Synthesis of Fluorous, Block−Brush Copolymers Containing Vinylidene Fluoride, Styrene, and Ethylene Oxide Blocks

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Macroscopic properties of polymeric materials largely depend on the macromolecular architecture of the constituent polymers. Design and synthesis of well-defined segmented copolymers (e.g., block and graft copolymers), which self-assemble into nanostructured morphologies, have attracted increasing interest in polymer science. Block segments may be chosen to have distinctly different physicochemical attributes—hydrophilic/hydrophobic, flexible/rigid, crystalline/amorphous[1−3]—which endow the resulting copolymer with intrinsic physical and chemical properties. Generally, graft copolymers exhibit similar features to block copolymers, with the addition that branched structures possess a lower melt viscosity, for a given molecular weight, which is advantageous for processing.

The use of macromonomers is a convenient method for preparing branched polymers.[4] However, graft copolymers obtained by conventional radical copolymerization of macromonomers often exhibit poorly controlled molecular weights and high polydispersities as well as large compositional heterogeneities from chain-to-chain. In contrast, the development of "living"/controlled radical polymerization has facilitated the precise synthesis of well-defined polymers with low polydispersities in addition to enabling synthetic chemists to prepare polymers with novel and complex architectures. In this context, atom transfer radical polymerization (ATRP), in which dormant halogenated initiators or chain ends are reversibly activated by transition metal complexes catalyst via halogen atom transfer, has attracted notable attention.[5]

Fluorous polymers possess low surface energy, high thermal and chemical stability, a low refractive index and dielectric constant, and good solubility in supercritical CO_2.[6−8] Semifluorous block copolymers, which combine the self-assembly characteristics of block copolymers with the unique properties of fluoropolymers,[9] have potential applications as surface modifiers[10] or surfactants for supercritical CO_2 processing.[11] Recently, Hillmyer et al. successfully synthesized two such kinds of styrene-based semifluorinated block copolymers by ATRP: one class with a perfluoroether pendent group and another with a perfluoroalkyl group. Small-angle X-ray scattering and differential scanning calorimetry (DSC) indicate distinct microphase separation of the block copolymers in the solid state.[12] More recently, Zhang and Russell reported the grafting of polystyrene (PS) and poly(*tert*-butyl acrylate) (P*t*BA) from poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) (P(VDF-*co*-CTFE)) using ATRP.[13] An established class of fluorous copolymer, perfluorosulfonated ionomers, such as Nafion, possess a perfluorinated backbone and pendent acidic functional side groups that phase-separate to yield highly (ionically) conductive materials and are widely used as proton conductive media in PEM fuel cells.[14,15] Previously, our group has used ATRP to prepare poly(vinylidene fluoride-*co*-hexafluoropropene) (P(VDF-*co*-HFP)) and sulfonated polystyrene block copolymers, (P(VDF-*co*-HFP)-*block*-SPS). Membranes formed from these materials exhibit a nanophase phase-separated morphology and high proton conductivity.[16,17]

ATRP is a powerful method for the preparation of block copolymers. Similarly, ATRP has been employed for the polymerization of macromonomers,[18−24] although these generally employ highly reactive methacrylic and acrylic macromonomers and use small molecule ATRP initiators. In contrast, very few reports on the polymerization of macromonomers initiated by a macroinitiator exist. Moreover, to the best of our knowledge, reports of the ATRP of styryl-based macromonomers, which inherently possess lower reactivity, are sparse. Herein, we report on the polymerization of a styryl-PEO macromonomer (PEOVB) initiated by a fluorous diblock macroinitiator and subsequently the synthesis of novel fluorous, block−brush copolymers. Trichloromethyl-terminated poly(vinylidene fluoride-*co*-hexafluoropropene) macroinitiator, P(VDF-*co*-HFP)-CCl_3, was prepared, as previously reported, by emulsion polymerization using chloroform as a chain transfer agent.[25] The preparation of the macromonomer was carried out under N_2 by reaction of PEO550 (Fluka, DP_{PEO} ~11) with excess sodium hydride (NaH) in dry benzene to afford the alkoxide, which was subsequently reacted with a 5-fold excess of 4-vinylbenzyl chloride (VBC) at room temperature.[26]

Scheme 1 illustrates two approaches for the preparation of fluorous, block−brush copolymers. One route involves random ATR copolymerization of styrene with PEO macromonomer, initiated by the fluorous macroinitiator; the other uses a fluorous macroinitiator to sequentially initiate the ATR block copolymerization of styrene and PEO macromonomer.

