size were cut and sonicated in dichloromethane followed by acetone and dried in vacuum oven for 25 h at 50 °C. Liquid bromine obtained from Merck, India, CuBr and $CuBr_2$ from Fluka, 2,2′-bipyridine and *N*-isopropyl acrylamide (NIPAA) from Aldrich were used without further purification. Tetrahydrofuran (THF) (hplc grade) was procured from Merck, India was used after drying.

2.2. Characterization

To substantiate surface grafting, attenuated total reflectance Fourier Transform infrared (ATR-FTIR) spectra were recorded using a *Perkin Elmer 16PC* FTIR spectrophotometer bearing an ATR attachment with a KRS-5 crystal at $\theta = 45°$. ESCA 3000 Electron spectrometer with twin anode, Al Kα (1486.6 eV) and Mg Kα (1253.6 eV) was used to understand the chemical changes on the polymer surface. The X-ray photoelectron spectroscopy (XPS) spectra were acquired at 50 eV pass energy, 5 mm slit width and two take off angles of 30 and 60°. Details of this electron spectrometer are described elsewhere [18]. Water compatibility of the neat/grafted samples was evaluated by measuring the contact angle (θ) using *RAME'-HART Inc.* NRL contact angle goniometer, Model No. 100-00 230. UV–Vis spectra were recorded on Hewlett Packard 8452A diode array spectrophotometer. Scanning electron micrographs were obtained from *Leica SEM Stereoscan-440*, Cambridge, UK.

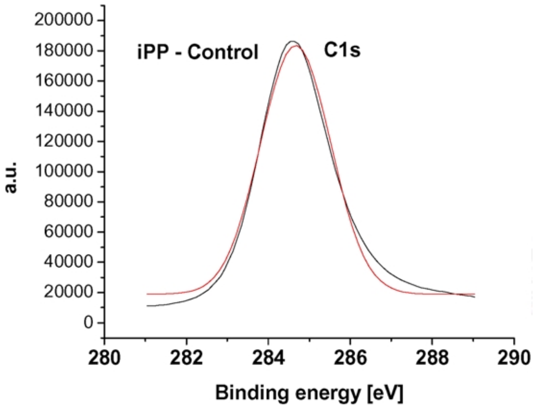


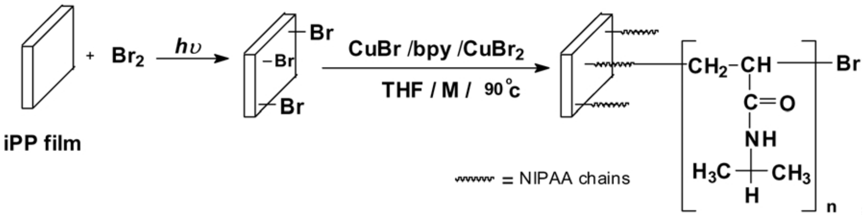
Fig. 1. C1s peak in XPS (raw and deconvoluted) spectra of iPP control sample.

2.3. Procedure for bromination of iPP film surface

Surface bromination of the polymer films was accomplished by a photo-bromination process similar to that reported by Vernekar et al. [18]. Two iPP films (4.5 × 1.5 cm^2) were suspended inside a Pyrex glass tube fitted with an inlet and outlet tube having stopcock for gas and a side arm with a septum in each experiment. The glass tube was purged with high purity argon gas for 15 min to replace the air inside the tube. Then ~0.1 ml of bromine was introduced into the tube via a syringe through the septum. After 5 min, when the tube is filled with bromine vapors, it is irradiated with 400 W, medium pressure mercury vapor (MPMV) lamp jacketed with cold-water circulation, from a distance of 10 cm, for a specific time. The reaction tube was maintained at 35 ± 2 °C. The films were removed after specific time, transferred in a fresh tube, flushed with argon and then stored under vacuum till further use.

2.3.1. Surface-initiated ATRP of NIPAA onto iPPBr

The solution mixture of monomer NIPAA (1.13 g, 0.2 M/l) and solvent THF (50 ml) was degassed by using three freeze–pump–thaw cycles and warmed to room temperature with continuous stirring. This degassed solution when transferred to a round-bottomed flask containing two iPPBr films (weighing, 79.21 and 82.47 mg, respectively, 0.39 mmol), CuBr (55 mg, 0.39 mmol), $CuBr_2$ (12 mg, 0.13 mmol) and bpy (273 mg, 1.17 mmol) under an argon atmosphere using a cannula, developed a brown color upon stirring. The reactor was maintained at 90 °C with stirring



Scheme 1.

