Macromolecules **2006,** *39,* 26−29

Articles

A Facile Route to Poly(acrylic acid) Brushes Using Atom Transfer Radical Polymerization

Neil D. Treat,[†] Neil Ayres,[‡] Stephen G. Boyes,[§] and William J. Brittain*[,‡]

Department of Polymer Science, The University of Southern Mississippi, Southern Station Box 10076, Hattiesburg, Mississippi 39406-0076; Department of Polymer Science, Goodyear Polymer Center, 170 University Ave., University of Akron, Akron, Ohio 44325; and Department of Chemistry and Geochemistry, Colorado School of Mines, 1500 Illinois Street, Golden, Colorado 80401

Received September 14, 2005; Revised Manuscript Received November 7, 2005

ABSTRACT: We report the preparation of a poly(acrylic acid) polymer brush from a flat silica substrate using a surface-initiated atom transfer radical polymerization of *tert*-butyl acrylate. Significantly, we use a chemical free deprotection strategy through pyrolysis of the *tert*-butyl esters to the corresponding carboxylic acids. This eliminates the possibility of loss of the polymer brush from the surface via acidolysis of the ester group in the surface bound initiator. We have verified the formation of the poly(acrylic acid) brush through ATR-FTIR, ellipsometry, water contact angle analysis, and XPS. We also demonstrate the stimuli-responsive nature of these brushes with respect to pH and added electrolyte concentration.

Introduction

Polymer brushes are assemblies of macromolecules that are tethered by one end to a surface or interface.[1,2] Attachment of the polymeric chains in close proximity to one another forces the polymers to adopt a stretched conformation in order to minimize segment−segment interactions.[3] As a result of these densely packed polymer topologies, the synthesis of polymer brushes has attracted increasing attention for applications in areas such as surface property tailoring,[4] chemical gating,[5−8] and nanolithographic patterning.[9]

Polymer brushes are rendered more complex when charged polymer molecules are used, i.e., polyelectrolytes. Surfaces decorated with polyelectrolyte brushes have garnered significant interest as they relate to stimuli responsive or “smart” surface coatings,[10] biosensors,[11] and colloidal stabilization.[12] Furthermore, polyelectrolyte surfaces can be used for the formation of inorganic nanoparticles, as we demonstrated in a recent publication.[13]

We,[13−16] and others,[17−22] utilize atom transfer radical polymerization (ATRP) for the synthesis of polymer brushes, employing the “grafting from” methodology. In this approach a molecule capable of initiating an ATRP polymerization is first immobilized on the surface.[23] The polymerization subsequently proceeds from these sites affording a relatively thick, covalently attached brush with a high grafting density.

ATRP is a well-established controlled/“living” radical polymerization technique that has been successfully applied to monomer systems that include styrenics, acrylates, and methacrylates.[24,25] The advantages of a controlled/“living” system include control over the brush thickness and the ability to prepare block copolymers through reinitiation of the dormant chain ends and subsequent regrowth of the polymer chains. However, ATRP cannot be used for some functional monomers. For example, (meth)acrylic acid which contains acid groups will poison the ATRP catalyst.[24]

A strategy to circumvent this problem is to polymerize *tert*-butyl (meth)acrylate, which proceeds to high conversion and yields polymers of narrow polydispersity that will readily reinitiate upon further addition of monomer.[26−31] The *tert*-butyl group acts is a protecting group and can be removed by acid hydrolysis giving the desired (meth)acrylic acid functionality. It should be noted here that the Huck group[32] has reported the direct aqueous polymerization of the sodium salt of acrylic acid from a surface; however, the chemical deprotection of the *tert*-butyl ester is a more common strategy for forming (meth)acrylic acid polymer brushes in the literature. This acid hydrolysis approach is problematic for polymer brushes because the anchoring moiety often contains an ester functional group; this group can also be cleaved leading to loss of the polymer brush from the surface. It is desirable to combine the benefits and control of the *tert*-butyl (meth)acrylate polymerization with a deprotection strategy that does not cleave the brush.

Herein we report an approach for the preparation of a poly(acrylic acid) brush without the need for acid hydrolysis. We also demonstrate the stimuli-responsive nature of the polyelectrolyte brush in response to pH and added electrolyte concentration.