Since chloro-based ATRP systems usually require high reaction temperature (130 °C), preliminary attempts to randomly copolymerize styrene with PEOVB (DP_{PEO} ~11) were conducted at 130 °C in *N*-methylpyrrolidinone (NMP) using CuCl/bpy as catalyst and P(VDF-*co*-HFP)-CCl_3 (number-average molecular weight (M_n), 6050 Da; polydispersity index (PDI), 1.58) as the macroinitiator. However, the copolymers obtained (M_n, 18 900 Da) possessed a high polydispersity index (PDI, 1.85), indicating "nonliving" radical polymerization behavior. When the polymerization temperature was decreased from 130 to 110 °C, and the reaction performed in a less polar solvent, *n*-butyl acetate (BA), the polydispersity index of the resultant polymer was reduced (M_n, 21 700 Da; PDI, 1.47). The resulting purified copolymer possessed a single gel permeation chromatography (GPC) peak, which had shifted to a higher molecular weight compared to the macroinitiator, as illustrated in Figure 1. ^{1}H NMR spectra of the macroinitiator and the resulting copolymer are shown in parts a and b of Figure 2, respectively. The groups of peaks centered at 3.0 ppm, corresponding to P(VDF-*co*-HFP) macroinitiator, are attributed to head−tail, head−head, and tail−tail structures of VDF sequences and to protons associated with HFP.[25] The same signature peaks are present in the copolymer (Figure 2b), but the copolymer possesses additional peaks at 6.5−7.4 ppm (aryl, 5H), 1.3−1.7 ppm (methylene, 2H), 1.8−2.0 ppm (benzylic, 1H), 3.3 ppm

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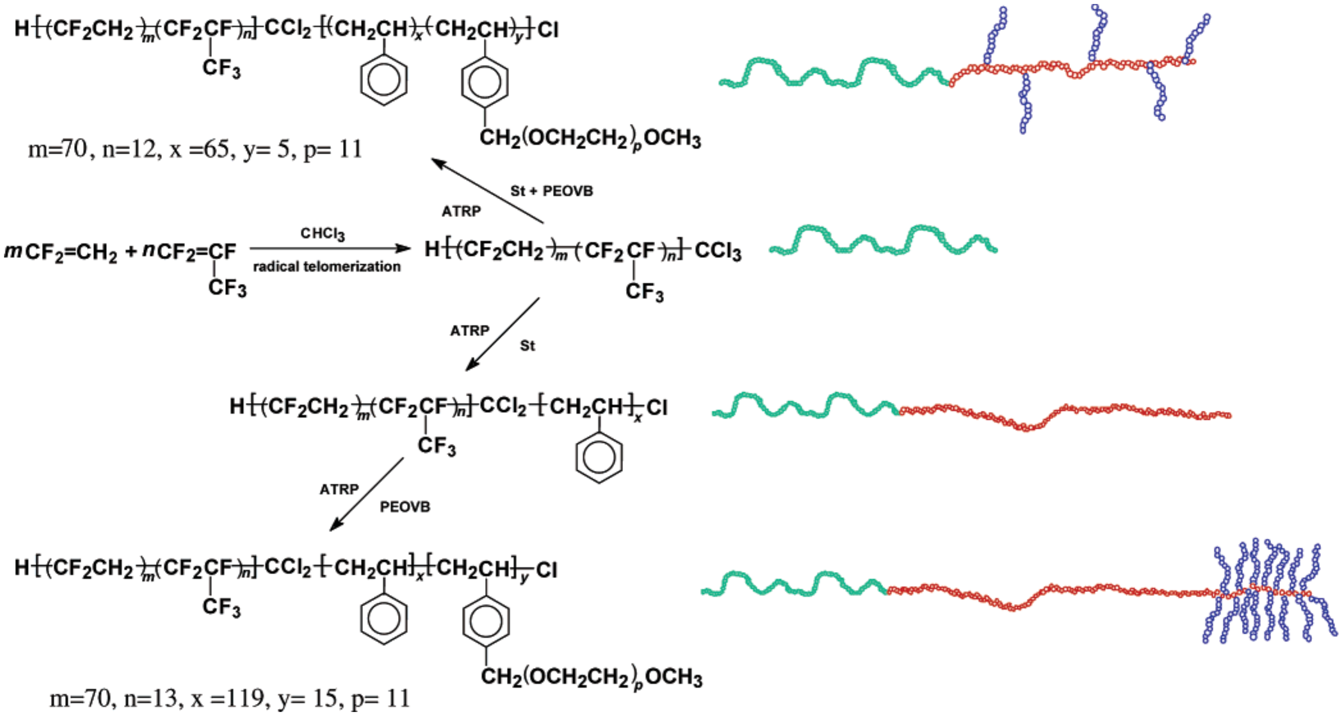
Scheme 1. Synthesis of Fluorous Block−Brush Copolymers via Fluorous Macroinitiators and ATRP of Styrene and PEO Macromonomer