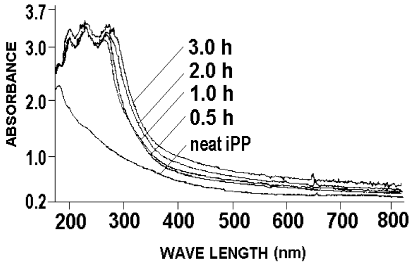


Fig. 2. The UV–vis spectra of iPP films brominated for different period.

during polymerization. Since the reaction medium (tetrahydrofuran) is a non-solvent for iPP the possibility of monomer (NIPAA) getting adsorbed in the iPP is neglected. This hypothesis is supported by the results of control as shown in Fig. 1. This figure shows C1s binding energy peak of iPP control film, where no visual asymmetry is apparent, indicating a clean hydrocarbon surface. The films were cleaned by soxhlet extraction for 12 h, followed by 5 min of sonication in fresh THF and acetone to remove any adhered monomer, dried in a vacuum oven for 24 h at 50 °C, weighed and then taken for further characterization.

3. Results and discussion

Brominated polyolefin surface is a preferred substrate for nucleophilic substitution reactions against fluorinated and chlorinated surfaces due to the better leaving-group ability of bromine (Br) compared to fluoride (F) and chloride (Cl) moieties [19]. Moreover, iPPBr replicates the structure of a macro-initiator (R–Br) essential for the surface initiated ATRP of NIPAA in the presence of CuBr and 2,2′-bipyridyl (bpy). Wang et al. [20] have discussed the initiation capacity of similar EPDM–Br macro-radical in detail. Scheme 1 represents the synthetic pathway which we have followed to grow polymer brushes from the surface of iPP films via photochemical bromination followed by surface initiated ATRP. The UV–Vis spectra of iPP films brominated for different period (Fig. 2) shows that iPP-Br films also contain long sequences of conjugated double bonds arising due to the simultaneous dehydrobromination during the bromination process. The XPS and ATR-FTIR analysis of the brominated iPP films (iPP-Br) confirmed the formation of Br moieties on the iPP film surface upon bromination. The XPS overlay (Fig. 3) of the brominated iPP film (iPPBr) for different irradiation time shows the increase in the intensity of the Br3d peak at 70.2 eV. Moreover, for the irradiation time less than 2 h, bromination is confined to the surface as evident from the XPS spectra with depth profiling results. As apparent from the figure, the intensity of the Br3d peaks for grazing angle (θ) = 30° (depth ~10 Å) is more than that for 60° (depth ~50 Å). This indicates that at higher angle, instrument is characterizing bulk as compared to the lower angle. This reaffirms that the bromination is confined to the film surface. The ATR-FTIR spectra (Fig. 4) of the same films revealed the C–Br stretching bands at 571, 640 and 661 cm^{-1}, further confirming the presence of Br moieties on the iPP surface with a small peak at ~1600 cm^{-1}, which can be due to C=C stretching vibration from unsaturation generated on the substrate back bone [18]. The structural features of iPP enhance both, the rate of bromination as well as dehydrobromination, which demonstrates that surface bromination of iPP also occurs regioselectively [18]. The first step in bromination reaction is the homolytic bond cleavage of bromine molecule into two bromine radicals upon exposure to radiation [21]. In the second step, the bromine radical abstracts a hydrogen atom from the tertiary carbon in the iPP backbone, which results in the formation of a radical center on the iPP chain. This radical center further reacts with bromine molecule to form C–Br moiety and bromine radical. Thus, this chain reaction continues till, Br substitutes all the tertiary hydrogen atoms.

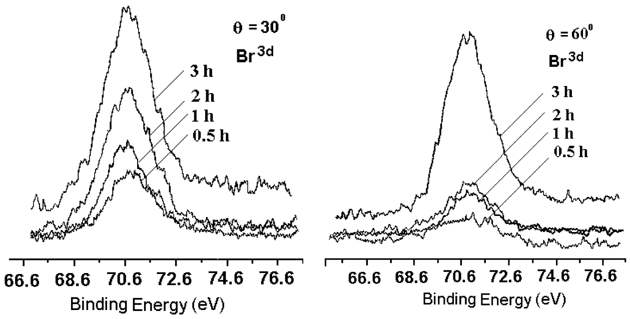


Fig. 3. The XPS overlay of the brominated iPP films (iPPBr) for different irradiation times.

