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Living Radical Polymerizations in Supercritical CO_2-Swollen Fluorinated Polymer Substrates

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Living radical polymerizations (LRPs) in supercritical CO_2-swollen polymer substrates were investigated. Atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) in supercritical CO_2-swollen polymer substrates produced interpenetration of PMMA chains in the mother polymer substrates. In addition, nitroxide-mediated polymerization (NMP) of styrene in supercritical CO_2-swollen polymer substrates resulted in interpenetration of polystyrene (PS) chains in the mother polymer substrates. The chain extensions of the penetrated PMMA chains by ATRPs of methacrylates were also performed. Chain extension ATRPs were carried out by immersing PMMA penetrated polymer substrate in a methanol solution for ATRP of another methacrylate. The chain extension was also successful. This is important for the development of the science and technology of polymer blends produced via living radical polymerizations.

Surface modification of soft matter, especially polymer materials, is important in order to obtain highly functionalized materials. Polymer materials can have many different surface properties. For instance, poly(tetrafluoroethylene) (PTFE) has extraordinarily low critical surface tension, on the other hand, some other polymers, e.g., poly(ethylene glycol) (PEG), possess high critical surface tension and are miscible to almost infinite dilution with water. If we could join them, the choices of the polymeric materials would be increased, however in most cases we need to employ expensive adhesive agents to join these two different types of surfaces because of the poor wettability between them. Because of the above-mentioned issues, surface modification of fluorinated polymer substrate by polymers is an important topic in polymer composites. The properties of PTFE, a common fluorinated polymer, are remarkable. It is known to be a typical corrosion resistant polymer. This means there is trade-off between corrosion resistance and poor wettability. This has made it difficult to make polymer composites including fluorinated polymers.

Watkins et al.,[1,2] proposed a promising new method to modify the surface of fluorinated polymers such as poly(chlorotrifluoroethylene) (PCTFE)[2] by free radical polymerization in supercritical CO_2 ($scCO_2$)-swollen PCTFE substrate. For example, free radical polymerization of styrene in $scCO_2$-swollen PCTFE substrate produced interpenetrated blends of polystyrene (PS) in a PCTFE surface (PCTFE-*intP*-PS). Because $scCO_2$ has high-diffusivity, mild critical temperature and pressure, and is chemically stable, it has been used as an efficient swelling agent and a medium for radical polymerization without causing serious damage to polymer materials undergoing $scCO_2$ swelling. Since application of $scCO_2$ as a reaction medium for free radical polymerizations has been well recognized to improve production and processing of polymers, especially for fluorinated polymers,[3] it is quite natural to combine $scCO_2$ impregnation and polymerization. The free radical polymerization in $scCO_2$-swollen polymer substrates enabled us to produce surface-modified fluorinated polymer without using any specific reagents.[4–6] $ScCO_2$ is well-known as a green solvent,[7] therefore further use may be attractive. In addition, $scCO_2$ is an atoxic fluid so $scCO_2$ impregnation may be applicable for treatment of biocompatible polymers.[8] These advantages have been utilized toward the most successful application of $scCO_2$, i.e., extraction of natural products, especially from foods, with high-efficiency and speed.[9]

Living radical polymerization (LRP) has been recognized as a powerful method to synthesize well-defined polymers with designed molecular weight, narrow polydispersity, defined end groups, and complex macromolecular architectures, such as comb, block, and star (co)polymers.[10] Especially for production of block copolymers and graft polymerization, LRP has been recognized as a powerful method to synthesize polymers with these unrivalled properties because of the wide range of available monomers and easier handling than other methods. Recently, it has become possible to obtain well-defined polymers with high molecular weight by applying high-pressure polymerization in LRPs,[11–14] Consequently, application of LRPs to $scCO_2$ impregnation polymerization may be a promising new development toward surface modification of polymer materials. Actually, performing LRP in $scCO_2$ have contributed to improved handling and synthesis of fluorinated polymers and their composites,[15–18] improvement of molecular weight control[19] and understanding of the reaction mechanism of reversible addition and fragmentation chain transfer (RAFT) polymerization.[20,21]

Here, we propose combining it with living radical polymerization (LRP), recognized as a powerful method to synthesize well-defined polymers,[10] to obtain highly functionalized polymer surfaces without using adhesives or causing serious damage to the surfaces.

Experimental

Materials. Styrene (99%, WAKO), methyl methacrylate (MMA, 99%, WAKO), and 2-hydroxyethyl methacrylate (HEMA, 99%, Aldrich) were purified by passing through a column filled with basic Al_2O_3. *N*-Isopropylacrylamide (NIPAM, 99%, WAKO) was used as received. The nitroxide-mediated polymerization (NMP) agent, 2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl benzoate (BS-TEMPO), was synthesized according to a procedure detailed by Hawker.[22] The purity of BS-TEMPO was better than 98% as verified by ^{1}H NMR analysis. Copper chloride (Cu^ICl, WAKO), 4,4′-dinonyl-2,2′-dipyridine (dNbipy, Aldrich), 2,2′-dipyridine (bipy, WAKO), and ATRP initiators, ethyl 2-bromoisobutyrate (EBIB, 98%, TCI) and methyl 2-chloropropionate (MCP, 96%, TCI), were used as received. Tris[2-(dimethylamino)ethyl]amine (Me_6TREN) was prepared as described in the literature.[23] Tetrahydrofuran (THF, HPLC grade, WAKO) and dimethylformamide (DMF, HPLC grade, WAKO) were used as eluents in size-exclusion chromatography. Methanol (dehydrated grade, WAKO), toluene (99%, WAKO), and hydroquinone (98%, WAKO) were used as received. The polymer blocks used in this study (poly(tetrafluoroethylene) (PTFE), fluorinated ethylene–propylene (FEP), perfluoroalkoxy polymer resin (PFA), poly(chlorotrifluoroethylene) (PCTFE), and Nylon 6 (Nylon) were all commercially available polymer plates or sheets purchased and used after cutting to adequate size (ca. $0.5 \times 0.5\,cm^2$).

Polymerizations. Sample preparations were carried out in a glove box purged with argon, and all chemicals were deoxygenated by argon bubbling before loading in the glove box. The polymerizing mixtures were prepared according to concentrations previously calculated. The concentrations for reaction mixtures with CO_2 were calculated from known mole fractions of monomer, and the other reagents were expanded to 6 mL with CO_2 under the assumption of a negligible excess volume of the mixture.