Experimental Section

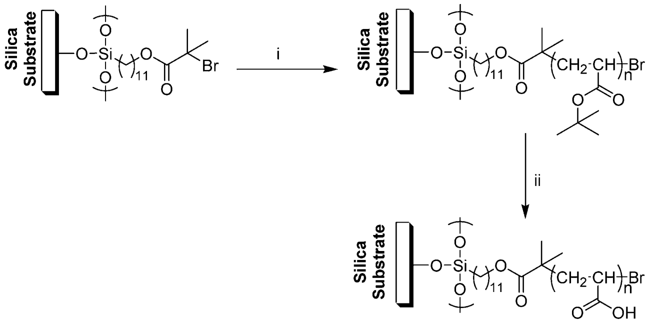
Materials. *tert*-Butyl acrylate (Aldrich, 98%) was passed through a column of activated basic alumina and degassed with high-purity nitrogen for 1 h prior to use. CuBr (Aldrich, 98%) was purified

---

[†] The University of Southern Mississippi.
[‡] Goodyear Polymer Center.
[§] Colorado School of Mines.
* To whom all correspondence should be addressed: Fax (330) 972-5290; e-mail wjbritt@uakron.edu.

10.1021/ma052001n CCC: $33.50

Scheme 1. Synthetic Route for the Formation of Si/SiO$_2$// Poly(acrylic acid) Brushes from a Silica Substrate



i) tert-Butyl acrylate, acetone, CuBr, PMDETA, 2-bromo-ethylisobutyrate, 60 °C, 4 h.
ii) 190 - 200 °C, 30 min.

was described in the literature.[33] *N*,*N*,*N′*,*N′*,*N″*-Pentamethyldiethylenetriamine (PMDETA, Aldrich 99%), ethyl 2-bromoisobutyrate (E2Br-iB, Aldrich, 98%), and anhydrous acetone (Aldrich, 99.8%) were used as received. Silicon wafers were purchased from Umicore Semiconductor Processing and cleaned prior to use in accordance with published procedure.[15] The synthesis and deposition of the surface bound initiator, (11-(2-bromo-2-methyl)propionyloxy)-undecyltrichlorosilane, have been reported previously.[34] All other reagents were purchased from either Aldrich or Fisher Scientific and used as received.

Instrumentation. FTIR-GATR spectra were recorded using a Nicolet system 370 spectrometer using a GATR accessory with Ge ATR crystal (Harrick Scientific). Spectra were recorded at 2 cm^{-1} resolution, and 256 scans were collected. Contact angles were determined using a Rame Hart NRL-100 contact angle goniometer equipped with a tilting stage. Drop volumes were 10 μL. Ellipsometric measurements were performed on a Gaertner model L116C ellipsometer with He−Ne laser ($\lambda = 632.8$ nm) and a fixed angle of incidence of 70°. For the calculation of the layer thickness, refractive indices of $n = 1.455$ (for silicon oxide), $n = 1.508$ (for tertiary and secondary initiator layers), $n = 1.466$ (for P(t-BA)), and $n = 1.527$ (for PAA) were used. X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer instrument using Al Kα radiation at the MATNET Surface Analysis Center at Case Western Reserve University. The takeoff angle of 45° with respect to surface normal, making the X-ray to electron angle 90°.

Typical ATRP Procedure for *tert*-Butyl Acrylate Polymerization from Flat Silicon Substrates. An initiator-modified silicon wafer was sealed in a 100 mL Schlenk flask, and the flask degassed by three vacuum purge/nitrogen fill cycles. CuBr (0.043 g, 0.3 mmol), acetone (13 mL, 176 mmol), and *tert*-butyl acrylate (17 mL, 116 mmol) were added to a separate 100 mL Schlenk flask along with a magnetic stirrer bar, sealed with a rubber septum, and degassed by purging with nitrogen for 1 h. PMDETA (0.094 mL, 0.45 mmol) was added to the mixture via syringe, and the solution was stirred at 60 °C until it became homogeneous (~5 min). The solution was then transferred to the flask containing the silicon wafer via cannula, followed by the addition of the free initiator (E2Br-iB) (0.022 mL, 0.15 mmol) via syringe. The polymerization was allowed to proceed at 60 °C for 4 h, after which the silicon wafer was removed and rinsed with THF. To remove untethered polymer chains, the silicon wafer was placed in a Soxhlet extractor and extracted with THF for 24 h followed by sonication in THF for 30 min.

Typical Procedure for Deprotection of *tert*-Butyl acrylate to Acrylic Acid. A poly(*tert*-butyl acrylate)-modified silicon wafer was placed in a crystallization dish. This was then added to an oven preheated to 200 °C and allowed to heat for 30 min. The wafer was then rinsed thoroughly with deionized (DI) water and blown with dry nitrogen.