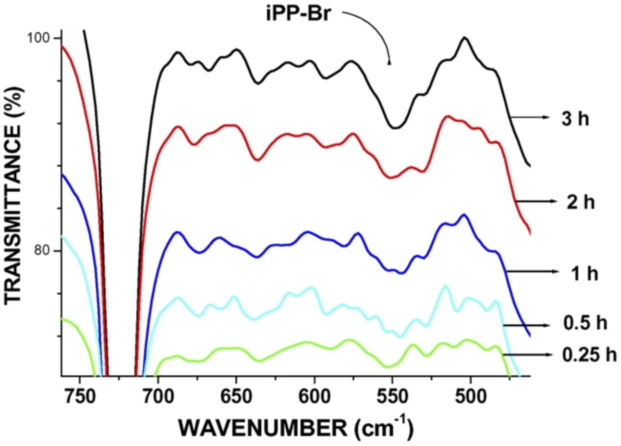


Fig. 4. ATR-FTIR overlay spectra of iPPBr for different bromination times.

Synthesis of controlled block and graft copolymers using the knowledge of ATRP is well accepted now [22,23]. Recent reports on surface initiated grafting onto gold, silicon wafers, glass filter and ceramic surfaces using CuCl/CuBr/2,2′-bipyridine system via ATRP has attracted a great attention. EPDM-*g*-PMMA in presence of EPDM–Br/MMA/CuBr/bpy at 90 °C in THF through ATRP is recently reported [20]. We have applied these concepts to the surface modification of iPP films. However, to ensure a sufficient

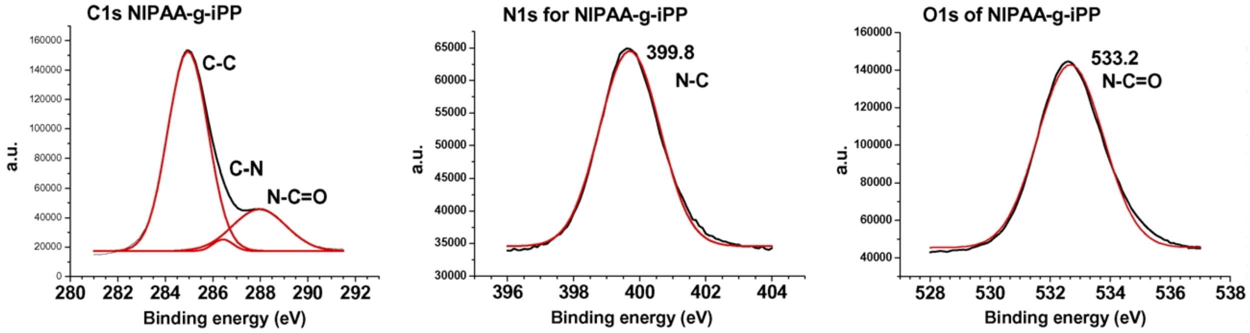


Fig. 5. The deconvoluted XPS spectra of the surface grafted NIPAA brushes.

concentration of deactivating Cu^{II} species in the solution and better control of ATRP, we added 30 mol% of $CuBr_2$ (with respect to CuBr) in the reaction medium. No gelation of the solution or homopolymerization of NIPAA was observed during grafting, indicating the control over the reaction. Here, gelation refers to the increase in the viscosity of the reaction medium due to the homopolymer formation, which is usually seen in the conventional free-radical polymerization. However, the reaction medium becomes colloidal and slightly viscous when reaction is continued for more than three days. In the ATR-FTIR spectrum of modified film, a broad peak at 3600–3400 cm^{-1} corresponding to N–H stretching and another at 1663 cm^{-1} corresponding to N–C=O stretching vibrations confirmed the formation of the grafted layer. The intensity of this peak increased progressively with the increase in the reaction time as a result of higher degree of grafting. Any peak arising due to the monomer adsorbed onto the film (hydrophobic) surface is quite unlikely since, the reaction was carried out in polar solvent and the films were thoroughly washed before analysis.

