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Synthesis of Ultrahigh Molecular Weight Poly(styrene-*alt*-maleic anhydride) in Supercritical Carbon Dioxide

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ABSTRACT: Radical copolymerization of styrene (St) and maleic anhydride (Man) was performed in supercritical carbon dioxide (SC CO_2) at 50−80 °C with 2,2′-azoisobutyronitrile as the initiator. A novel, ultrahigh molecular mass St−Man alternative copolymers ($M_w > 10^6$) has been synthesized. The NMR spectra demonstrated that the copolymers obtained possess strictly alternating structure. Aqueous solutions of the alternative copolymers exhibit lower critical solution temperatures (LCST). These LCST's are highly sensitive to changes in the molecular weight and pH. St/MAn copolymerization in SC CO_2 as the solvent yielded higher molecular weight products and more cis configuration linkage of cyclic MAn units in the copolymer chains than those made in common organic solvents. These facts demonstrate that SC CO_2 as the solvent plays an important role in the copolymerization of styrene with maleic anhydride, originating from the special intermolecular interactions between SC CO_2 and St−Man alternative copolymer.

Introduction

Considerable attention has been paid to the preparation of alternating copolymers from which special materials with different functionalities could be designed and manufactured.[1,2] In addition, the well-defined alternating copolymers (such as styrene-*alt*-maleic anhydride, styrene-*alt*-maleimide, etc.) exhibit unique properties such as superior thermal stabilities, fire resistance, photo-, X-ray, and E-beam sensitivities, catalytic and chiroptical activities, and extremely low band gap materials.[3−6] The alternating styrene−maleic anhydride copolymer, poly(St-*alt*-Man), is one of the most thoroughly investigated systems. The free radical copolymerization of styrene (St) and maleic anhydride (MAn) yields an alternating copolymer.[7−10] The mechanism of alternation was explained by the formation of a donor−acceptor complex between the two monomers.[11−13] However, there are other explanations for the alternation copolymerization.[14] The sequence distribution and stereochemistry of the St−Man copolymer have been investigated.[15−17] However, the molecular weights of the copolymers prepared by conventional free radical methods were too low to be used for structure materials. Moreover, their composition tends to shift to higher molar fraction of St as the polymer chain size increases.[18]

To prepare alternating copolymer of St and Man with controlled molecular weight and narrow molecular weight distribution, the controlled living radical copolymerization methods, such as atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT) process, have been applied to the copolymerization of St and Man.[19−21] However, they are all unsuccessful to prepare strictly alternating copolymer of St and Man despite the living nature of the copolymerization. Furthermore, low molecular weight and long reaction time limited the usefulness of this type of reaction process for industrial applications.[22]

The charge-transfer complex of St and MAn, favoring alternating copolymerization, has been verified by many researchers.[11−13,23] Low temperature, high pressure, and weak polarity can enhance the formation of the charge-transfer complex. Therefore, the supercritical carbon dioxide (SC CO_2) is a preferred alternative for the alternating copolymerization of St and MAn due to its nonpolarity, low dielectric constant, and unusually tunable versatile properties in solvent strength, viscosity, and so on.[24]

SC CO_2 can dissolve the comonomers of St and Man, but not for the copolymer of St and Man according to Beckman.[25] Therefore, St/Man copolymerization in SC CO_2 is precipitation polymerization, in which the locus of polymerization shifts to the interior of polymer particles with the increase of polymer chains. However, SC CO_2 can enhance the transportation of monomers into polymer particles due to its low viscosity and large swelling effects, resulting in high chain propagation rate. In addition, as the diffusion of the active polymer chains becomes restricted due to chain entanglements, the termination rate decreases. Consequently, the overall reaction rate increases, and the copolymers of high molecular weight are produced. The mechanisms of heterogeneous polymerizations in SC CO_2, for various monomer systems including methyl methacrylate and styrene, have been investigated by Desimone and O'Neill and Johnston.[26,27] Furthermore, SC CO_2 exhibits specific interactions with copolymers possessing electron-donating functional groups (e.g., carbonyl groups), which can lower the glass transition temperature and plasticize these copolymers.[28,29] Thus, the copolymerization of St and MAn conducted in the presence of SC CO_2 will reduce precipitation of the resulting alternative copolymer, consequently resulting in both higher yields and higher molecular weight poly(St-*alt*-Man).