Polymerizations in $scCO_2$-swollen polymer substrates were carried out by the following procedure. 3 mL of the monomer, initiator, and catalyst solution was loaded into an autoclave (i.v. = 6 mL) together with polymer substrates which undergo impregnation and polymerization in the glove box. Then, the autoclave was sealed and loaded with CO_2 until the pressure reached 45 MPa using a HPLC pump (JASCO, SCF-Get) with a Peltier cooling device to condense gaseous CO_2 into liquid. Impregnation of monomer was performed at 35 °C for 2 h. Then, the polymerizations were carried out at scheduled temperature for scheduled time. After the scheduled reaction time passed, the autoclave was removed from the oil bath and depressurized by releasing CO_2 to terminate the polymerizations. 10 mL of 1 wt % hydroquinone/acetone solution was added to the polymerized solution to quench polymerization. The synthesized polymer was collected and the molecular weight distribution of the polymer was measured by gel permeation chromatography. The treated polymer substrates were immersed in toluene for 1 day to remove free polymer chains from the surfaces.

Chain extension polymerizations were carried out by the following procedure. Monomer, initiator, and catalyst were weighed and dissolved in methanol in the glove box. The polymer substrates which were interpenetrated with PMMA by $scCO_2$ swelling ATRP were immersed in the methanol solution, then the test tube was sealed and inserted to an aluminum block heater. After the scheduled time passed, the test tube was removed from the heater and brought outside of the glove box. 10 mL of 1 wt % hydroquinone/acetone solution was added to the polymerized solution to terminate polymerizations. The synthesized polymer was collected and the molecular weight distribution of the polymer was measured by gel permeation chromatography. The polymer substrates were immersed in methanol for 1 day to remove free polymer chains from the surfaces.

Characterizations. Attenuated total reflection Fourier transfer infrared (ATR-FTIR) spectrometry (Digilab, FTS-7000) was employed to measure ATR-FTIR spectra of polymer block surfaces. Transmission FTIR spectra were also measured (Jasco, FT/IR 680 plus) to examine whether synthesized polymer chains penetrated inside the mother fluorinated polymer substrates or not. Contact angle with nylon blocks and water was measured with a contact angle meter (Kyowa interface science, CA-D) and the contact angles listed in this study are averaged values of at least 5 measurements at different positions on the substrate. Field emission scanning electron microscopy (FE-SEM, Hitachi High-Technologies, S-4800) was employed to take images of polymer surfaces. Solution-state NMR was measured using a 400 MHz FT-NMR system (JEOL, JNM-ECX400) at 25 °C.

Gel permeation chromatographic (GPC) analysis was carried out at 35 °C on a JASCO GPC-900 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30-cm mixed columns (Shodex GPC KF-803L, exclusion limit: 7×10^4 and KF-805L, exclusion limit: 4×10^6), and a differential refractometer. Tetrahydrofuran (THF) was used as an eluent at a flow rate of $1\,mL\,min^{-1}$. The GPC system was basically calibrated with PS and PMMA standards (Polymer Standard Service, PSS-Kit, (PS): $M_p = 682\text{–}1.67 \times 10^6$ D, (PMMA): $M_p = 102\text{–}9.81 \times 10^5$ D). In the case of DMF being used as an eluent, the column set was changed to a guard column (Shodex GPC KD-G), two 30-cm mixed columns (Shodex GPC KD-804, exclusion limit: 4×10^5 and KD-805, exclusion limit: 4×10^6), The flow rate was set to $1\,mL\,min^{-1}$ and the calibration was complemented by poly(ethylene oxide) standards (Polymer Laboratories, $M_p = 2.0 \times 10^3\text{–}1.0 \times 10^6$ D).

Results and Discussion

ATRP of Methyl Methacrylate (MMA) in $scCO_2$-Swollen Polymer Substrates. ATRP of MMA in $scCO_2$-swollen polymer substrates ($scCO_2$ swelling ATRP of MMA) was performed in order to check whether synthesized poly(methyl methacrylate) (PMMA) chains were interpenetrated in the mother polymer matrixes after the polymerization and formed stable surface modifier layer after washing by good solvents.

Because PMMA has strong IR absorption corresponding to stretching of ester groups, the determination of successfully interpenetration in the surface of the polymer blocks can be evaluated by attenuated total reflection Fourier transfer infrared (ATR-FTIR) spectroscopy. The polymer substrates (poly(tetrafluoroethylene) (PTFE), fluorinated ethylene–propylene (FEP), perfluoroalkoxy polymer resin (PFA), poly(chlorotrifluoroethylene) (PCTFE), and Nylon 6 (Nylon)) were treated by scCO$_2$ swelling ATRP of MMA. ATRP of MMA was performed using ethyl 2-bromoisobutyrate (EBIB) as an initiator and 4,4′-dinonyl-2,2′-dipyridine (dNbipy) stabilized Cu^{I}Cl (CuCl/dNbipy$_2$) as a catalyst. The concentration of EBIB, CuCl/dNbipy$_2$, and MMA was 1.0 mM, 5.1 mM, and 4.5 M, respectively. The conditions of impregnation were 35 °C, 45 MPa, and 2 h to restrict unfavorable polymerization. After impregnation, the temperature of the system was raised to 80 °C and kept there for 3 h. The scCO$_2$ swelling ATRP treated polymer blocks were immersed in toluene and stirred overnight. The modified polymer blocks were dried and stored in a vacuum oven maintained at 40 °C.

The molecular weight of the free PMMA synthesized simultaneously in the autoclave was $M_n = 120000\,\mathrm{g\,mol^{-1}}$ with $M_w/M_n = 1.16$. The monomer conversion of the polymerization was calculated from the weight ratio of residual monomer and synthesized polymer and was $X = 30\%$. It is common that M_n of synthesized polymer by LRPs is proportional to the monomer conversion of the system. In our case, the M_n value calculated from the conversion, $M_{n,theo}$, is $135000\,\mathrm{g\,mol^{-1}}$, this is close enough to the actual M_n value. The small discrepancy might be due to evacuation of the monomer during depressurizing. The gaseous monomer was lost with CO$_2$. By considering the facts that the molecular weight distribution of the free PMMA synthesized was smaller than 1.2 and the discrepancy between actual M_n and $M_{n,theo}$ was not so large, it can be said that the polymerization performed had living polymerization characteristics.