The XPS spectra (Fig. 5) show the peaks with binding energies (eV) 286.0 (C–N) and 288.2 (HN–C=O) in the C1s, 399.8 (N–C) in the N1s and 533.2 (N–C=O) in the O1s regions, respectively. The intensities of these peaks were substantially high for spectra recorded at grazing angle 30° than at 60°, indicating that the grafting is confined to the surface. These results are again supported by the drop in the water contact angle (θ) from 94° for neat iPP to 70° for iPPBr and 45° for iPP-*g*-NIPAA. Thus, the water compatibility of the NIPAA grafted surface is considerably higher than that of the neat sample. XPS overlay spectra for N1s of NIPAA-*g*-iPP is also shown in Fig. 6. The surface morphology of grafted film in SEM image (Fig. 7b) showed that the films were microscopically homogeneous as compared to neat film (Fig. 7a). Since the reorganization

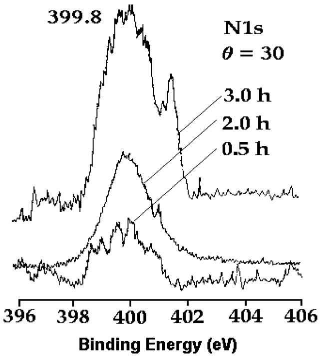


Fig. 6. XPS overlay spectra for N1s of NIPAA-*g*-iPP (iPP films with different bromination time).

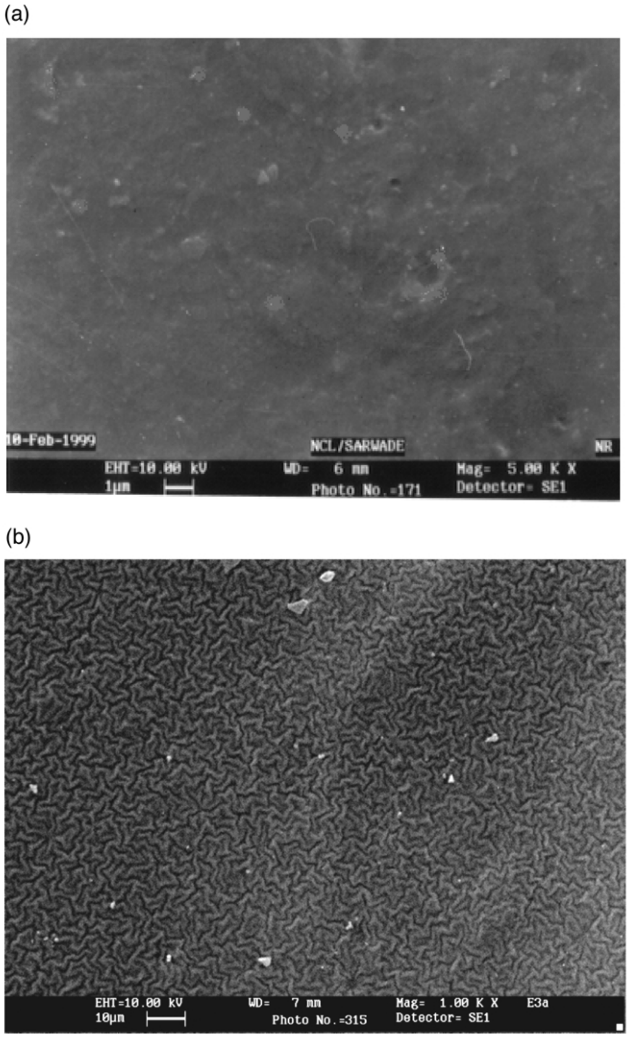


Fig. 7. SEM micrograph (a) smooth surface of neat PP (b) uniform carpeting of NIPAA brushes on NIPAA-*g*-iPP film surface.

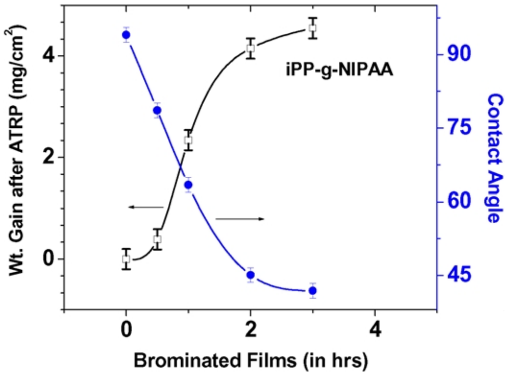


Fig. 8. Time dependence of weight gain and change in contact angle of NIPAA-*g*-iPP films.