(ether methyl, 3H), 4.5 ppm (benzyl methylene, 2H), and 3.6 ppm (polyoxyethylene, 44H). GPC and ^{1}H NMR spectroscopy confirm the formation of the block−brush copolymer P(VDF-*co*-HFP)-*block*-PS-*graft*-PEO. The compositional ratio of styrene to PEO was 70:30 (wt %) calculated from the ratio of NMR peak areas for aryl and oxyethylene groups. The molecular formula was estimated from a combination of GPC and NMR spectroscopic data to be P[(VDF)$_{65}$-*co*-(HFP)$_{12}$]-*block*-{(PS)$_{70}$-*graft*-[(PEO)$_{11}$]$_5$} which describes a polymer comprising of 65 units of VDF copolymerized with 12 units of HFP, the block of which is coupled to a random copolymer of styrene and styryl-PEO, which is equivalent to a styrenic main chain block 70 units long, onto which 5 blocks of PEO, each containing 11 oxyethylene units, are attached.

Sequential block copolymerization of styrene, followed by the styryl-PEO macromonomer, onto the fluorous macroinitiator, as indicated in Scheme 1 (lower Scheme), was more challenging due to the lower reactivity of the macromonomer and the added steric hindrance resulting from the high density of PEO side chains. The following synthetic procedure was found successful: Styrene was first polymerized onto P(VDF-*co*-HFP)-CCl$_3$ (M_n, 6500 Da; PDI, 1.69) as macroinitiator at 110 °C in BA using CuCl/bpy as catalyst. After 14 h, the diblock copolymer P(VDF-*co*-HFP)-*block*-PS was obtained and purified (M_n, 18 800 Da; PDI, 1.38). Macromonomer PEOVB (DP$_{\mathrm{PEO}}$ ∼11) was initiated by, and polymerized onto, the terminal unit of the above purified diblock copolymer, using CuCl/dNbpy. The macromonomer conversion reached 14.6% after 45 h. GPC curves of the macroinitiator, diblock, and block−brush copolymer are shown (Supporting Information). During polymerization, the block copolymers maintained a monomodal distribution and increased in molecular weight. The block−brush copolymer possessed a low polydispersity (PDI, 1.18). The molecular weight, 28 100 Da (M_n), measured by GPC using polystyrene standards, is lower than the theoretical value, 43 200 Da, calculated from the extent of macromonomer conversion and reflects that the densely grafted copolymers possess smaller hydrodynamic volumes than linear polymer standards.[27] The molecular formula was estimated from a combination of GPC and NMR spectroscopic data to be P[(VDF)$_{70}$-*co*-(HFP)$_{13}$]-*block*-{(PS)$_{119}$-*comb*-[(PEO)$_{11}$]$_{15}$} which describes a polymer comprising of 70 units of VDF copolymerized with 13 units of HFP, to which a block of 119 styrene units is attached, followed by a block of 15 styryl-PEO segments, each containing 11 oxyethylene units.

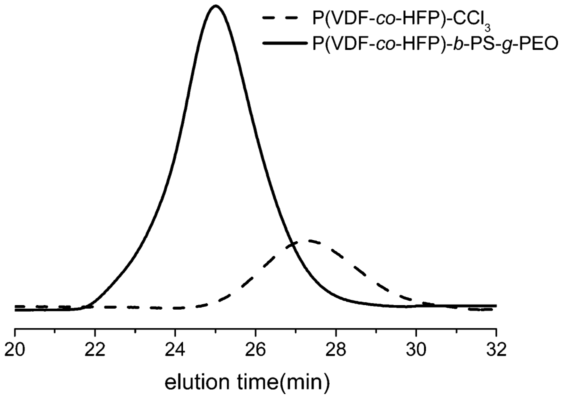


Figure 1. Gel permeation chromatography (GPC, RI detector) trace of trichloromethyl-terminated poly(vinylidene fluoride-*co*-hexafluoropropene) (P(VDF-*co*-HFP)-CCl$_3$) macroinitiator (dashed line, the curve is inverted for clarity) and the resulting block−brush copolymer P(VDF-*co*-HFP)-*block*-polystyrene(PS)-*graft*-poly(ethylene oxide) (PEO) (solid line). Polymerization conditions: $[\mathrm{S}]_0/[\mathrm{PEOVB}]_0/[\mathrm{macroinitiator}]_0/[\mathrm{CuCl}]_0/[2,2'\text{-bipyridyl}]_0 = 246/21.6/1/3.4/6.8$; $T = 110$ °C; $t = 64$ h.