The surface state of the modified polymer blocks was checked by ATR-FTIR spectroscopic analysis. Figure 1 depicts the ATR-FTIR spectra of polymer substrates before and after scCO$_2$ swelling ATRP of MMA. It is clearly seen that the spectrum of treated substrates showed a peak corresponding to C=O stretching of the ester group of PMMA around 1700 cm^{-1}. In addition, the spectra of the treated polymer substrates also showed absorption signals around 2800–3000 cm^{-1} due to C–H stretching modes. These facts suggest the successful interpenetration of PMMA for FEP, PFA, PCTFE, and Nylon substrates. However no signal corresponding to PMMA was seen for the PTFE substrate.

In order to elucidate whether synthesized polymer chains penetrated the mother fluorinated polymer substrates, transmission FTIR spectra of the fluorinated polymers were also measured. Since fluorinated polymers are transparent to IR radiation in the range of 2650–4300 cm^{-1}, the deeply penetrated polymer chains in the fluorinated polymer substrates can be detected by transmission FTIR. As shown in Figure 2, one can clearly see the peaks corresponding to C–H stretching modes in the spectrum of treated PTFE.

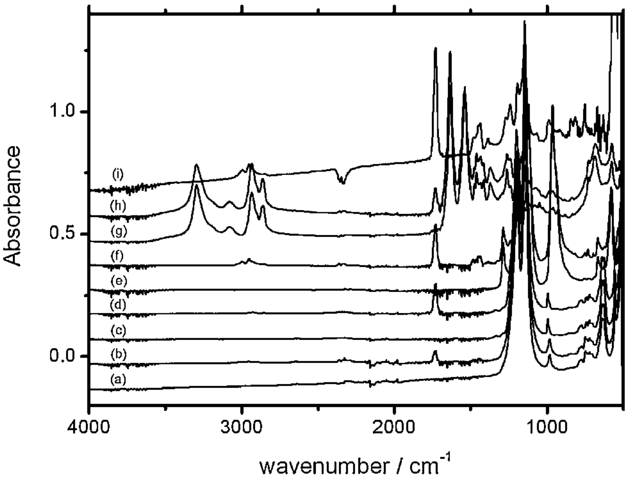

Figure 1. ATR-FTIR spectra of polymer substrates. (a) Untreated FEP, (b) scCO$_2$ swelling ATRP treated FEP, (c) untreated PFA, (d) scCO$_2$ swelling ATRP treated PFA, (e) untreated PCTFE, (f) scCO$_2$ swelling ATRP treated PCTFE, (g) untreated Nylon, (h) scCO$_2$ swelling ATRP treated Nylon, and (i) bulk PMMA substrate.

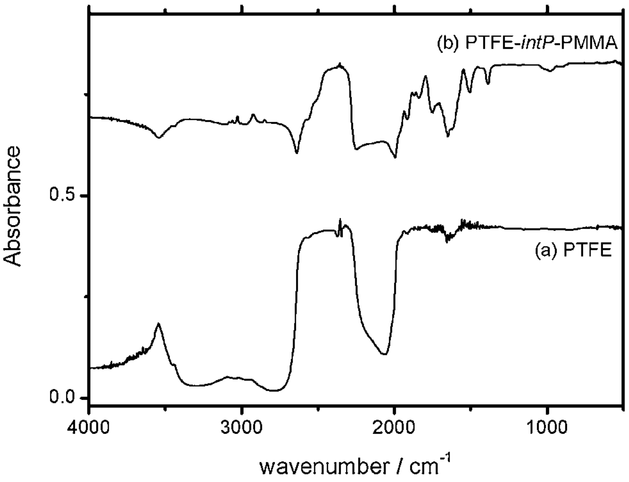

Figure 2. Transmission FTIR spectra of PTFE blocks. (a) Untreated and (b) the scCO$_2$ swelling ATRP of MMA treated. The spectrum (b) is the differential spectrum of treated and untreated substrates whereas the spectrum (a) is not. As one can see in the spectrum (a), PTFE is transparent in the regions 4300–2600 and 2250–2000 cm^{-1}. We only used the absorption spectrum in the range of 2650–4300 cm^{-1} to elucidate the penetration of PMMA. The transmission FTIR absorption spectrum in the range of 2650–500 cm^{-1} was not considered for discussion because all the polymer blocks used in this study were not transparent in the region. Actually, as one can see in the spectrum of PTFE, the absorbance is saturated in the range of 2650–500 cm^{-1}.

The next question was the extent of penetration of PMMA chains generated by the scCO$_2$ swelling ATRP of MMA. The ATR-FTIR spectrum of PTFE after reaction did not exhibit any peaks corresponding to PMMA, however the transmission FTIR spectrum did. This may imply the shallowly penetrated PMMA chains were torn off from the PTFE surface, although the deeply penetrated PMMA chains were not. We briefly examined whether the treatment totally blended the mother