Herein, we report the preparation of poly(St-*alt*-Man) with ultrahigh molecular weights in SC CO_2. The radical copolymerization of St and Man was performed in SC CO_2 with 2,2′-azoisobutyronitrile (AIBN) as the initiator. Gel permeation

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chromatography (GPC), matrix-assisted laser desorption ionization mass spectrometer (MALDI), and laser light scattering (LLS) were used to determine the molecular weight of the copolymers. It was shown that a novel St−Man copolymer with the molecular weight higher than 10^6 was obtained. The structure and properties of St−Man copolymers synthesized were derived from IR, chemical, and DSC analyses. The compositional analysis and the sequence structural information on the copolymer obtained from DEPT experiments of the ^{13}C NMR demonstrated that the copolymers obtained possess strictly alternating structure. St/MAn copolymerization in SC CO_2 as the solvent yielded higher molecular weight products compared to that in other organic solvents. These facts demonstrate that SC CO_2 as the solvent plays an important role in the copolymerization of styrene with maleic anhydride. SC CO_2 possesses properties that make them an attractive media for polymerization reactions. Conducting copolymerization reactions at supercritical conditions provides opportunities to manipulate the reaction environment (solvent properties) by changing pressure, thus to enhance the solubilities of monomers and copolymers and interphase transport of monmers. Moreover, the specific intermolecular interaction between SC CO_2 and St−Man copolymer was considered in the study. Poly(St-*alt*-MAn) with a ultrahigh molecular weight has not only excellent mechanical property, but also reactive anhydride groups for postfunctionalization. Morover, the novel copolymer exhibits desirable thermal and pH responsive properties and notable biocompatibility. The novel copolymer can be potentially useful for membrane fabrication, functionalization, and supermolecular assembly on membrane surfaces, which will be reported in later publications.

Experimental Section

Materials and Equipment. Styrene (St) was washed thrice with a 10% NaOH solution and thrice with water to remove inhibitor. It was stored at −10 °C after drying over calcium chloride. It was freshly distilled under reduced pressure before use. AIBN was recrystallized twice from absolute methanol. Maleic anhydride (MAn) was recrystallized thrice from chloroform. The solvents *N*,*N*-dimethylformide (DMF), tetrahydrofuran (THF), and diethyl ether were purchased in the anhydrous form. DMF was dried over 4 Å molecular sieves, and THF and diethyl ether were dried over sodium wires. Carbon dioxide (>99%) was kindly provided by Hangzhou Special Gas Factory and was used as received.

Copolymerizations of Styrene and Maleic Anhydride. Copolymerizations were conducted in SC CO_2 in a thermostated, 1 L stainless steel autoclave with an internal diameter of 8 cm. A magnetically coupled impeller was used to mix the contents of the reactor. The reactor was charged with 1.7×10^{-3} mol of AIBN, and then the system was purged with a flow of carbon dioxide prior to the addition of monomer. The desired amount of St/Man comonomers (St/Man ratio, 1:1) was then added to the system under a carbon dioxide blanket. An ISCO model no. 500D automatic syringe pump was used to pressurize the reactor with CO_2 to ∼32 MPa or below, and the reaction mixture was heated to 35 °C for 5 h in order to dissolve the comonomers and AIBN and then subsequently heated to 50−80 °C for copolymerization. As the reaction vessel was heated, the remaining CO_2 was added to the system, if needed, until the desired pressure was reached. Once the final reaction condition was obtained, the reaction was allowed to proceed under magnetic stirring for 6−20 h. At the end of the reaction, the reactor was cooled, and the CO_2 was slowly vented through a pressure let-down valve from the reactor before removal of the polymer product. To quantify the reaction yields, the reaction reactor was rinsed with DMF to remove any residual polymer product. The copolymers obtained were then reprecipitated from DMF solution into diethyl ether to obtain pure copolymers for the composition analysis. This procedure was repeated three times in the case of each sample. The product was then dried in a vacuum at 120 °C overnight. The copolymer conversion determined gravimetrically was more than 90% in all cases. The resultant copolymer exhibited a yellowish-white appearance.

Element Analysis. The element analysis of the copolymer was performed on a EA 1112, and the content of Man units in the copolymer was determined.

GPC Analysis. A Waters 150/C-AL gel permeation chromatograph (GPC) with three 950 mm MixB columns of linear, 103 Å, and 104 Å porosities and a 410 differential refractometer was used at 110 °C to determine the molecular weights and the molecular weight distributions. DMF was used as the mobile phase with a flow rate of 1.0 mL/min, and the instrument was calibrated using PS standards (narrow standard).

