Macromolecules **2004,** *37,* 8239−8248

Copolymerization of Acrylonitrile with Methyl Methacrylate and 2-Chlorostyrene in Supercritical CO_2

Sang-Do Yeo[†] and Erdogan Kiran*

Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Received February 4, 2004; Revised Manuscript Received August 11, 2004

ABSTRACT: Free-radical precipitation copolymerizations of acrylonitrile with methyl methacrylate and 2-chlorostyrene were carried out using AIBN as initiator at 70 °C and 220 bar in carbon dioxide at a total comonomer concentration of 13.6 wt %. Polymerizations were carried out without the use of stabilizers with different feed comonomer molar ratios of 100:0; 98:2; 96:4; 94:6; 90:10; 50:50, and 0:100 acrylonitrile: methyl methacrylate or acrylonitrile:2-chlorostyrene. The preliminary experiments conducted in a view cell showed that these systems that are initially homogeneous solutions undergo phase separation within about 3 h of polymerization time upon formation of polymer chains that are no longer completely miscible in the polymerization medium. Polymerizations that were carried out in a 50 mL high-pressure batch reactor for 20 h under rotational agitation of an impeller at 200 rpm resulted in end products that were either free-flowing powder, or soft solid, or gel (as observed upon depressurization and opening the reactor). The actual physical form was found to be dependent on the initial feed comonomer ratio. Homopolymerization of acrylonitrile led to powders, homopolymerization of 2-chlorostyrene resulted in a soft solid, and homopolymerization of methyl methacrylate resulted in a gel. In the copolymers, those with high acrylonitrile content resulted in powders and became gellike with increasing methyl methacrylate or soft solid with increasing 2-chlorostyrene content. Polymer yield which was about 50% in homopolymerizations was found to decrease in copolymerizations as the acrylonitrile content in the feed mixture was reduced. The number-average molecular weights of the polymers were in the range from 40 000 to 300 000, with polydispersities in the range from 1.4 to 4.8. The polymers were characterized by FTIR, DSC, TGA, ^{1}H NMR, and ^{13}C NMR, and the morphologies were evaluated with electron microscopic studies. The acrylonitrile:methyl methacrylate molar ratios in the copolymers as calculated from ^{1}H NMR were lower than the respective feed comonomer ratios used in their polymerizations. These ratios were even lower in the acrylonitrile−2-chlorostyrene copolymers, suggesting relatively lower reactivity ratios in copolymerizations involving 2-chlorostyrene.

Introduction

Use of supercritical fluids, especially carbon dioxide as a solvent medium for polymerization, is of growing technological interest because of (a) their greater environmental acceptability, (b) the greater ease of removal of the solvent, and (c) the greater ability to tune the properties of the polymerization medium.[1−4] These polymerizations which are intrinsically high-pressure processes are also of increasing scientific interest in that they display a complex interplay of phase equilibria, thermodynamics, and kinetics (both chemical and physical) as the system undergoes compositional changes with the progress in polymerization. The ability of the growing chains to remain in the solution depends on the solvent power of the supercritical fluid medium. The polymerization medium is typically a mixture of the supercritical fluid such a carbon dioxide and the monomer that has not yet reacted at the prevailing time, temperature, and pressure during polymerization. The thermophysical properties such as the melting and/or glass transition temperatures of the polymers that are produced are affected (lowered) in the presence of residual monomer and the supercritical fluid. The fluid composition and the extent to which the transitions are shifted influence the final morphology and the physical state of the polymer when the system pressure is lowered for final recovery of the polymer.

Because of the low solubility of the majority of polymers in supercritical carbon dioxide, special stabilizers have been developed[5] and used in various dispersion polymerizations which typically lead to spherical polymer particles. Dispersion polymerization of styrene, acrylonitrile, methyl methacrylate, and several other monomers have been reported.[4−7] However, the presence of stabilizers that cannot be easily removed from the polymer becomes a concern for some applications. Precipitation polymerization is an alternative approach which produces stabilizer-free polymers. These polymerizations, as the name implies, are polymerizations in which polymer precipitates when they reach a certain chain length or reach the limit of solubility because of changes in the “*effective solvent*” composition.