of the polymer chains is unlikely, the homogeneity of the films suggests that the grafting is uniform throughout the surface. To demonstrate the living character of the surface initiated ATRP, we discontinued the reaction after 24 h, washed the films, weighed them after drying and again continued the grafting onto these films in a fresh reaction system for 48 h. The films exhibited a significant rise in the weight initially from 79.12 to 87.5 mg (after 24 h) and 98.9 mg (after 48 h). However, the thickness of the grafted layer was not determined due to the limitations of elipsometric analysis for the polymeric samples. We also observed a gradual increase in the weight of the films with increase in bromination and grafting reaction time with corresponding decrease in the contact angle (Fig. 8). This observation suggests that the reaction proceeds in a controlled manner.

4. Conclusions

It is obvious from the results that photo-bromination is a very efficient technique to generate macro-initiators on the polymer surface for grafting functional monomers via ATRP. The degree and depth of bromination can be easily tuned to get optimal allyl/alkyl bromide moieties onto the film surface. Surface-initiated ATRP of NIPAA from the iPP film has been accomplished in a controlled manner. The grafting is uniform over the total film, presumably because polymerization is limited to the surface and minimal homopolymer is formed in solution. Terminating the reaction and reinitiating it in the same system substantiated the living nature of the graft copolymer. The living character of ATRP can be further used to grow block co-polymer brushes from this pre-modified surfaces.

Acknowledgements

Authors thank Dr S. Sivaram, Director, National Chemical Laboratory, Pune, for the critical discussions and C.S.I.R., New Delhi, India for the Senior Research Fellowship.

References

[1] Chan CM. Polymer surface modification and characterization. Munich: Hanser; 1994.
[2] Garbassi F, Morra M, Occhiello E. Polymer surfaces: from physics to technology. Chichester, UK: Wiley; 1994.
[3] Harmer MA. Langmuir 1991;7:2010–2.
[4] Holmes-Farley SR, Bain CD, Whitesides GM. Langmuir 1988;4:921–37.
[5] Ferguson GS, Whitesides GM. In: Schrader ME, Loeb GI, editors. Modern approaches to wettability: theory and applications. New York: Plenum Press; 1992. p. 143–77.
[6] Kong X, Kawai T, Abe J, Iyoda T. Macromolecules 2001;34:1837–44.
[7] Jordan R, Ulman A. J Am Chem Soc 1998;120:243–7.
[8] Ingall MDK, Honeyman CH, Mercure JV, Bianconi PA, Kunz RR. J Am Chem Soc 1999;121:3607–13.
[9] Weck M, Jackiw JJ, Rossi RR, Weiss PS, Grubbs RH. J Am Chem Soc 1999;121:4088–9.
[10] Boer B, Simon HK, Werts MPL, Van der Vegte EW, Hadziioannou G. Macromolecules 2000;33:349–56.
[11] Ramakrishnan A, Dhamodharan R, Rühe J. Macromol Rapid Commun 2002;23:612–6.
[12] Yamamoto K, Miwa Y, Tanaka H, Sakaguchi M, Shimada S. J Polym Sci Part A: Polym Chem 2002;40:3350–9.
[13] Xianyi C, Christian P, Steven PA. Polym Prepr (American Chemical Society, Division of Polymer Chemistry) 2002;43:265–6.
[14] Jeyaprakash JD, Samuel S, Dhamodharan R, Jurgen R. Macromol Rapid Commun 2002;23:277–81.
[15] Kim J, Huang W, Miller MD, Baker GL, Bruening ML. J Polym Sci Part A: Polym Chem 2003;41:386–94.
[16] Prucker O, Schimmel M, Tovar G, Knoll W, Rühe J. Adv Mater 1998;10:1073–7.
[17] Shah RR, Merreceyes D, Husseman M, Rees I, Abbott NL, Hawker CJ, Hedrick JL. Macromolecules 2000;33:597–605.
[18] Balamurugan S, Mandale AB, Badrinarayanan S, Verneker SP. Polymer 2001;42(2501):2512.
[19] March J. Advanced organic chemistry, 3rd ed. New Delhi: Wiley Eastern; 1986.
[20] Wang X, Luo N, Ying S. Polymer 1999;40:4515–20.
[21] Calvert JG, Pitts JN. Photochemistry. New York: Wiley; 1960.
[22] Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117:5614.
[23] Grimaud T, Matyjaszewski K. Macromolecules 1997;30:2216.