NMR. The ^{13}C NMR spectra of the copolymers were obtained on a Bruker AMX400 spectrometer using DMSO-d_6 or acetone-d_6 as the solvent and tetramethylsilane as the internal standard. Experiments on the copolymer samples were performed at 75.46 MHz using a recycle time of 2 s and a *J*-modulation time of 3.7 ms. ^{1}H and ^{13}C $\pi/2$ pulse times were 22 and 15 μs, respectively. DEPT subspectra were generated using the following combination[38] of the $\pi/4$ and $3\pi/4$ experiments: $CH_2 = (\pi/4) + 1.15\ (3\pi/4)$, together with the procedure used to calculate the styrene-centered sequence distributions from the CH_2 subspectrum.[30]

Fourier Transform Infrared Spetra. FT-IR spectra of the copolymer samples were recorded on a Bruker Vector 22 FT-IR spectrophotometer.

DSC Analyses. The thermal properties of the polymers were determined using a TA DSC Q100 calorimeter. Thermal history of the products was removed by scanning to 350 °C with the heating rate of 10 °C/min. After cooling the sample at the rate of 10 °C/min to room temperature, it was reheated at 10 °C/min to 300 °C, and the second scan DSC thermogram was obtained.

Measurement of LCST. The LCST's of St−MAn alternative copolymer solutions were measured using the cloud point method. LST 200 turbidimeter was used to trace the phase transition by monitoring the scattered ray of a white light beam at 90°. The turbidity of solution was recorded as NTU with formazine solution as standard. The phase transition temperature was defined as the inflection point of the NTU vs temperature curve, as determined by the maximum in the first derivative. The concentration of the polymer solutions was 0.5 wt %, and the heating rate was 1.0 °C min^{-1}.

Results and Discussion

Molecular Weight of St−Man Copolymers. The copolymerization of St with Man exhibits some interesting features. Man itself does not homopolymerize, and its copolymerization with St has a strong tendency toward alternation, indicated by the reported reactivity ratios.[31] Convincing evidence was published a few years ago indicating that the St/Man copolymerization obeys the charge-transfer-complex (CTC) model.[1] It was reported that there is an equilibrium between CTC, St, and Man, and the equilibrium constant (K_c) determines the manner of copolymerization.[12] $K_c < 0.01$ L/mol, no alternating copolymerization occurs, and the copolymerization proceeds randomly rather than in alternating manner; $K_c > 0.1$ L/mol, and free radical alternating copolymerization can occur easily, while $1 < K_c < 5$ L/mol, spontaneous ionic polymerization happens.[32] In addition, K_c is determined by the reaction temperature and solvents, which decreases with the increase of the temperature and the solvent polarity.[12,33]

However, there are stronger interaction and weaker mobility of chain segments owing to more polar groups (e.g., carbonyl group) in an alternative copolymer of styrene and maleic anhydride. The solubility of poly(St-*alt*-Man) in common solvents decreases dramatically with increasing molecular weight of the copolymer. Thus, the alternative copolymer chains are easily precipitated during the copolymerization of styrene and

Table 1. Radical Copolymerization of Styrene and Maleic Anhydride in Supercritical Carbon Dioxide[a]

no.	monomer concn (mol/L)[b]	polym solvent	polym temp (°C)	conv (%)	M_w (10^6 g/mol)	MWD	Man%[c]
1	0.5	SC CO_2	60	89.8	8.44 [d]	3.20	51.83
2	0.5	SC CO_2	70	91.5	4.59	2.58	51.48
3	0.5	SC CO_2	80	92.6	1.99 (1.46)[e]	2.52	50.21
4	0.5	butanone	70	92.8	0.049 (0.045)	2.45	49.46
5[f]		DMF	60	28	0.011	2.3	48.0
6[g]		decalin	60	55.7	0.0039		50.5
7[g]		DMB	60	50.4	0.0037		49.24

[a] Polymerization was carried out with SC CO_2 as the solvent at 20.5 MPa pressure and AIBN 0.0017 mol/L, except no. 4 in which the solvent is butanone. [b] Total monomer concentration, St/MAn mol ratio 1:1. [c] Determined by element analysis. [d] Determined at 110 °C by GPC using DMF as eluent. [e] Determined at 25 °C by LLS using water as solvent. [f] Cited from ref 37. [g] Cited from ref 38, DMB = 1,3-dimethoxylbenzene.

maleic anhydride, resulting in an alternative copolymer with a low molecular weight. As a result, it is very difficult to synthesize poly(St-*alt*-Man) of high molecular weights.