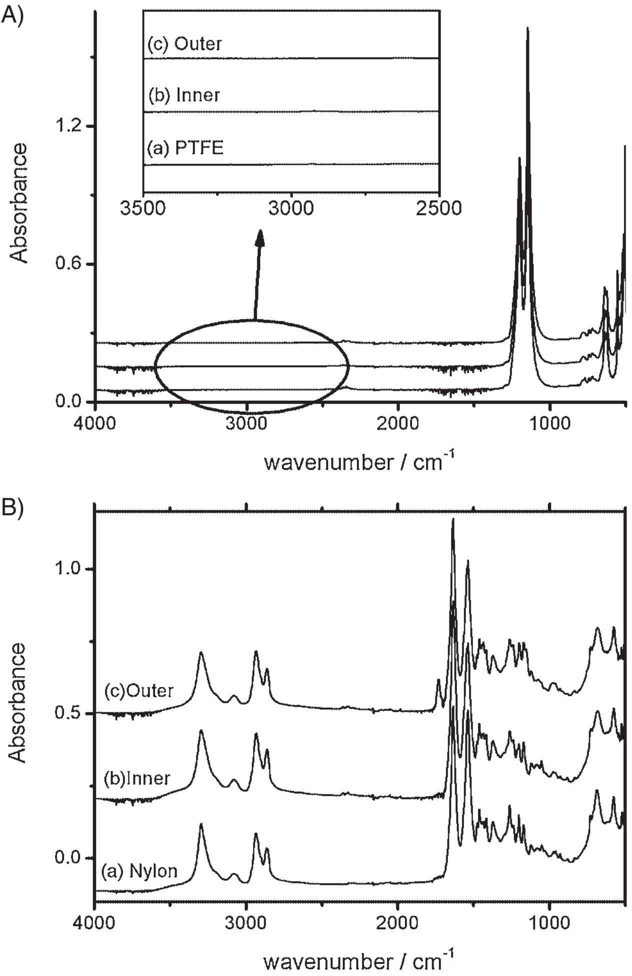

Figure 3. (A) ATR-FTIR spectra of PTFE blocks. (a) Untreated, (b) the inside of $scCO_2$ swelling ATRP of MMA treated, and (c) the surface of $scCO_2$ swelling ATRP of MMA treated. (B) ATR-FTIR spectra of Nylon blocks. (a) Untreated, (b) the inside of $scCO_2$ swelling ATRP of MMA treated, and (c) the surface of $scCO_2$ swelling ATRP of MMA treated.

polymer and PMMA. A PTFE and Nylon block were split into two pieces at the middle thickness of the blocks after treatment. The thickness of the PTFE and Nylon blocks before dividing were 2 mm. ATR-FTIR spectra were measured for the freshly produced surfaces. Figure 3 displays ATR-FTIR spectra of the PTFE (A) and Nylon (B) blocks before and after the division. We can see neither ester C=O peaks nor C–H peaks in the spectrum of the newly produced (inner) Nylon and PTFE surfaces. If the PMMA was totally blended with the PTFE and Nylon blocks, these peaks due to PMMA should appear in the spectra (b) shown in Figure 3. From this, it is suggested that the penetration of synthesized PMMA chains were limited to the surface area of the polymer blocks, probably from the surface to tens of micrometers inside the polymer substrates. This is what we intended to do. The impregnation polymerization was successfully achieved by surface modification of polymer substrates not by blending the polymers. The reason there is no PMMA was detected on the treated PTFE surface would be smaller affinity between PTFE and PMMA than that between Nylon and PMMA. The peak intensity of C=O stretching of PMMA on each polymer substrate detected by ATR-FTIR directly reflects the amount of shallowly penetrated PMMA, i.e., it can be a scale of the affinity between mother polymer substrate and PMMA and the extent of the swelling by $scCO_2$. According to the interfacial energy of the polymer substrates and PMMA, the assumption can be supported because the interfacial energy discrepancy between PTFE and PMMA was the largest of all the combinations.

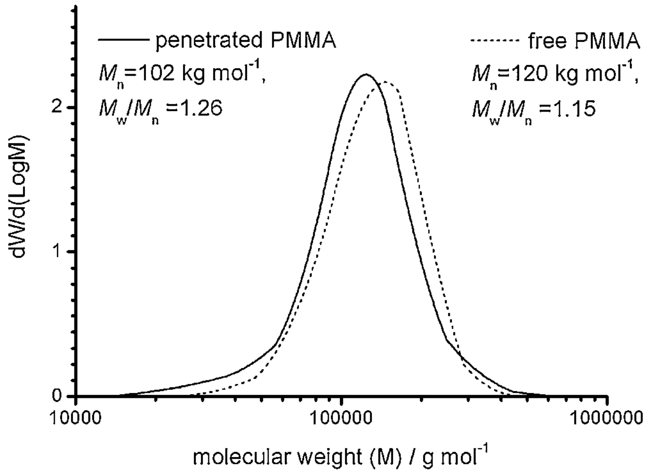

Figure 4. The molecular weight distributions of the PTFE-penetrated PMMA and free PMMA synthesized by $scCO_2$ swelling ATRP of MMA.

The molecular weight of the penetrated PMMA chains was also examined. As mentioned above, the polymer chains initially penetrated in the polymer surface gradually eluted from the surface. The elution of PMMA was accomplished by 1 week immersion of the treated PTFE in toluene and chloroform. The eluted PMMA from the PTFE surface was collected and the molecular weight distribution measured by GPC. The molecular weight distributions of the eluted and free PMMA are depicted in Figure 4. The molecular weight of penetrated PMMA was $M_n = 102000\,\mathrm{g\,mol^{-1}}$ with $M_w/M_n = 1.26$. The mean number molecular weight of penetrated PMMA was slightly smaller than that of free PMMA. It is common that monomer concentration affects the rate of polymerization. The monomer concentration in PTFE matrix would be smaller than that in the $scCO_2$ solution. It is reasonable to believe the rate of polymerization and the molecular weight of the PMMA synthesized in PTFE matrix were smaller than those of the free PMMA chains simultaneously polymerized in solution. In addition, the peaks corresponding to aromatic C–H stretching were observed the transmission FTIR spectrum of the treated PTFE shown in Figure 2. This indicates some amounts of dNbipy were still trapped in the PTFE. The presence of ATRP catalyst implies that the ATRP of MMA also took place in the PTFE matrix. According to these results, it is suggested that the penetrated PMMA are a mixture of the PMMA chains synthesized in the PTFE matrix and synthesized outside and penetrated in the PTFE.

NMP of Styrene in $scCO_2$-Swollen Polymer Substrates. In the above sections, we examined ATRP of MMA in $scCO_2$-swollen polymer substrates. The next target was establishing

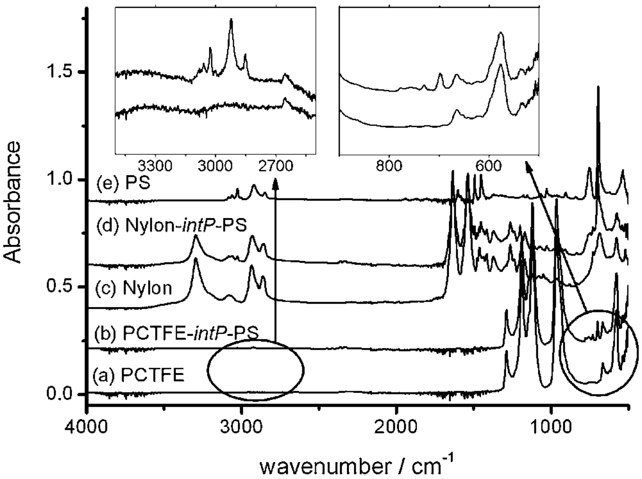

Figure 5. ATR-FTIR spectra of polymer substrates. (a) Untreated PCTFE, (b) scCO$_2$ swelling NMP treated PCTFE, (c) untreated Nylon, (d) scCO$_2$ swelling NMP treated Nylon, and (e) bulk PS substrate.