A special feature of the solvent effect in polymerizations in supercritical fluids is that, in addition to the ability to tune the solvent properties and influence the course of polymerization as in altering the propagation rate,[8] the end products may be highly swollen with the fluid which impacts the final morphology of the polymer recovered. Depending upon the thermal transitions of the polymer (T_g and T_m) and the extent to which they may have been lowered in the supercritical fluid media, the end product may be a viscous liquid or a sticky porous gel or a soft solid or free-flowing powder. In the case of copolymers, depending upon the composition and sequence distribution, one or two glass transition tem-

---

[†] Permanent address: Department of Chemical Engineering, Kyungpook National University, Daegu, 702-701 Korea.

* Corresponding author: Tel 540-231-5561; Fax 540-231-5022; e-mail ekiran@vt.edu.

10.1021/ma040030c CCC: $27.50

peratures may be observed. In random or statistical copolymers that are formed in free-radical copolymerizations, only one T_g is observed which is intermediate to the T_g of the respective homopolymers and closer to the T_g of the component that is present in higher amount in the copolymer. The agglomeration or the free-flowing nature of the end products is therefore expected to depend strongly on the copolymer composition. Particulate morphology is expected to be produced more with copolymers with high T_g. Consequently, the feed composition and the reactivity ratios that determine the copolymer compositions become important factors influencing the final outcome.

In this paper we report on the free-radical precipitation polymerization of acrylonitrile and its copolymerization with methyl methacrylate and 2-chlorostyrene in supercritical carbon dioxide. These comonomers were selected to provide a contrast because of the nearly 20 °C difference in the glass transition temperatures of their respective homopolymers (with a T_g of about 100 °C for poly(methyl methacrylate) and about 120 °C for poly(2-chlorostyrene)) and because of the chemical structure differences arising from aromaticity and the chlorine atom that may influence the solvent effects, polymer miscibility, the reactivity ratios, and final polymer morphology.

Miscibility of acrylonitrile in carbon dioxide and its free-radical precipitation polymerizations in carbon dioxide have already been reported in the literature.[9−11] These mixtures show a continuous critical mixture curves between the critical temperature of carbon dioxide (31.1 °C) and acrylonitrile (262.8 °C), passing through a pressure maximum at 140 bar at around 150 °C.[9] Homopolymerization of acrylonitrile in CO_2 has been reported at pressures up to 300 bar in the temperature range from 50 to 65 °C.[10,11]

Copolymerization and terpolymerization are techniques that are traditionally employed to render polyacrylonitrile melt processable.[12] Even though some studies have appeared in the patent literature on copolymerization of acrylonitrile with styrene in carbon dioxide,[13,14] the precipitation copolymerization of acrylonitrile with methyl methacrylate and with 2-chlorostyrene in supercritical carbon dioxide, to our knowledge, has not been previously reported.

Experimental Section

Materials. Acrylonitrile (AN), methyl methacrylate (MMA), and 2-chlorostyrene (CS) were purchased from Aldrich Co. All the monomers were purified by using a prepacked inhibitor remover column (Aldrich Co.) before use. The free radical initiator 2,2′-azobis(isobutyronitrile) (AIBN) was obtained from Aldrich Co. Supercritical fluid chromatography grade CO_2 was obtained from Air Products and Chemicals Inc. (Allentown, PA).

Apparatus. Majority of the polymerization experiments were carried out in a 50 mL high-pressure batch reactor (model MC-05-05S1, Pressure Products Industries Inc., Warminster, PA). The unit was equipped with a magnetically driven overhead impeller and a tachometer that allowed the measurement of agitation speed of the impeller.

Polymerization. The known amounts of liquid monomers and the free-radical initiator AIBN were loaded to the reaction vessel. Next, a gentle stream of gaseous CO_2 was passed through the reactor in order to remove any entrapped air from the vessel. Carbon dioxide was introduced up to 63 bar at room temperature from a preloaded CO_2 transfer vessel. The amount of CO_2 loaded to the view cell was calculated by measuring the weight of transfer vessel before and after the charge. After charging, the system was isolated and the reactor was heated to 70 °C, causing a subsequent pressure increase of the reactor to 220 bar. After the temperature and pressure were stabilized at 70 °C and 220 bar, the system was agitated with an impeller rotational speed of 200 rmp and polymerization was carried out for 20 h. The system was then cooled to room temperature, and CO_2 was vented. The physical form and the overall appearance of the polymer were noted. The polymer was then transferred to a high-vacuum chamber to remove any unreacted monomer residues. The yield of the polymer product was determined gravimetrically.