Recently, the study conducted by Kazarian et al.[28] suggests that specific intermolecular interactions between carbon dioxide and copolymers containing carbonyl groups enhance the capability of CO_2 to swell and plasticize the copolymers. As a consequence of this intermolecular interactions, the free volume and segment mobility of the copolymers are increased, which leads to a higher diffusion rate of low molecular weight molecules in the copolymer matrix and a lower viscosity for the reaction system.[29,34] The St−Man alternative copolymer contains many carbonyl groups with strong interactions with CO_2. Thus, it is expected that using SC CO_2 will reduce polymer precipitation during the copolymerization and result in a poly(St-*alt*-Man) of a high molecular weight. Some research on decreasing precipitation of polymer chains in heterogeneous polymerization has been reported.[26,27] For example, in polymerization of methyl methacrylate (MMA), the fluorinated grafted stabilizers were used to decrease flocculation in order to obtain acceptable poly(methyl methacrylate) (PMMA) with high molecular weight.[35,36]

In the present work, the copolymerization of St and Man was performed at 60−80 °C using SC CO_2 as the solvent. The resulting copolymer of St and Man has not only an alternative sequence structure but also an extremely high molecular weight of higher than 10^6. Typical examples of St/Man copolymerization in SC CO_2 are shown in Table 1 and compared with the St/Man copolymerization performed in conventional solvents under similar conditions.

The molecular weight of the resulting copolymers was determined by gel permeation chromatography (GPC), laser light scattering (LLS), and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF mass spectrometry). However, the molecular weight of the copolymer synthesized in SC CO_2 was too high to be determined by MALDI−TOF mass spectrometry. For the St/Man copolymers prepared in SC CO_2, no. 3 sample with lower molar mass could be determined by LLS, and other samples with higher molar mass had negative value in LLS determination, owing to the limitation of our instrument. Therefore, other methods, such as intrinsic viscosity technology, will be considered in a later publication. Table 1 shows that the copolymerization of St and Man in SC CO_2 can produce extreme high molecular weight copolymers while much lower molecular weight was obtained when conventional solvents were used. The element analysis of the copolymer indicates that the copolymerization possess alternative trends, which was verified by ^{13}C NMR discussed in a later section. In addition, the elemental analysis indicated that the resulting copolymers prepared in SC CO_2 appear to have positive deviations from alternation, contrary to the negative deviations of the resulting copolymers prepared in other organic solvent. The molecular weight distributions (MWDs) of the copolymer samples are presented in Figure 1. It is shown MWDs of the copolymer samples obtained in SC CO_2 as the solvent are different from that for butanone as the solvent. MWDs of the former samples shift to higher molecular weights and converse for the latter sample. These facts demonstrate that SC CO_2 as the solvent plays an important role in the copolymerization of styrene with maleic anhydride. SC CO_2 possesses properties that make them attractive as media for copolymerization reactions.

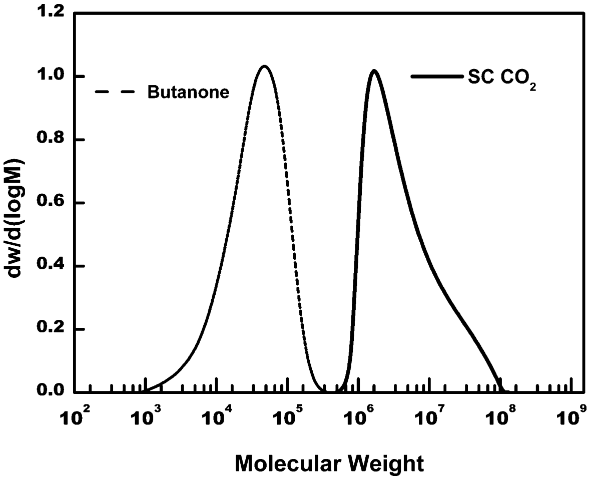


Figure 1. Molecular weight distribution of the St−MAn copolymers prepared in SC CO_2 (—) and butanone (- - -) at 60 °C, 20.5 MPa, and AIBN 0.0017 mol/L.