Figure 3 shows atomic force microscopy(AFM) images of thin films of P(VDF-*co*-HFP)-*block*-PS-*graft*-PEO and P(VDF-*co*-HFP)-*block*-PS-*comb*-PEO spin-cast on mica from chloroform solution. Chloroform is a better solvent for the PS and PEO segments than for the fluorous segment. The latter are more quickly depleted of solvent during solvent evaporation which leads to elevated P(VDF-*co*-HFP) block domains (bright regions). The PS domains possess a higher surface energy than the fluorous domains, while the PEO block exhibits a prefer-

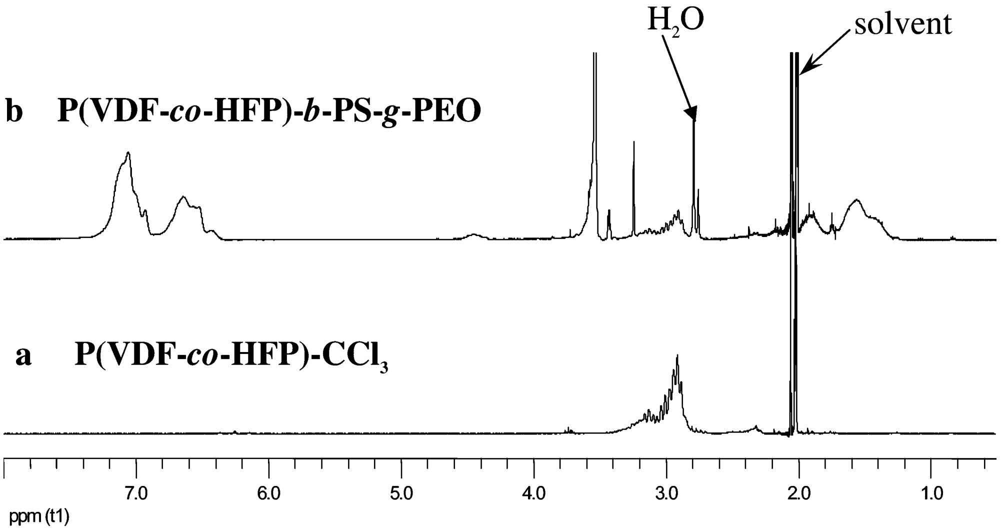


Figure 2. ^{1}H NMR spectra of trichloromethyl-terminated poly(vinylidene fluoride-*co*-hexafluoropropene) (P(VDF-*co*-HFP)-CCl_3) macroinitiator (a) and the resulting block−brush copolymer P(VDF-*co*-HFP)-*block*-polystyrene (PS)-*graft*-poly(ethylene oxide) (PEO) (b) (in acetone-d_6).