Table 1. Comonomer Charge to the Reactor and the Comonomer Feed Ratios[a]

experiment designation	AN (g)	MMA (g)	CS (g)	molar ratios AN:MMA or AN:CS (%:%)
PAN	7.5			pure AN
PMMA		7.5		pure MMA
PCS			7.5	pure CS
PAN−PMMA (98/2)	7.22	0.28		98:2
PAN−PMMA (96/4)	6.96	0.54		96:4
PAN−PMMA (95/5)	6.82	0.68		95:5
PAN−PMMA (94/6)	6.69	0.81		94:6
PAN−PMMA (90/10)	6.20	1.30		90:10
PAN−PMMA (50/50)	2.60	4.90		50:50
PAN−PCS (98/2)	7.12		0.38	98:2
PAN−PCS (96/4)	6.76		0.74	96:4
PAN−PCS (94/6)	6.42		1.08	94:6
PAN−PCS (90/10)	5.81		1.69	90:10
PAN−PCS (50/50)	2.07		5.43	50:50

[a] Molecular weights of acrylonitrile (AN), methyl methacrylate (MMA), and 2-chlorostyrene (CS) are 53.06, 100.12, and 138.60 g/mol, respectively. Nominal total mass of pure monomer or comonomer mixtures charged in each experiment was 7.5 g.

Table 1 summarizes the actual amount of monomers and comonomers charged to the reactor for these polymerization experiments. Polymerizations were performed with the pure monomers AN, MMA, and CS as well as with monomer mixtures of AN + MMA and AN + CS. The monomer mixtures were loaded to reactor with the initial molar ratios of 98:2, 96:4, 94:6, 90:10, and 50:50 (both for AN:MMA and AN:CS systems). With AN + MMA, an additional mixture with initial molar ratio of 95:5 was also explored. In all the experiments, 47.5 g of CO_2 was charged to the reactor. Total mass of the pure monomers or the comonomer mixtures charged was kept constant at 7.5 g for each run. This corresponds to a monomer/comonomer concentration of 13.6 wt % in CO_2 in all experiments. As initiator, 0.03 g of AIBN was used for every experiment, which corresponds to an initiator concentration of 0.4 wt % with respect to monomer.

Phase Behavior Observation. A number of polymerization experiments were also conducted in a view cell in order to observe the phase separation conditions that set in during the course of polymerization. The view cell is equipped with a magnetic stirring bar, two sapphire windows, and an optical sensor.[15] The system permits visual observations or optical monitoring of the changes in the transmitted light intensity (of a white light source) that takes place with the onset of polymer phase separation. The polymerizations were performed with selected comonomer systems in Table 1, and all the feed concentrations and experimental conditions were kept identical to the batch reactor experiments. The intensity of the transmitted light was recorded as a function of time during the polymerization reaction, and the experiment was continued until the onset of polymer precipitation was detected. Typically, the view cell experiments were conducted for 3 h.

Characterization. Morphological features of the polymers were examined using a field emission electron microscope (FESEM) (LEO 1550). The specimen was sputter-coated with gold−palladium in the thickness of 6 nm. Molecular weights were determined using a gel permeation chromatograph (GPC) (Waters 1515) equipped with a Waters Styragel HT 6E column (7.8 × 300 mm) with *N*-methylpyrrolidone (NMP) as the solvent. The measurements were carried out at 30 °C with an

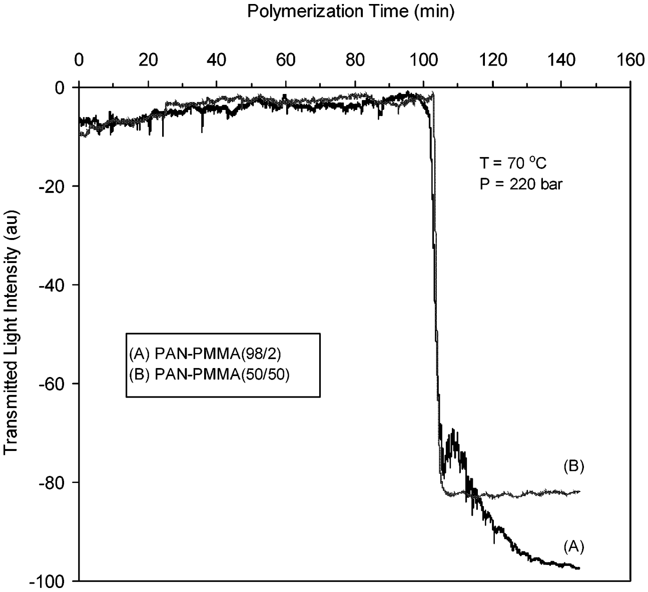

Figure 1. Change in transmitted light intensity with polymerization time during copolymerization of acrylonitrile with methyl methacrylate for feed comonomer ratios of 98:2 and 50:50 at 70 °C and 220 bar.