The effects of SC CO_2 on St/Man copolymerization may be explained as follows. First, because of a depletion of electron density on the carbon atom, CO_2 is a weak Lewis acid and interacts with oxygen atom of carbonyl groups having lone pair electron as Lewis base.[28] The specific acid−base interaction can decrease electron density of Man and facilitate the formation of CTC between St and Man. The donor−acceptor complex monomer (CTC) has a far greater reactivity toward the propagating radical compared to free monomer (St and Man).[1,12] Second, the specific intermolecular interactions between carbon dioxide and copolymers containing carbonyl groups enhance the capability of SC CO_2 to swell and plasticize St−Man alternative copolymers, which increase the free volume of the copolymer and promote interphase transport of monomers.[28] So, the chain propagation of the St−Man alternative copolymer still is high, although the polymerization locus shifts to the interior of polymer particles with the increase of polymer chains. Third, the termination rate decrease because chain entanglements restrict the mobilibity of the active polymer chains. As a result, the overall polymerization reaction is in favor of the polymer chain propagation and the formation of high molecular weight copolymer. Finally, for the intermolecular interactions between SC CO_2 and St−Man copolymers, the CO_2−Man interactions

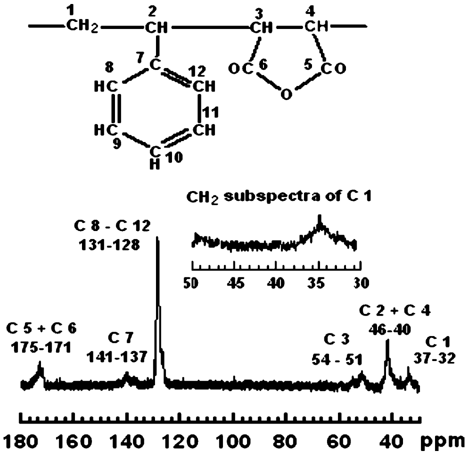


Figure 2. Typical ^{13}C NMR spectrum of an alternating St−MAn copolymer prepared with [MAn] = [St] = 0.25 mol/L, [AIBN] = 0.0017 mol/L in SC CO_2 at 60 °C and 20.5 MPa.

likely enhance the solubility of St−Man copolymer and restrain the copolymer precipitation, which result in the high molecular weight copolymer. However, the mechanism of St/Man copolymerization in SC CO_2 needs further study, which will be reported in a later publication.

Structure and Composition of St−MAn Copolymer. The copolymers formed in SC CO_2 were analyzed by ^{13}C NMR to identify the microstructure. The quaternary aromatic “next to polymer chain” carbon[39] and the methylene (−CH_2−) “polymer chain” carbon[15] of St(1) units were reported to be sensitive to the ST(1)-centered triad sequence distribution observed by the ^{13}C NMR spectra. Figure 2 shows a typical ^{13}C NMR spectrum of a St−MAn alternating copolymer where the peaks were assigned with the chemical shifts according to Butler et al.[17] Indeed, the styrene quaternary carbon exhibits a main peak between 136 and 140 ppm related to the alternating MAn−St−MAn triad; no peak corresponding to MAn−St−St or St−St−St triads appears between 142 and 145 ppm. In the aliphatic carbons region, the three broad peaks between 30 and 60 ppm, also related to the alternating triad,[16] were observed.

Yet, the ^{13}C NMR spectrum in the aliphatic region did not give efficiently sequence information because the signals due to methine and methylene carbons are partially overlapped. So, DEPT subspectra for the methylene were generated using the combination of the $\pi/4$ and $3\pi/4$ experiments: $CH_2 = (\pi/4) + 1.15(3\pi/4)$. For St−Man copolymers, three distinct CH_2 regions, 33−37, 37−42, and 42−47 ppm, were assigned to Man−St−Man, St−St−Man + Man−St−St, and St−St−St triad sequences, respectively, according to Maurizio[18] and Barron et al.[15] Figure 2 shows the methylene subspectra of the St−MAn copolymer (Table 1, no 1). Only one broad methylene signal at 33−38 ppm of MAn−St−MAn is observed, demonstrating that the St−MAn copolymers prepared in SC CO_2 possess the strictly alternating sequence structure. As a conclusion, the alternate structure, which is usually obtained by conventional radical copolymerization of styrene and maleic anhydride, remains preserved in the presence of SC CO_2.

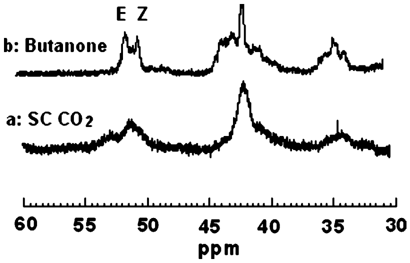


Figure 3. Aliphatic region parts of ^{13}C NMR spectrum of the alternating St−MAn copolymer prepared in SC CO_2 (a) and butanone (b) at 60 °C, 20.5 MPa, and AIBN 0.0017 mol/L.