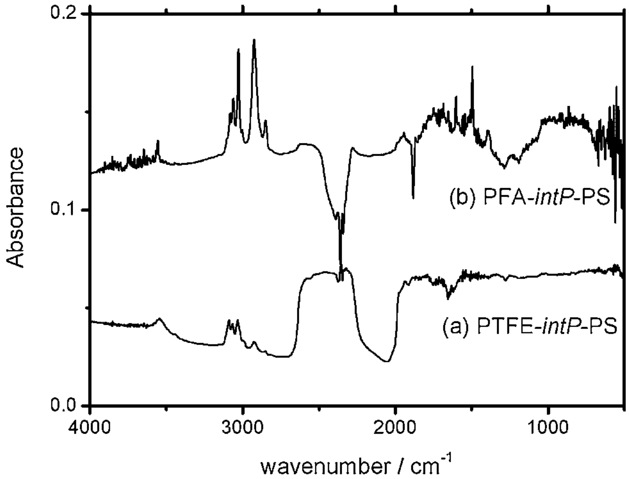

Figure 6. Transmission FTIR spectra of the scCO$_2$ swelling NMP of styrene-treated PTFE (a) and PFA (b) blocks. Both spectra are differential spectra of treated and untreated substrates.

NMP in scCO$_2$-swollen polymer substrates. We performed NMP of styrene in scCO$_2$-swollen polymer substrates. However it was rather difficult to identify the IR absorption peaks due to polystyrene (PS) chain interpenetrated in polymer substrates. The ATR-FTIR absorption spectrum of PS showed a strong peak at 700 cm^{-1} as shown in Figure 5e so we decided to check the existence of PS chain on the surface of the polymer substrates by comparing ATR-FTIR spectra around 700 cm^{-1} and of course, around 2700–3000 cm^{-1} where the absorption band of C–H stretching was seen before and after the treatment.

We performed scCO$_2$ swelling NMP of styrene using 2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl benzoate (BS-TEMPO) as an initiator. Just as the scCO$_2$ swelling ATRP of MMA, PTFE, FEP, PFA, PCTFE, and Nylon substrates were treated by the scCO$_2$ swelling NMP of styrene. The concentration of BS-TEMPO and styrene was 2.2 mM and 4.4 M, respectively. The conditions of impregnation were 40 °C, 45 MPa, and 3 h. After the impregnation, the temperature of the system was raised to 120 °C and kept for 2 h. The treated polymer blocks were cleaned by immersing in toluene with agitation overnight. The molecular weight of the free PS synthesized simultaneously in the autoclave was $M_n = 37000\,\mathrm{g\,mol^{-1}}$ with $M_w/M_n = 1.18$. The monomer conversion of the polymerization was calculated from the weight ratio of residual monomer and synthesized polymer and was $X = 26\%$. The same as ATRP of MMA, the M_n of PS synthesized by NMP should be proportional to the monomer conversion of the system. In this case, the M_n value calculated from the conversion, $M_{n,\mathrm{theo}}$, is $54000\,\mathrm{g\,mol^{-1}}$. This is a bit far from the actual M_n value, however styrene self-initiates polymerization at 120 °C. The actual initiator (macroradical) concentration in the NMP system would be higher than the initial concentration of BS-TEMPO. Therefore, the living characteristics of the polymerization should be checked by the molecular weight distribution. The molecular weight distribution of the free PS synthesized was smaller than 1.2 and the discrepancy between actual M_n and $M_{n,\mathrm{theo}}$ was not so large, hence it can be said that the polymerization performed had living polymerization characteristics.

After the modified polymer blocks were dried in a vacuum oven maintained at 40 °C for more than 1 day, ATR-FTIR spectra were measured. Figure 5 depicts the ATR-FTIR spectra of PCTFE and Nylon blocks before and after scCO$_2$ swelling NMP of styrene. We can clearly see the peaks around 700 cm^{-1} corresponding to the PS in the spectra of PCTFE and Nylon after the treatment. The left hand side inset of Figure 5 also shows an absorption band around 3000 cm^{-1}. It is small but the peaks due to C–H stretching of PS can be seen. Therefore, it can be said that successful modification was done to produce PCTFE-*intP*-PS and Nylon-*intP*-PS. Unfortunately, there was no peak observed corresponding to PS in the spectra of the other loaded polymer substrates. However, transmission FTIR spectra of the styrene-treated fluorinated polymers exhibited peaks corresponding to PS as the MMA-treated fluorinated polymer did. Figure 6 depicts the transmission FTIR spectra of the scCO$_2$ swelling NMP of styrene-treated PTFE and PFA. One can clearly see the peaks corresponding to C–H stretching modes in the spectrum of NMP of styrene-treated PTFE and PFA, i.e., all the fluorinated polymers which did not exhibit the PS peaks in the ATR-FTIR spectra. This implies the penetration of PS chains, however the PS chains in the interface was extracted by emersion in toluene.

The reason PS chains could not be found on PTFE, FEP, and PFA might be the small molecular weight of PS polymerized by the scCO$_2$ swelling NMP of styrene. When the molecular weight of penetrated PS is small, the penetrated PS chains can be easily eluted by toluene. Actually, the molecular weight of the free PS synthesized simultaneously in the autoclave was smaller than that of PMMA synthesized by the scCO$_2$ swelling ATRP of MMA. The temperature for the NMP was very close to most of the α transition temperatures of the fluorinated polymers e.g., PTFE: 126 °C, FEP: 70–126 °C, and PCTFE: 150 °C.[24] This implies the penetration could be easier in the scCO$_2$ swelling NMP of styrene than the scCO$_2$ swelling ATRP of MMA.