injection volume of 20 μL and a flow rate of 1 mL/min. Chemical components of the polymers were identified by FTIR (BIO-RAD, FTS-40A). The specimen were prepared by compressing mixtures of 0.5 mg of polymer sample and 200 mg of KBr into a 12 mm diameter circular disks. Molecular composition and structure of polymer were determined by ^{1}H NMR (Varian, Inova 400) and ^{13}C NMR (Varian, Unity 400) with the resonance frequencies of 400 and 100 MHz, respectively. Samples for NMR characterizations were prepared by dissolving the polymers in DMSO-d_6 at a concentration of 20 mg/mL for ^{1}H NMR and 300 mg/mL for ^{13}C NMR analyses. Thermal characterizations were carried out using thermogravimetric analysis (TGA) (TA Instruments 2950) and differential scanning calorimetry (DSC) (TA Instruments 2920). A heating rate of 10 °C/min was used in generating the TGA and DSC scans.

Results and Discussion

Phase Separation Behavior. Preliminary polymerization experiments were carried out in the view cell for copolymerization of AN with MMA for feed concentrations with a molar AN to MMA ratios of 98:2 and 50:50. Copolymerization of AN with CS were carried out also with 98:2 and 50:50 molar ratios in the feed. Figure 1 shows the change in the transmitted light intensity during polymerization. The data shown correspond to the time period after the system temperature reached 70 °C. These polymerization mixtures were initially all clear and homogeneous. As shown in Figure 1, during copolymerization of AN with MMA, after about 100 min of polymerization time a sharp drop in the transmitted light intensity was observed irrespective of the initial feed composition. However, for the feed composition of 98(AN):2(MMA), this initial reduction in transmitted light intensity was followed by a second drop. With this system, rapidly moving polymer particles could be visually noted in the cell. The transmitted light intensity continued to decrease with polymerization time as a result of the high turbidity caused by the increasing amount of polymer particles. In copolymerization in the 50:50 mixture, the transmitted light intensity did not show further decrease after the initial phase separation, and the system sustained a level of transparency. In this system, fine droplets of gellike polymer particles were visually observed, which were consistent with the translucency of the system even after phase separation. With this system, polymer that forms is thus observed to be highly swollen in the reaction medium.

In copolymerization of acrylonitrile with 2-chlorostyrene, a small amount of a white solid precipitate was formed immediately after the physical mixing of these monomers at ambient conditions. These solid particles remained in the system after CO_2 addition. For the feed monomer ratio of 98:2, the solid particles appeared to dissolve as the system temperature was increased to 70 °C. The homogeneous polymerization mixture was observed to undergo phase separation after about 65 min polymerization time compared to about 100 min in the AN + MMA case. Similar to the AN + MMA case, this major phase separation step was also followed by a second phase separation process shortly after. Even though could not be visually confirmed, these two-stage phase separations are suggestive of either polymerization proceeding in two phases prior to their phase separation or imply existence of chains that display different growth kinetics. For the feed monomer ratio of 50(AN):50(CS), as in the AN + MMA case, transmitted light intensity changes indicated only one phase separation step. In this system, white solid precipitates were also observed at the beginning. The origin of these white solids is not clear. It may be similar to a phenomenon that has been reported in the literature in copolymerization of styrene with vinylidene cyanide.[16]

The polymerization experiments in the view cell were terminated after 180 min, which was sufficiently beyond the observation of the phase separation conditions. All