Typical Procedure for pH Studies. A clean PAA-modified silicon wafer was placed in a solution with a specified pH. This was stirred for 20 min and wafer was blown dry with air and the brush thickness recorded.

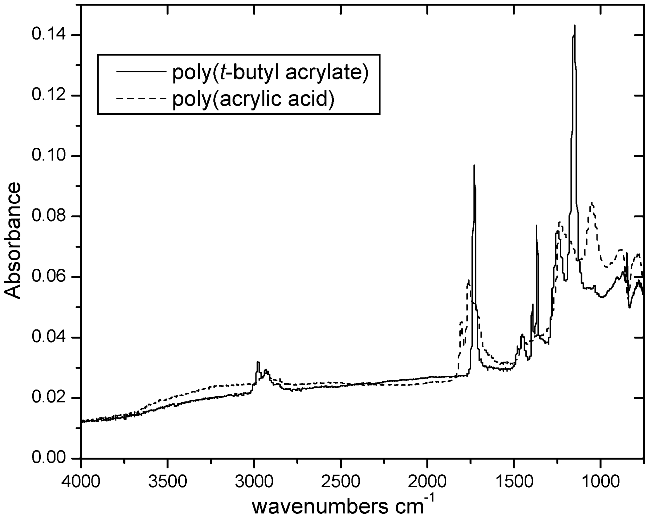


Figure 1. ATR-FTIR spectra of Si/SiO$_2$//poly(*tert*-butyl acrylate) (solid line) and Si/SiO$_2$//poly(acrylic acid).

Table 1. Water Contact Angle and Ellipsometry Data for the Polymer Brush Samples Studied in This Work

sample	water contact angle[a] (deg) Θ_a	water contact angle[a] (deg) Θ_r	thickness[b] (nm)
Si/SiO$_2$//poly(*tert*-butyl acrylate)	93	71	36
Si/SiO$_2$//poly(acrylic acid)	48	34	16

[a] The standard deviation of contact angles was <2°. [b] Thickness was determined by ellipsometry, and typical error on thickness measurement is ±1 nm.

Typical Procedure for Salt Concentration Studies. A clean, deprotonated PAA-modified silicon wafer was placed in a solution with a specified salt concentration. This was stirred for 20 min, and then the wafer washed with DI water, and blown dry with air and the brush thickness recorded.

Results

The experimental procedure for the synthesis of a poly(*tert*-butyl acrylate) brush and subsequent transformation to a poly(acrylic acid) brush is outlined in Scheme 1. The synthesis of the poly(*tert*-butyl acrylate) brush was confirmed by ATR-FTIR, contact angle analysis, and ellipsometry. The ATR-FTIR spectrum (Figure 1) contained the expected peaks at 1730 cm^{-1} (C=O stretch) and 2977 cm^{-1} (asymmetric CH$_3$ stretching vibration) and a doublet at 1368/1392 cm^{-1} (symmetric methyl deformation mode). The contact angles recorded (93° advancing and 71° receding) correlated well with literature values while the thickness of the film was 36 nm (Table 1).

The poly(*tert*-butyl acrylate) chains were converted to poly(acrylic acid) via pyrolysis.[35] This was achieved by simply heating the samples in a clean oven set to ~190−200 °C for 30 min. It has been reported that the pyrolysis of *tert*-butyl esters sometimes requires the addition of an acidic phenolic group.[35] However, in our hands no such treatment was required for successful and repeatable pyrolysis reaction. Following pyrolysis the polymer brush thickness decreased to 16 nm, while the contact angles decreased to 48° and 34° for advancing and receding angles (Table 1). The ATR-FTIR spectrum showed a broad peak at 2900−3400 cm^{-1}, a broadening of the peak at 1730 cm^{-1}, and the loss of the peaks associated with the pendant methyl groups (Figure 1).

The stimuli-responsive nature of the obtained poy(acrylic acid) brush was also investigated. Initially we examined the response of brush thickness to pH; the results of this study are shown in Figure 2. A silicon wafer bearing a poly(acrylic acid)

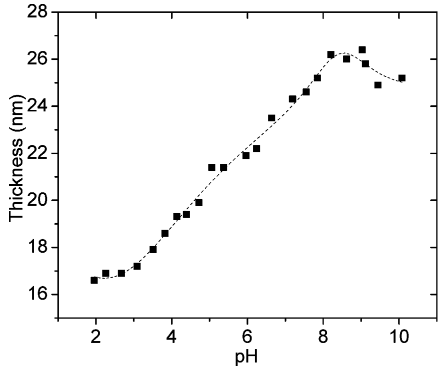


Figure 2. Plot of the polymer brush height (nm) of a Si/SiO$_2$//poly(acrylic acid) brush vs solution pH (20 min immersion). The dotted line is merely a guide for the eye.