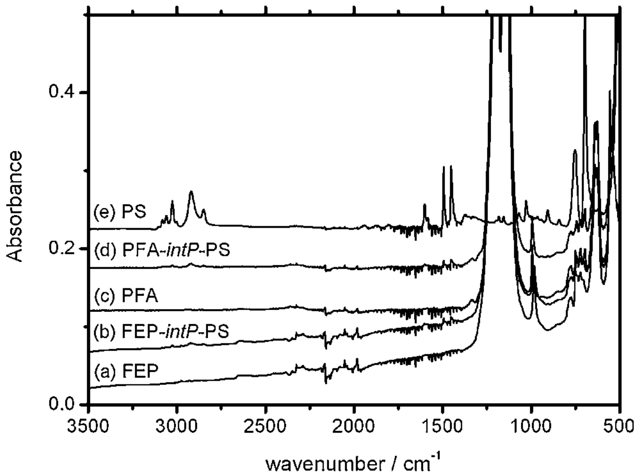

Figure 7. ATR-FTIR spectra of polymer substrates. (a) Untreated FEP, (b) $scCO_2$ swelling NMP treated FEP, (c) untreated PFA, (d) $scCO_2$ swelling NMP treated PFA, and (e) bulk PS substrate. Very small peaks due to interpenetrated PS in polymer substrates are seen around 3000–2700, 1500, and 700 cm^{-1} in spectra (b) and (d).

We thought that the reason we could not find interpenetrated PS chains on the PTFE, FEP, and PFA surfaces might be the smaller molecular weight of the PS. It can be said that longer PS chains can stay better with the polymer chains than shorter PS chains. In order to examine this, we increased polymerization time from 2 and 6 h to obtain larger molecular weighted PS in $scCO_2$ swelling NMP of styrene. The molecular weight of the free PS synthesized simultaneously in the autoclave was increased as $M_n = 92000\,\mathrm{g\,mol^{-1}}$ with $M_w/M_n = 1.25$. The monomer conversion of the polymerization was calculated from the weight ratio of residual monomer and synthesized PMMA and was $X = 58\%$. The M_n value calculated from the conversion, $M_{n,theo}$, was $121000\,\mathrm{g\,mol^{-1}}$, this is close enough to the actual M_n value when we consider the self-initiation of styrene as mentioned above and the molecular weight distribution of the free PMMA was still close to 1.2, it could be said that the polymerization kept living polymerization characteristics. Figure 7 depicts the ATR-FTIR spectra of FEP and PFA substrates before and after the 6 h of $scCO_2$ swelling NMP of styrene. Very small peaks due to interpenetrated PS in polymer substrates are seen around 3000–2700, 1500, and 700 cm^{-1} in the spectra of Figures 7b and 7d. This suggests the successful interpenetration of PS for FEP, PFA, PCTFE, and Nylon substrates. However no signal corresponding to PS is seen for the PTFE substrate at this time. It may require much larger molecular weight PS to remain in the PTFE substrate. The same thing can be said for $scCO_2$ swelling ATRP of MMA, if we synthesize larger molecular weight PMMA by $scCO_2$ swelling ATRP of MMA, the interpenetration of PMMA to PTFE can occur.

Chain Extension of Interpenetrated Polymer Chain. As mentioned in the introduction, if chain extension of interpenetrated polymer chains in mother polymer substrates is possible, we can increase the variety of the surface modifications of polymer materials. Because LRPs leave substituents which can re-initiate the LRP at chain ends of the synthesized polymer chains, one can extend the chains by the previously employed LRP. The graft polymerization of another monomer can also be possible so that the method will increase the combinations of surface polymer composites. Here, chain extension ATRP of *N*-isopropylacrylamide (NIPAM) and 2-hydroxyethyl methacrylate (HEMA) in methanol was performed.

The ATRP of NIPAM was carried out at 40 °C for 24 h in methanol solution. The concentration of methyl 2-chloropropionate (MCP, initiator), tris[2-(dimethylamino)ethyl]amine (Me_6TREN) stabilized Cu^ICl ($CuCl/Me_6TREN$, catalyst) and NIPAM was 53 mM, 53 mM, and 5.3 M, respectively. The untreated fresh PCTFE substrate was immersed together with a MMA penetrated PCTFE substrate in the solution for comparison. After the polymerization, the PCTFE substrates were immersed in methanol for 1 day to totally remove the free PNIPAM from the PCTFE blocks. The monomer conversion of the polymerization was calculated from the weight ratio of residual monomer and synthesized polymer and it was almost full conversion. The molecular weight of the free PNIPAM synthesized simultaneously in the methanol solution was analyzed by GPC. It was $M_n = 15000\,\mathrm{g\,mol^{-1}}$ with $M_w/M_n = 1.19$ according to standard PEO calibration. The same as ATRP of MMA, the M_n of PNIPAM synthesized by the ATRP should be proportional to the monomer conversion of the system. In this case, the M_n value calculated from the conversion, $M_{n,theo}$, is $11300\,\mathrm{g\,mol^{-1}}$. The discrepancy would be due to the calibration of the GPC measurement. Nevertheless, the molecular weight distribution of the free PNIPAM was smaller than 1.2. It can be said that the performed polymerization had living polymerization characteristics.

The ATRP-treated PCTFE blocks were dried and stored at 40 °C in a vacuum oven. The ATR-FTIR spectra were measured to check whether the chain extension polymerization was successful. As we can clearly see the difference in the ATR-FTIR spectra shown in Figure 8, the spectrum after the reaction have peaks corresponding to PNIPAM, i.e., a broad peak of N–H stretching around 3300 cm^{-1}, and two sharp peaks of amide C=O stretching at 1500–1700 cm^{-1}. This represents the successful extension of the interpenetrated PMMA by PNIPAM. The reference spectrum of the fresh PCTFE immersed in the extension ATRP of NIPAM (PCTFE-*immersed*-PNIPAM) exhibited quite small peaks of amide C=O stretching. Although the intensity of the peaks were incomparably smaller than that exhibited in the spectrum of the PCTFE-*intP*-PMMA-*b*-PNIPAM substrate. The transmission FTIR spectra of the PCTFE substrates were also measured and are displayed in Figure 9. No peak corresponding to N–H stretching (3300 cm^{-1}) of PNIPAM was observed in the reference spectrum of the PCTFE-*immersed*-PNIPAM. From the FTIR analysis, it can be said that negligible amounts of free PNIPAM chains synthesized in the ATRP solution shallowly penetrated the PCTFE surface. There are a series of reports that PMMA thin films can be swollen by methanol which is regarded as a poor solvent for PMMA.[25] In accordance with this information, it would be natural to believe that a quite small amount of PNIPAM chains shallowly penetrated the PCTFE surface. Therefore, the shallowly penetrated PNIPAM