The composition of MAn unit in St/MAn copolymer were analyzed by relative areas of the carbonyl carbon peak to the total aromatic carbon peaks from ^{13}C NMR spectrum with gated decoupling to remove NOE according to eq 1

$$\mathrm{MAn\%} = 5 \times I_{5,6}/(2I_{8-12} + 5I_{5,6}) \qquad (1)$$

where $I_{5,6}$ and I_{8-12} are integral values of the peaks the carbonyl carbon and total aromatic carbon, respectively. MAn% is the molar percentage of MAn in the copolymer, and all the values listed in Table 2 are close to 50% and in good agreement with the compositions determined from the element analysis (Table 1). This is another evidence of the alternating structure of the copolymer. However, the compositions calculated from the two methods conformably show that the St−Man copolymers have positive deviations in SC CO_2 and negative deviations in other organic solvent, compared with strictly alternative structure. This could be due to the special intermolecular interaction of CO_2 and the carbonyl groups of MAn units.

In present paper, both cis and trans configurations of the cyclic MAn units in St−Man copolymers can be observed in Figure 3. The peak for C-3 shows fine structure in which 51.5 and 52.5 ppm can be related to cis and trans configurations of the MAn portion, respectively.[17,40] The relative amount of cis and trans configurations of anhydride units in the copolymers were determined from ^{13}C NMR spectra and listed in Table 2 and compared with the St/Man copolymerization performed in conventional solvents under similar conditions.

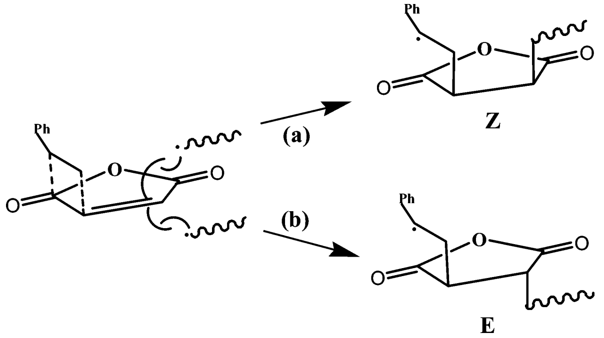
Of all the MAn units, 67.3, 45.0, 54.0, and 58.3% of the linkages were found to be in the cis configuration for copolymers made in SC CO_2, butanone, DMF, and $CHCl_3$, respectively. The cis configuration was considered to be formed by a participation of the 1:1 electron donor−acceptor complex formed between St and MAn in the propagation step. Higher % of cis configuration may be conveniently explained by a participation of the charge-transfer complex of styrene and maleic anhydride.[40]

Table 2. Composition and Microstructure Analytic Data of the St−MAn Copolymers Prepared in Different Solvents

		copolymers of styrene and maleic anhydride			
				configurations of MAn unit[c]	
entry	polym solvent	M_w (10^6 g/mol)[a]	composition, MAn% [b]	cis (%)	trans (%)
1[d]	SC CO_2	4.59	51.0	67.3	32.7
2[e]	butanone	0.049	48.3	45.0	55.0
3[f]	DMF		50	54.0	46.0
4[g]	$CHCl_3$		50	58.3	41.7

[a] Determined by GPC. [b] Calculated by relative areas of the carbonyl carbon peak to the total aromatic carbon peaks from the ^{13}C NMR spectrum. [c] Calculated by the relative areas of the peaks at 51.5 and 52.5 ppm in ^{13}C NMR spectra. [d] Entry 1 is no. 2 sample of the copolymer in Table 1. [e] Entry 2 is no. 4 sample of the copolymer in Table 1. [f] Entry 3 is cited from ref 40. [g] Entry 4 is cited from ref 41.

Scheme 1. Proposed Mechanism for the Formation of Z (cis)- and E (trans)-Man Units via CTC Complex Addition, Showing Attack by the Radical Chain Yielding (a) a Z-Man Unit and (b) an E-Man Unit



Butler et al. proposed a stereoregulatory mechanism based on the maximum orbital overlap theory of Mullikin, for the formation of a cis succinimide unit in copolymers of N-substituted maleimide with vinyl ethers, which was used for explanation of St/Man copolymerization by Brown.[42,43] The mechanism, adapted to the present case, is presented in Scheme 1.