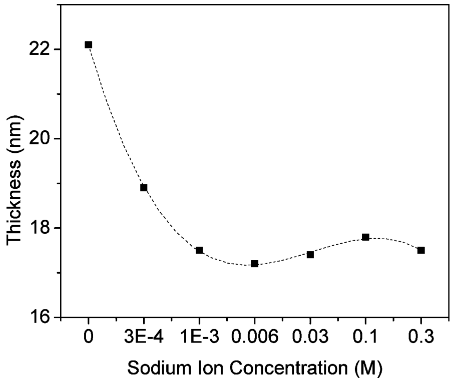


Figure 3. Plot of Si/SiO$_2$//poly(acrylic acid) brush thickness vs [NaCl]. The dotted line is merely a guide for the eye.

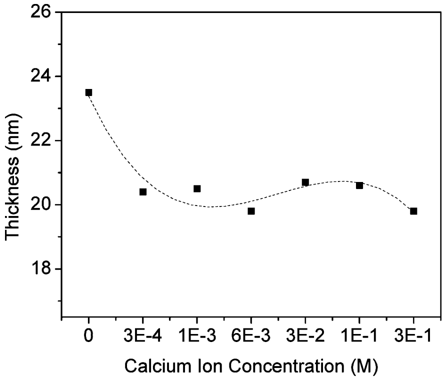


Figure 4. Plot of Si/SiO$_2$//poly(acrylic acid) brush height (nm) vs [CaCl$_2$]. The dotted line is merely a guide for the eye.

brush was immersed in an aqueous solution, and the pH was adjusted from 2 to 10. With increasing pH there was a concomitant increase in brush height from 16 to 26 nm at pH 9. The increase in thickness of a poly(acrylic acid) brush in response to added base has been previously reported, and we were pleased to see that our results closely matched the published data.[36] Interestingly, upon a further increase in pH to a value of 10 the brush decreased in thickness.

We then probed the response of a fully deprotonated brush to added electrolyte. For this we chose a monovalent (NaCl) and a divalent (CaCl$_2$) salt; the results of these experiments are shown in Figures 3 and 4. As expected, the brush height decreased upon addition of electrolyte. With increasing [NaCl] the brush height decreased from 22 to 17 nm while increasing [CaCl$_2$] caused the brush height to decrease from 24 to 20 nm. It appears from visual inspection of Figures 3 and 4 that the divalent salt results in a faster collapse of the brush height.

Discussion

We have used pyrolysis to convert of a *tert*-butyl ester to the corresponding carboxylic acid.[35] The reaction is proposed to proceed via a six-membered transition state to yield the acid and liberate isobutylene as a side product. Significantly, this is a chemical-free approach that excludes the possibility of cleavage of the polymer brush through acidolysis of the ester linkage in the immobilized initiator layer. We characterized the product of the reaction using ATR-FTIR, contact angle analysis, ellipsometry, and XPS.

The appearance of the broad peak at ≈2900−3400 cm^{-1} is reflective of the OH functionality of the brush, while the loss of the CH$_3$ stretch and the methyl deformation doublet indicates the loss of the *tert*-butyl group. The decrease in both the advancing and receding contact angles shows that the brush now possesses a lower surface energy due to the loss of the hydrophobic *tert*-butyl functionality and formation of acid groups that produce a more wettable, hydrophilic surface. The thickness change (of nearly half the brush height) corresponds to the loss of the mass of the $-C(CH_3)_3$ groups within the brush and agrees with literature values.[3] Upon comparison of the thickness change in our work with that found by Wu et al.,[3] we find that the pyrolysis reaction proceeded to 85 ±7 %, accounting for the accuracy of the measurement. Finally, XPS data (not shown) show a change in the surface composition of 77.5:22.5 (C:O) to 69:28 (C:O) upon the pyrolysis reaction. This correlates to the decrease in the amount of carbon in the film with respect to oxygen upon transformation of the *tert*-butyl ester to the acid. These four separate characterization techniques demonstrate that the pyrolysis of a *tert*-butyl ester to a carboxylic acid was successful within a polymer brush.