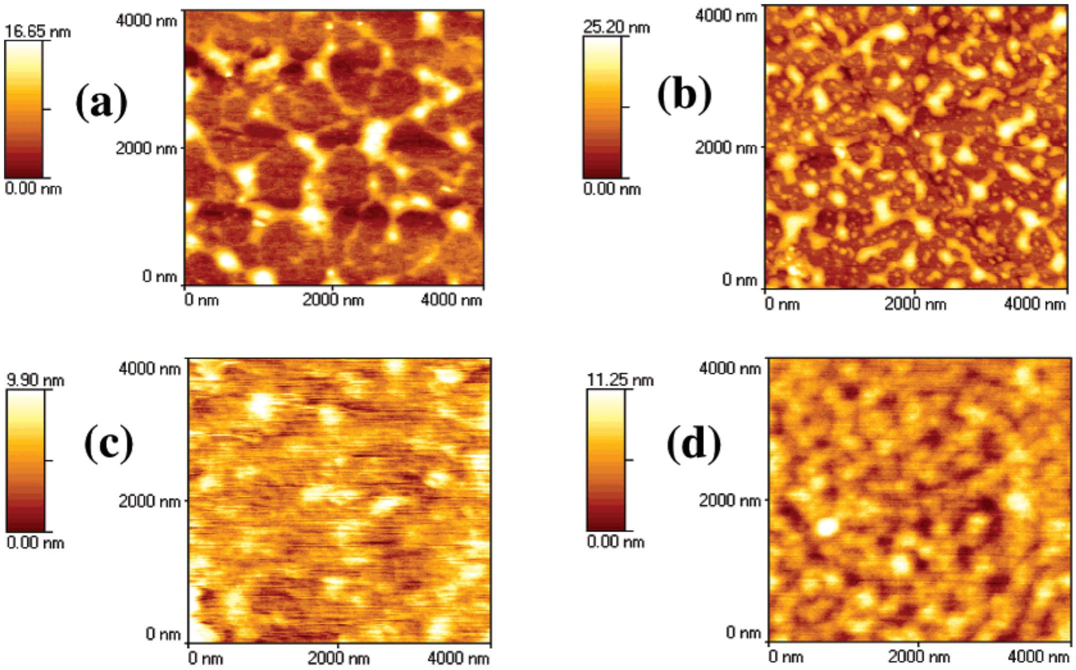


Figure 3. Atomic force microscopy (AFM) images of spin-cast films of poly(vinylidene fluoride-*co*-hexafluoropropene) (P(VDF-*co*-HFP))-*block*-polystyrene (PS)-*graft*-poly(ethylene oxide) (PEO): (a) before annealing; (b) annealed at 120 °C under vacuum for 2 h. AFM images of P(VDF-*co*-HFP)-*block*-PS-*comb*-PEO: (c) before annealing; (d) annealed at 120 °C under vacuum for 2 h.

ential interaction to the mica substrate due to its polar nature. Therefore, the depressed regions (dark regions) comprise largely of hydrophobic PS and hydrophilic graft PEO domains. The latter is believed to be located either underneath the PS or radially extended around the PS domains—further work is required to accurately clarify the morphology and will be the subject of a future report. In contrast, AFM images of the diblock copolymer macroinitiator P(VDF-*co*-HFP)-*block*-PS show a bicontinuous phase structure, not atypical for thin film copolymers (Supporting Information). Nevertheless, the "island in sea" morphology was also observed for a variety of graft and block copolymer systems, for example, poly(vinyl acohol)-*graft*-polystyrene.[28] Annealing the films at 120 °C leads to an increase in the topographical contrast and a change in surface morphology. P(VDF-*co*-HFP)-*block*-PS-*graft*-PEO evolves from a connected "island" morphology (Figure 3a) into a larger number of dispersed smaller fluorous domains (Figure 3b), presumably as a result of surface rearrangement and the migration of fluorous segments to the surface, as observed for other types of fluorous copolymers reported in the literature.[29] The block−comb-like copolymer P(VDF-*co*-HFP)-*block*-PS-*comb*-PEO possesses a smoother surface topography (Figure 3c,d) than the block−random graft structure for reasons that are not yet understood but most likely due to the increased regularity and periodic nature of the segments. Differential scanning calorimetry (DSC) measurements showed that both fluorous block−brush copolymers exhibit three glass transition temperatures (T_g). For the block−random graft copolymer, T_gs of fluorous, PEO, and polystyrene segments were −35, −89, and 36 °C, respectively. While for the comb copolymer, the corresponding T_gs were observed at −66, −102, and 46 °C. The T_gs of pure P(VDF-*co*-HFP) and PEO homopolymers were approximately −29 and −95 °C, respectively. The T_g of the PS segment in the copolymers is much lower than PS homopolymer ($T_g \sim 100$ °C) due to the PS domains being surrounded by low-T_g fluoropolymer and low-T_g PEO.

In summary, the combined use of a fluorous macroinitiator and ATRP of macromonomers provides a route to the synthesis of new types of fluorous, block−brush copolymers: (P(VDF-*co*-HFP)-*block*-PS-*graft*-PEO) and (P(VDF-*co*-HFP)-*block*-PS-*comb*-PEO). These preliminary studies may be extended through modification of the starting materials to prepare novel materials with low polydispersities, choice of backbone, control of side chain length, and sequential distribution, in addition to the incorporation of crystallizable or noncrystallizable side chains. Thermal analysis confirmed that the obtained ABC fluorous, block−brush copolymers possess three glass transition temperatures. A preliminary morphological study by AFM reveals that the block−brush copolymers exhibit appreciable nanophase separation, which changes upon annealing. Moreover, because of the presence of hydrophilic PEO domains, the above copolymers may exhibit interesting responses to the presence of water and changes in morphology—these topics are the subject of an ongoing investigation and will be reported separately.