This shows that addition of the growing radical chain to the side of the CTC complex that is syn to the styrene unit leads the addition of an Man unit in the cis (Z) configuration (a), while attack from the opposite side (b) yields the trans (E) configuration. CTC complex participation following this mechanism can therefore lead to the addition of both cis- and trans-Man units to the growing radical chain. CO_2 has a large quadrupole moment and both Lewis acid and base sites.[28] As a Lewis acid, the C atom of CO_2 easily interacts with oxygen atom of carbonyl group as Lewis base. Because both benzene ring and oxygen atom of CO_2 are electron donors and there is electrostatic repulsion, CO_2 may more easily get access to the carbonyl group of Man from the side of CTC complex which is far from the St unit. Because of the steric hindrance of CO_2, the growing radical chain more easily attacks the complex from the side that is syn to the St unit, which could result in more Man units in the cis configuration.

Thermal Property of St–MAn Copolymer. DSC thermograms of St/MAn alternative copolymers with molecular weights of 8.44×10^6 (A), $4. 59 \times 10^6$ (B), and 1.99×10^6 (C) prepared in SC CO_2 are shown in Figure 4.

The St/MAn alternative copolymers, without exception, show a single phase transition corresponding to the glass transition, which is not a perfect platform and similar to a peak shape due to thermal aging. Compared to styrene homopolymer with T_g of 102 °C, the St/MAn alternative copolymers with more rigid structure, originating from cyclic anhydride in the main chains of the copolymer, possess higher T_g ranging from 160 to 202 °C. Furthermore, the dependence of T_g on the molecular weight of St/MAn alternative copolymer can be seen in Figure 4. The T_g of the St/MAn alternated copolymers increases concomitantly with the molecular weight in the present work.

Thermosensitive and pH-Sensitive Property of St–MAn Copolymer. It has been reported that amphiphilic graft copolymers based on maleic anhydride copolymers possess temperature and pH-responsive property and exhibit the lower critical solution temperature (LCST) changing with the length of grafted chains.[44,45] However, the St–MAn copolymers made in conventional organic solvents have not been found to possess thermosensitive and pH-sensitive property so far. In the present paper, we report that the thermosensitive and pH-sensitive property of the ultrahigh molecular weight poly(St-*alt*-MAn).

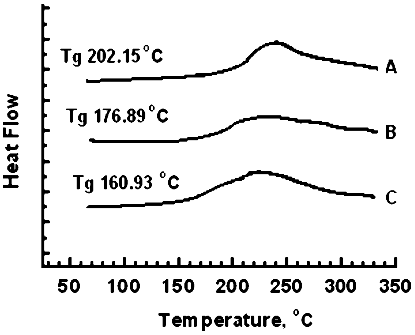


Figure 4. DSC thermograms of the alternating St–MAn copolymers with the molecular weights of M_w 8.44×10^6 (A), 4.59×10^6 (B), and 1.99×10^6 (C), prepared in SC CO_2.

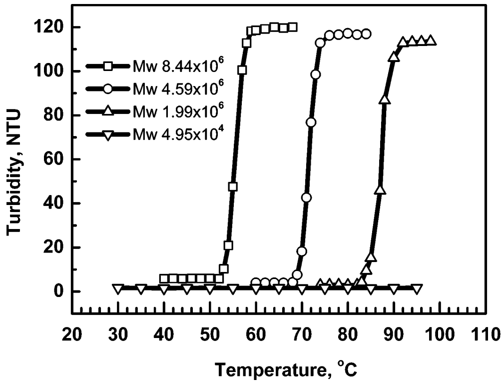


Figure 5. Phase transitions of the alternating St–MAn copolymer solutions at pH 3.5: (□) M_w 8.44×10^6, (○) M_w 4.59×10^6, (△) M_w 1.99×10^6, and (▽) M_w 4.95×10^4.

Figure 5 shows the phase transitions of several St–MAn alternative copolymers solutions with different molecular weights. The LCST's of the St–MAn alternative copolymer solutions are dependent on the molecular weight of the poly(St-*alt*-MAn). St–MAn alternative copolymer with M_w of 4.9×10^4 was easily dissolved in water and did not exhibit LCST, which could be due to the too strong interaction between water and carboxyl groups in the copolymer chains, originating from the hydrolysis of anhydride. Yet, the alternative copolymers with M_w of higher than 10^6 exhibit LCST's in water solutions. The phase transition temperatures decrease with the increasing molecular weight of the alternative copolymer (Figure 5). It is reasonable that the copolymer–copolymer interaction, owing to hydrophobic interaction of phenyl groups and intra/intermolecular hydrogen bonds with the carboxyl groups, could be remarkably enhanced with the increasing copolymer chain length and equal to the copolymer–solvent interaction. IR spectra of hydrolyzed St–MAn copolymer are shown in Figure 6, where the intrinsic peaks of anhydride disappear and that for carboxyl groups appear.