The expansion of the polyelectrolyte brush upon addition of base is an example of the well-known “polyelectrolyte effect”. Essentially, as the acid groups along the polymer backbone become deprotonated, the like charges experience Coulombic repulsions forcing the polymer to adopt an extended conformation, reflected by an increase in brush thickness.[36] At the point where the chain becomes fully ionized all of the counterions should remain trapped within the brush layer,[37] and the thickness of the brush will be determined by a balance between the swelling effect of the counterions and chain elasticity.[38,39] It was thus interesting to observe that at high pH values the brush appears to collapse. This can be explained by two potential mechanisms. First, at these high pH values, the ester group in the surface immobilized initiator may be hydrolyzing, resulting in the brush cleaving from the surface. A second mechanism could be as follows: As a fully ionized brush retains its counterions within the polymer layer to retain electroneutrality,[37] the addition of further ions (through continued addition of base) will have a similar effect to adding salt and induce chain collapse through screening of the charges along the polymer backbone, or alternatively, through a decrease in the Manning charge condensation layer.

The prior statement succinctly explains the results for the change in brush height in response to added electrolyte (Figures 3 and 4). In our experiment we began with a fully ionized brush and then swiftly transferred this extended brush into a salt solution of predetermined molarilty. We first examined the case of a monovalent salt, NaCl. As expected, upon addition of electrolyte the brush contracts from 22 to 17 nm where upon addition of further salt has no effect. This agrees well with molecular dynamics simulations where the end-to-end distance of a polyelectrolyte chain was modeled against the inverse Debye length.[40] The end-to-end distance was seen to decrease until it reached a neutral chain value where upon addition of further salt had a negligible effect. The molecular dynamic studies suggest the ionic density of counterions and salt ions about the chains determined the structure of the polyelectrolyte chains. Within the volume of the chain, the ion density increased as the electrolyte concentration increased; thus, the repulsions between monomers distant along the chain become increasingly screened, and the chains contract even when counterion condensation occurs. For flexible chains (we consider the polyelectrolyte brush studied in this paper to be relatively flexible, certainly with respect to polymers such as DNA), the Coulomb energy can be decreased by bending the chains and bring more oppositely charged particles closer together. The system entropy will increase since the chains have access to more conformations, thus increasing the free energy.

Figure 4 shows the collapse of the polymer brush height upon addition of a divalent counterion. The collapse of a polyelectrolye brush in a high salt concentration of divalent salts has been described previously, both experimentally[41] and theoretically.[42] Two points can be seen from the graph: First, the overall shape of the curve clearly resembles the case for the monovalent species; the brush collapses to a limiting value at which the addition of further electrolyte concentration has no discernible effect. Second, the collapse in brush height occurs faster than for NaCl. (It should be remembered here that the curves in Figures 3 and 4 are only intended as guides for the eye.) The increased rate of collapse is expected, as the counterions now possess a +2 charge. Simplistically, this can be rationalized in terms of increased modes of counterion condensation, e.g., between single *mer* units, two units on the same chain, or two units on separate chains.

Conclusions

We have reported a facile route to controlled poly(acrylic acid) brushes from a planar silica surface utilizing a chemical free deprotection strategy of poly(*tert*-butyl acrylate). Namely, we have used the pyrolysis reaction of *tert*-butyl esters to produce a carboxylic acid and isobutylene as a side product. Upon transformation of the ester to the acid there was a decrease in film thickness and surface energy of the film as evidenced by ellipsometry and water contact angle analysis. The success of the reaction was further confirmed by ATR-FTIR and XPS spectroscopy. Furthermore, we have shown the responsive nature of these brushes to stimuli such as pH and electrolyte concentration.

Acknowledgment. This work was supported by the National Science Foundation (DMR-0423786 and DMR-0353746 (The University of Akron REU site, The Department of Polymer Science)), and the authors thank Dr. Wayne Jennings at CWRU MATNET Surface Analysis Center for the XPS data.