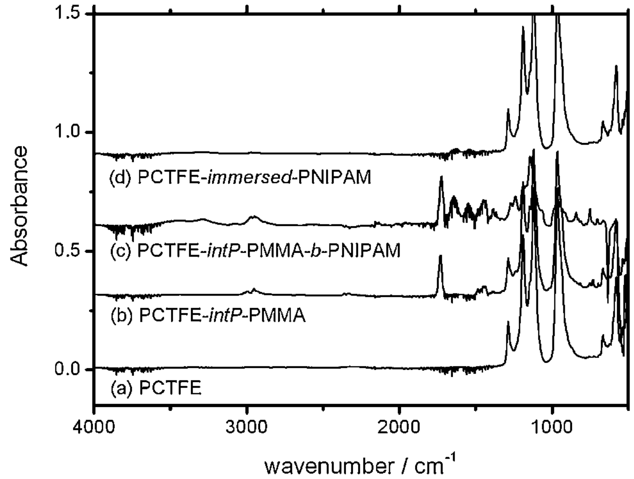

Figure 8. ATR-FTIR spectra of PCTFE substrates. (a) Untreated PCTFE, (b) scCO$_2$ swelling ATRP of MMA treated, (c) scCO$_2$ swelling ATRP of MMA subsequent chain extension ATRP of NIPAM treated, and (d) fresh PCTFE immersed in the ATRP of NIPAM solution. The peaks around 3300–3000 and 1650–1500 cm^{-1} in the spectrum (c) denotes the successful extension of the penetrated PMMA chains in PCTFE by PNIPAM was successful. The slight peaks around 1650–1500 cm^{-1} in the spectrum (d) denote that a quite small amount of PHEMA penetrated PCTFE (see text).

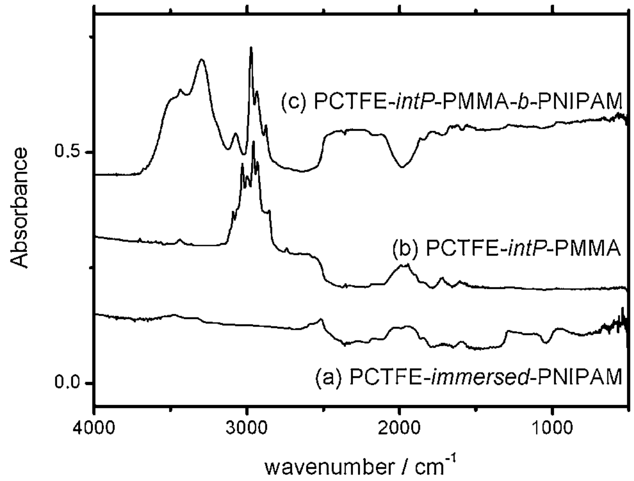

Figure 9. Differential transmission FTIR spectra of the PCTFE substrates between before and after surface modifications. (a) Fresh PCTFE immersed ATRP of NIPAM, (b) scCO$_2$ swelling ATRP of MMA treated PCTFE, and (c) scCO$_2$ swelling ATRP of MMA subsequent chain extension ATRP of NIPAM treated PCTFE.

in the PCTFE surface would be eluted by methanol as with the shallow penetration of PNIPAM. The contact angle measurement between water and PCTFE substrates was also performed in order to check the interface properties of the PCTFE. The contact angle (θ) was measured 10 times at different positions of the surfaces and averaged. The results are listed in Table 1. θ was obviously increased with modification of the PCTFE substrate by more hydrophilic polymers. This also supports the successful interpenetration of PMMA and extension by PNIPAM. The reason the θ of PCTFE-*intP*-PMMA was larger than that of PMMA could be the small molecular weight of PMMA. The surface of PCTFE was not fully covered by PMMA.

Table 1. Contact Angle (θ) between Water and Polymer Surfaces

No.	Substrate	Surface modification	θ/degree
1	PCTFE	None	94.0
2	Nylon	None	60.2
3	PMMA	None	63.6
4	Si wafer	Spin casted PHEMA	53.1
5	PCTFE	*intP*-PMMA	77.3
6	PCTFE	*intP*-PMMA-*b*-PNIPAM	65.2
7	Nylon	*intP*-PMMA	61.9
8	Nylon	*intP*-PMMA-*b*-PHEMA	58.5

In addition to the extension of interpenetrated PMMA in PCTFE, the extension of interpenetrated PMMA in Nylon substrate was also examined. Since the compatibility between PMMA and Nylon is better than that between PMMA and PCTFE, the chain end group of interpenetrated PMMA may be submerged deeper inside of the Nylon substrate than that in PCTFE. The Nylon-*intP*-PMMA was prepared by the scCO$_2$ swelling ATRP of MMA as described above. The interpenetration of PMMA in the Nylon was confirmed by ATR-FTIR analysis. The extension of interpenetrated PMMA in Nylon substrate was performed by ATRP of HEMA in methanol. The untreated fresh Nylon substrate was immersed together with a MMA penetrated Nylon substrate in the solution for comparison. The ATRP of HEMA was carried out at 40 °C for 4 h with the concentration of EBIB, CuCl/bipy$_2$, and HEMA being 22 mM, 25 mM, and 4.4 M, respectively. The ATRP of HEMA treated polymer blocks were immersed in methanol for 1 day to remove the free PHEMA. The monomer conversion of the polymerization was calculated from the weight ratio of residual monomer and synthesized PHEMA and was $X = 70\%$. The molecular weight of the free PHEMA synthesized simultaneously in the system was $M_n = 28000\,\text{g mol}^{-1}$ with $M_w/M_n = 1.22$ according to standard PEO calibration. The M_n value calculated from the conversion, $M_{n,\text{theo}}$, is 18200 g mol^{-1}, this is a bit far from the actual M_n value in this case, however the molecular weight distribution of the free PHEMA was still close to 1.2. This can be interpreted as the presence of living polymerization characteristics.

The modified Nylon block was carefully dried in a vacuum oven maintained at 40 °C for 1 day. It is difficult to identify the PHEMA on the Nylon-*intP*-PMMA by FTIR because the FTIR spectra of PMMA and PHEMA are similar. Therefore, we compared the contact angle with water and the Nylon blocks for checking the extension. The contact angles are also listed in Table 1. The contact angle was increased when PMMA was immobilized onto the Nylon surface and decreased again after PHEMA was further immobilized. From this result, the successful extension ATRP of HEMA from the end group of interpenetrated PMMA in the Nylon substrate was indicated.