The reason for the temperature-induced phase separations of solutions of LCST polymers lies in the balance of the polymer–solvent, polymer–polymer, or solvent–solvent interactions in the system.[46] Therefore, the carboxyl groups of the alternative copolymers have two opposing functions: on one hand, these acid groups form intra/intermolecular hydrogen bonds with the other acid groups in the copolymer, and on the other hand, they are capable of forming hydrogen bonds with water. These two functions affect the LCST in opposite ways, depending on the alternating copolymer chain length.

For our St–MAn alternating copolymers, the hydrophobic units and hydrophilic units are evenly distributed, such that the effects of incorporating hydrophilic units on the intra/intermolecular interactions should be even larger than that seen in

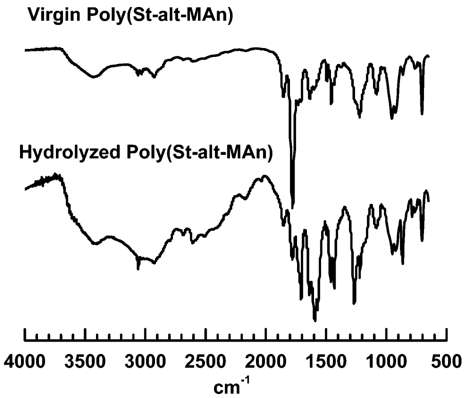


Figure 6. IR spectra of virgin and hydrolyzed samples of the alternating St−MAn copolymer (M_w 8.44 × 10^6) prepared in SC CO_2.

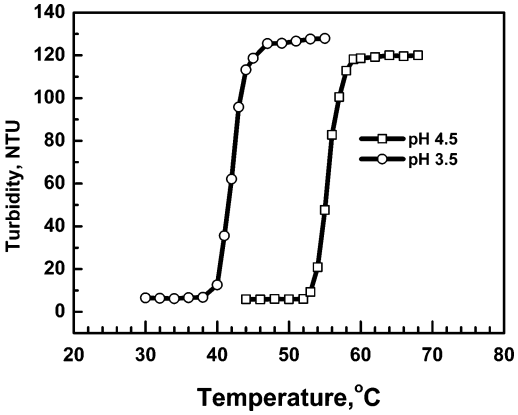


Figure 7. Dependence of the phase transition of the alternating St−MAn copolymer solution on pH: (○) pH 3.5 and (□) pH 4.5, with M_w of 8.44 × 10^6.

random copolymers. Here, the ionization of the carboxylic groups should not only disrupt the intra/intermolecular hydrogen bonding but also suppress the hydrophobic−hydrophobic interaction between styrene units.

Figure 7 shows the pH-dependent phase transition of St-MAn alternative copolymer in water. The poly (St-*alt*-MAn) with M_w of 8.44 × 10^6 has a LCST of 55 °C at pH 4.5 and 42 °C at pH 3.2, respectively. This alternating copolymer is not water-soluble below pH 2.2, even at 0 °C. Apparently, the hydrogen bonding between the acid groups reduces the copolymer−water interactions and prevents solvation of the copolymer in acidic conditions.

Conclusion

SC CO_2 possesses properties that make them attractive as the media for polymerization reactions. The solvent properties of SC CO_2 can be manipulated by changing pressure for controlling the solubilities of monomers and copolymers and eliminating interphase transport limitations on polymerization rates. Moreover, because of the specific intermolecular interactions between CO_2 and anhydride groups, SC CO_2 could increase the free volume and segment mobility of the St−MAn alternative copolymer, which decreases the precipitation of the St−MAn alternative copolymer from the solvent. Thus, an ultrahigh molecular weight poly(St-*alt*-MAn) was obtained in the St/MAn copolymerization with SC CO_2 as the solvent. Higher cis configuration linkage of the cyclic MAn units was found in the poly(St-*alt*-MAn) in the SC CO_2 system. This suggests that SC CO_2 is in favor of the formation of the charge-transfer complex of styrene and maleic anhydride. An ultrahigh molecular weight poly(St-*alt*-MAn) not only remained the excellent thermal stability and exhibited temperature and pH responsive properties in an aqueous solution, which have potential applications for biomedical and functional membrane materials.

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