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Supporting Information Available: Experimental procedures, methods of characterization, and preparation of PEOVB macromonomer. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Varghese, S.; Lele, A. K.; Srinivas, D.; Sastry, M.; Mashelkar, R. A. *Adv. Mater.* **2001**, *13*, 1544−1548.

(2) Luo, D.; Haverstick, K.; Belcheva, N.; Han, E.; Saltzman, W. M. *Macromolcules* **2002**, *35*, 3456−3462.

(3) Pispas, S.; Kioulafa, E. S.; Hadjichristidis, N.; Mavromoustakos, T. *Macromol. Chem. Phys.* **2002**, *203*, 1317−1327.

(4) Ito, K. *Prog. Polym. Sci.* **1988**, *23*, 581−620.

(5) (a) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615. (b) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990. (c) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3745.

(6) Wang, J.; Mao, G.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1997**, *30*, 1906−1914.

(7) Feiring, A. E.; Wonchoba, E. R. *Macromolecules* **1998**, *31*, 7103−7104.

(8) McHugh, M. A.; Park, I. H.; Reisinger, J. J.; Ren, Y.; Lodge, T. P.; Hillmyer, M. A. *Macromolecules* **2002**, *35*, 4653−4657.

(9) Hillmyer, M. A.; Lodge, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1−8.

(10) Iyengar, D. R.; Perutz, S. M.; Dai, C. A.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1996**, *29*, 1229−1234.

(11) McClain, J. B.; Betts, D. E.; Canelas, D. A.; Samulski, E. T.; DeSimone, J. M.; Londono, J. D.; Cochran, H. D.; Wignall, G. D.; Chillura, M. D.; Triolo, R. *Science* **1996**, *274*, 2049−2052.

(12) Radhakrishnan, K.; Switek, K. A.; Hillmyer, M. A. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 853−861.

(13) Zhang, M.; Russell, T. P. *Macromolecules* **2006**, *39*, 3531−3539.

(14) (a) Banerjee, S.; Curtin, D. E. *J. Fluorine Chem.* **2004**, *125*, 1211−1216. (b) Yang, Z. Y.; Rajendran, R. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 564−567. (c) Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535−4585.

(15) Souzy, R.; Ameduri, B. *Prog. Polym. Sci.* **2005**, *30*, 644−687.

(16) Shi, Z.; Holdcroft, S. *Macromolecules* **2005**, *38*, 4193−4201.

(17) Rubatat, L.; Shi, Z.; Diat, O.; Holdcroft, S.; Frisken, B. J. *Macromolecules* **2006**, *39*, 720−730.

(18) Roos, S. G.; Mueller, A. H. E.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 8331−8335.

(19) Shinoda, H.; Miller, P. J.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 3186−3194.

(20) Hong, S. C.; Jia, S.; Teodorescu, M.; Kowalewski, T.; Matyjaszewski, K.; Gottfried, A. C.; Brookhart, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2736−2749.

(21) Shinoda, H.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 6243−6248.

(22) Neugebauer, D.; Zhang, Y.; Pakula, T.; Sheiko, S. S.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 6746−6755.

(23) Yamada, K.; Miyazaki, M.; Ohno, K.; Fukuda, T.; Minoda, M. *Macromolecules* **1999**, *32*, 290−293.

(24) Deimede, V.; Kallitsis, J. K. *Chem.—Eur. J.* **2002**, *8*, 467−473.

(25) Shi, Z.; Holdcroft, S. *Macromolecules* **2004**, *37*, 2084−2089.

(26) Chao, D.; Itsuno, S.; Ito, K. *Polym. J.* **1991**, *23*, 1045−1052.

(27) (a) Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 9413−9415. (b) Neugebauer, D.; Zhang, Y.; Pakula, T.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 8687−8693.

(28) Pientka, Z.; Oike, H.; Tezuka, Y. *Langmuir* **1999**, *15*, 3197−3201.

(29) (a) Inoue, Y.; Watanabe, J.; Takai, M.; Ishihara, K. *J. Biomater. Sci., Polym. Ed.* **2004**, *15*, 1153−1166. (b) Park, I. J.; Lee, S. B.; Choi, C. K. *J. Appl. Polym. Sci.* **1994**, *54*, 1449−1454.

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