Conclusion

ATRPs of MMA and NMP of styrene in supercritical CO_2-swollen polymer substrates (PTFE, FEP, PFA, PCTFE, and Nylon) were investigated. For all the mother polymer substrates tested in this study, the penetrations of PMMA and PS were possible. The penetration of the polymers was confirmed by transmission FTIR spectra. However, stable surface modifications were somewhat difficult. Except for PTFE, both ATRP of MMA and NMP of styrene could stably modify (penetrate) the synthesized polymer chains into the polymer surfaces. The PMMA and PS penetrated by $scCO_2$ swelling LRPs may be eluted by good solvents depending on the depth of the penetration and the molecular weight of the penetrated polymers. The ATR-FTIR spectra show that both the ATRP of MMA and NMP of styrene successfully produced PMMA- and PS-modified surfaces of the mother polymer substrates. In addition, there was not significant difference between the molecular weight distributions of penetrated PMMA and free PMMA. This may imply the penetrated PMMA was a mixture of the synthesized PMMA outside and inside of the mother polymer substrates. The possibility of the chain extension ATRP from the penetrated PMMA chains in PCTFE and Nylon were also investigated. Both ATRP of NIPAM from the chain end of PMMA penetrated into PCTFE in methanol and ATRP of HEMA from the chain end of PMMA penetrated into Nylon in methanol were performed. The ATR-FTIR spectrum indicates the extensions of interpenetrated PMMA chains were successful. The contact angle between water and the surfaces varied in incremental steps with immobilization of polymers. The results obtained in this study may indicate that the LRPs in $scCO_2$-swollen polymer surfaces are advantageous in designing of new polymer composites and surface modifications.

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References

1 J. J. Watkins, T. J. McCarthy, *Macromolecules* **1994**, *27*, 4845.

2 J. J. Watkins, T. J. McCarthy, *Macromolecules* **1995**, *28*, 4067.

3 J. M. DeSimone, Z. Guan, C. S. Elsbernd, *Science* **1992**, *257*, 945.

4 A. I. Cooper, *J. Mater. Chem.* **2000**, *10*, 207.

5 O. Muth, T. Hirth, H. Vogel, *J. Supercrit. Fluids* **2000**, *17*, 65.

6 Z. Liu, Z. Dong, B. Han, J. Wang, J. He, G. Yang, *Chem. Mater.* **2002**, *14*, 4619.

7 *Supercritcal Carbon Dioxide in Polymer Reaction Engineering*, ed. by M. F. Kemmere, T. Mayer, WILEY-VCH Verlag GmbH & Co. KGaA, **2005**.

8 T. Hoshi, T. Sawaguchi, R. Matsuno, T. Konno, M. Takai, K. Ishihara, *J. Supercrit. Fluids* **2008**, *44*, 391.

9 L. T. Taylor, *Supercritical Fluid Extraction (Techniques in Analytical Chemistry Series)*, New York, Wiley-Interscience Publication, **1996**.

10 For reviews: a) *Handbook of Radical Polymerization*, ed. by K. Matyjaszewski, T. P. Davis, New York, Wiley and Sons, **2002**. b) *ACS Symposium Series*, ed. by K. Matyjaszewski, Vol. 685, **1998**; *ACS Symposium Series*, ed. by K. Matyjaszewski, Vol. 768, **2000**; *ACS Symposium Series*, ed. by K. MatyjaszewskK, Vol. 854, **2003**; *ACS Symposium Series*, ed. by K. Matyjaszewski, Vol. 944, **2006**. c) C. J. Hawker, A. W. Bosman, E. Harth, *Chem. Rev.* **2001**, *101*, 3661. d) M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689. e) G. Moad, D. H. Solomon, *The Chemistry of Radical Polymerization*, Elsevier, Amsterdam, **2006**. f) W. A. Braunecker, K. Matyjaszewski, *Prog. Polym. Sci.* **2007**, *32*, 93. g) H. Fischer, *Chem. Rev.* **2001**, *101*, 3581. h) A. Goto, T. Fukuda, *Prog. Polym. Sci.* **2004**, *29*, 329.

11 T. Arita, M. Buback, O. Janssen, P. Vana, *Macromol. Rapid Commun.* **2004**, *25*, 1376.

12 T. Arita, Y. Kayama, K. Ohno, Y. Tsujii, T. Fukuda, *Polymer* **2008**, *49*, 2426.

13 J. Rzayev, J. Penelle, *Macromolecules* **2002**, *35*, 1489.

14 J. Rzayev, J. Penelle, *Angew. Chem., Int. Ed.* **2004**, *43*, 1691.

15 J. Xia, T. Johnson, S. G. Gaynor, K. Matyjaszewski, J. DeSimone, *Macromolecules* **1999**, *32*, 4802.

16 S. Villarroya, J. Zhou, C. J. Duxbury, A. Heise, S. M. Howdle, *Macromolecules* **2006**, *39*, 633.

17 J. Zhou, S. Villarroya, W. Wang, M. F. Wyatt, C. J. Duxbury, K. J. Thurecht, S. M. Howdle, *Macromolecules* **2006**, *39*, 5352.

18 B. Grignard, C. Jérôme, C. Calberg, R. Jérôme, C. Detrembleur, *Eur. Polym. J.* **2008**, *44*, 861.

19 F. Aldabbagh, P. B. Zetterlund, M. Okubo, *Macromolecules* **2008**, *41*, 2732.

20 T. Arita, B. Sabine, B. Michael, V. Philipp, *e-Polymers* **2004**, 003.

21 T. Arita, S. Beuermann, M. Buback, P. Vana, *Macromol. Mater. Eng.* **2005**, *290*, 238.

22 C. J. Hawker, J. L. Hedrick, *Macromolecules* **1995**, *28*, 2993.

23 M. Ciampolini, N. Nardi, *Inorg. Chem.* **1966**, *5*, 41.

24 D. L. Kerbow, C. A. Sperati, in *Polymer Handbook*, 4th ed., ed. by J. Brandrup, E. H. Immergut, E. A. Grulke, John Wiley & Sons, Inc., **1999**, Vol. 1, Chap. V, p. V/31.

25 K. Tanaka, Y. Fujii, H. Atarashi, K.-i. Akabori, M. Hino, T. Nagamura, *Langmuir* **2008**, *24*, 296.