References and Notes

(1) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31.
(2) Milner, S. T. *Science* **1991**, *251*, 905.
(3) Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Ruhe, J. *Polymer Brushes: Synthesis, Characterization, Applications*, 2004.
(4) Mayes, A. M.; Kumar, S. K. *MRS Bull.* **1997**, *22*, 43.
(5) Granville, A. M.; Brittain, W. J. *Macromol. Rapid Commun.* **2004**, *25*, 1298.
(6) Ito, Y.; Park, Y. S.; Imanishi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 2739.
(7) Ito, Y.; Nishi, S.; Park, Y. S.; Imanishi, Y. *Macromolecules* **1997**, *30*, 5856.
(8) Park, Y. S.; Ito, Y.; Imanishi, Y. *Chem. Mater.* **1997**, *9*, 2755.
(9) Kong, X.; Kawai, T.; Abe, J.; Iyoda, T. *Macromolecules* **2001**, *34*, 1837.
(10) Moya, S.; Azzaroni, O.; Farhan, T.; Osborne, V. L.; Huck, W. T. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 4578.
(11) Tugulu, S.; Arnold, A.; Sielaff, I.; Johnsson, K.; Klok, H.-A. *Biomacromolecules* **2005**, *6*, 1602.
(12) Jusufi, A.; Likos, C. N.; Ballauff, M. *Colloid Polym. Sci.* **2004**, *282*, 910.
(13) Boyes, S. G.; Akgun, B.; Brittain, W. J.; Foster, M. D. *Macromolecules* **2003**, *36*, 9539.
(14) Zhao, B.; Brittain, W. J. *Macromolecules* **2000**, *33*, 8813.
(15) Granville, A. M.; Boyes, S. G.; Akgun, B.; Foster, M. D.; Brittain, W. J. *Macromolecules* **2004**, *37*, 2790.
(16) Boyes, S. G.; Brittain, W. J.; Weng, X.; Cheng, S. Z. D. *Macromolecules* **2002**, *35*, 4960.
(17) Ohno, K.; Morinaga, T.; Koh, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2005**, *38*, 2137.
(18) Zhou, F.; Jiang, L.; Liu, W.; Xue, Q. *Macromol. Rapid Commun.* **2004**, *25*, 1979.
(19) Li, H.; Zhang, H.; Xu, Y.; Zhang, K.; Ai, P.; Jin, X.; Wang, J. *Mater. Chem. Phys.* **2005**, *90*, 90.
(20) Pyun, J.; Kowalewski, T.; Matyjaszewski, K. *Polym. Brushes* **2004**, 51.
(21) Iwata, R.; Suk-In, P.; Hoven, V. P.; Takahara, A.; Akiyoshi, K.; Iwasaki, Y. *Biomacromolecules* **2004**, *5*, 2308.
(22) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem. Soc. Rev.* **2004**, *33*, 14.
(23) Zhao, B.; Brittain, W. J. *Prog. Polym. Sci.* **2000**, *25*, 677.
(24) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
(25) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.
(26) Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716.
(27) Zhang, Q.; Remsen, E. E.; Wooley, K. L. *J. Am. Chem. Soc.* **2000**, *122*, 3642.
(28) Ma, Q.; Wooley, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4805.
(29) Cheng, G.; Boeker, A.; Zhang, M.; Krausch, G.; Mueller, A. H. E. *Macromolecules* **2001**, *34*, 6883.
(30) Francis, R.; Lepoittevin, B.; Taton, D.; Gnanou, Y. *Macromolecules* **2002**, *35*, 9001.
(31) Burguiere, C.; Chassenieux, C.; Charleux, B. *Polymer* **2002**, *44*, 509.
(32) Osborne, V. L.; Jones, D. M.; Huck, W. T. S. *Chem. Commun.* **2002**, 1838.
(33) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1947**, *2*, 1.
(34) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.
(35) Klemm, L. H.; Antoniates, E. P.; Lind, C. D. *J. Org. Chem.* **1962**, *27*, 519.
(36) Biesalski, M.; Johannsmann, D.; Ruhe, J. *J. Chem. Phys.* **2002**, *117*, 4988.
(37) Seidel, C. *Macromolecules* **2003**, *36*, 2536.
(38) Pincus, P. *Macromolecules* **1991**, *24*, 2912.
(39) Santangelo, C. D.; Lau, A. W. C. *Eur. Phys. J. E* **2004**, *13*, 335.
(40) Stevens, M. J.; Plimpton, S. J. *Eur. Phys. J. B* **1998**, *2*, 341.
(41) Zhang, Y.; Tirrell, M.; Mays, J. W. *Macromolecules* **1996**, *29*, 7299.
(42) Zhulina, E. B.; Borisov, O. V.; Birshtein, T. M. *Macromolecules* **1999**, *32*, 8189.

MA052001N