Table 2. Molecular Weights, Polydispersities, Yields, and the Physical State of Polymers Produced

experiment designation	M_n	M_w	M_w/M_n	yield (%)	physical state[a]
PAN	54 000	124 000	2.3	49	powder
PMMA	115 000	171 000	1.5	51	gel
PCS	116 000	309 000	2.7	54	soft solid
PAN−PMMA(98/2)	59 000	205 000	3.5	41	powder
PAN−PMMA(96/4)	66 000	190 000	2.9	33	agglomerated powder
PAN−PMMA(94/6)	56 000	177 000	3.2	21	agglomerated powder
PAN−PMMA(90/10)	65 000	227 000	3.5	*b*	gel
PAN−PMMA(50/50)	169 000	255 000	1.5	*b*	gel
PAN−PCS(98/2)	49 000	127 000	2.6	54	powder
PAN−PCS(96/4)	55 000	235 000	4.3	38	agglomerated powder
PAN−PCS(94/6)	53 000	253 000	4.8	34	agglomerated powder
PAN−PCS(90/10)	40 000	184 000	4.6	*b*	gel
PAN−PCS(50/50)	317 000	663 000	2.1	52	soft solid

[a] Based on the visual observations made immediately after the recovery of polymer from the reactor. [b] Are not reported due to difficulty in recovering the gellike polymer completely.

further polymerization experiments and characterizations were carried out in the batch reactor.

Polymerization in Batch Reactor. All polymerizations in the batch reactor were continued for 20 h. Based on the view-cell experiments described above after about 2−3 h into polymerization, the character of the system changes from being homogeneous to heterogeneous. However, in the batch reactor setup, under intense agitation with an impeller speed at 200 rpm, polymer particles that form are expected to remain suspended, and further polymerization beyond the initial phase separation continues in polymer particles swollen in a mixture of monomer plus CO_2. The physical forms of the end products from these polymerization experiments that were observed immediately after depressurization and venting the CO_2 from the system are included in Table 2. Homopolymerization of acrylonitrile resulted in free-flowing powders, which is consistent with the high crystalline melting temperature (593 K) and glass transition temperature (370 K) for this polymer.[17] Homopolymerization of MMA resulted in a gel, consistent with the relatively lower glass transition temperature of PMMA and its further reduction in the presence of residual monomer and dissolved CO_2. Homopolymerization of 2-chlorostyrene resulted in a soft solid, once again consistent with the higher glass transition of this polymer compared to that of PMMA. In the case of copolymers, the systems with high acrylonitrile content resulted in powders. They became more gellike with increasing MMA content or became soft solids with increasing CS content in the copolymer.

Polymer yield was about 50% in homopolymerizations. In copolymers, a reduction in yield (to about 21% in the AN + MMA system and to about 34% in the AN + CS system) was noted as the acrylonitrile content in the feed mixture was reduced from 98 to 94 mol %. The reasons for this reduction in yield is at the moment not clear.

The copolymers were tested for their solubility in different solvents under ambient conditions. They could be dissolved in DMF, but no solubility could be detected in acetone. With the AN−MMA copolymer (94/4), additional solubility evaluations were carried out at high pressures in acetone at pressures up to 300 bar and temperatures up to 100 °C in a view cell to test for the presence of any extractable homopolymer (PMMA) fractions (which was done by expanding and collecting the solvent phase). No PMMA could be detected, providing further confirmation that the polymerizations have indeed led to the formation of copolymers and not to mixtures of homopolymers.

(a) Molecular Weight. As shown in Table 2, the number- and weight-average molecular weights, M_n and M_w, ranged from 40 000 to 300 000 and from 120 000 to 600 000, respectively, and the polydispersity (M_w/M_n) ranged from 1.4 to 4.8. It was found that the exceptionally high molecular weights were obtained from the initial molar ratio of 50:50 for both copolymer systems. No bimodal distributions were noted in any of the GPC results. Absence of bimodality can be viewed as an additional indicator that the polymerizations of monomer mixtures have resulted in copolymers and not mixtures of homopolymers. The formation of higher molecular weight polymers from 50:50 comonomer feed compositions may in part suggest that the growing polymer chains are more soluble in this reaction medium where the molecules can stay longer in the solution phase, and the chain buildup can proceed further before the precipitation takes place. Or, the polymerization effectively continues in the highly swollen polymer (gellike) particles that have phase-separated. Polymerization in precipitated particles can also result in autoacceleration effects that may lead to higher molecular weights. Relatively low polydispersities and absence of bimodality are suggestive of polymerization proceeding under homogeneous-like conditions. The molecular weights that have been obtained appear consistent with those reported for homopolymerization

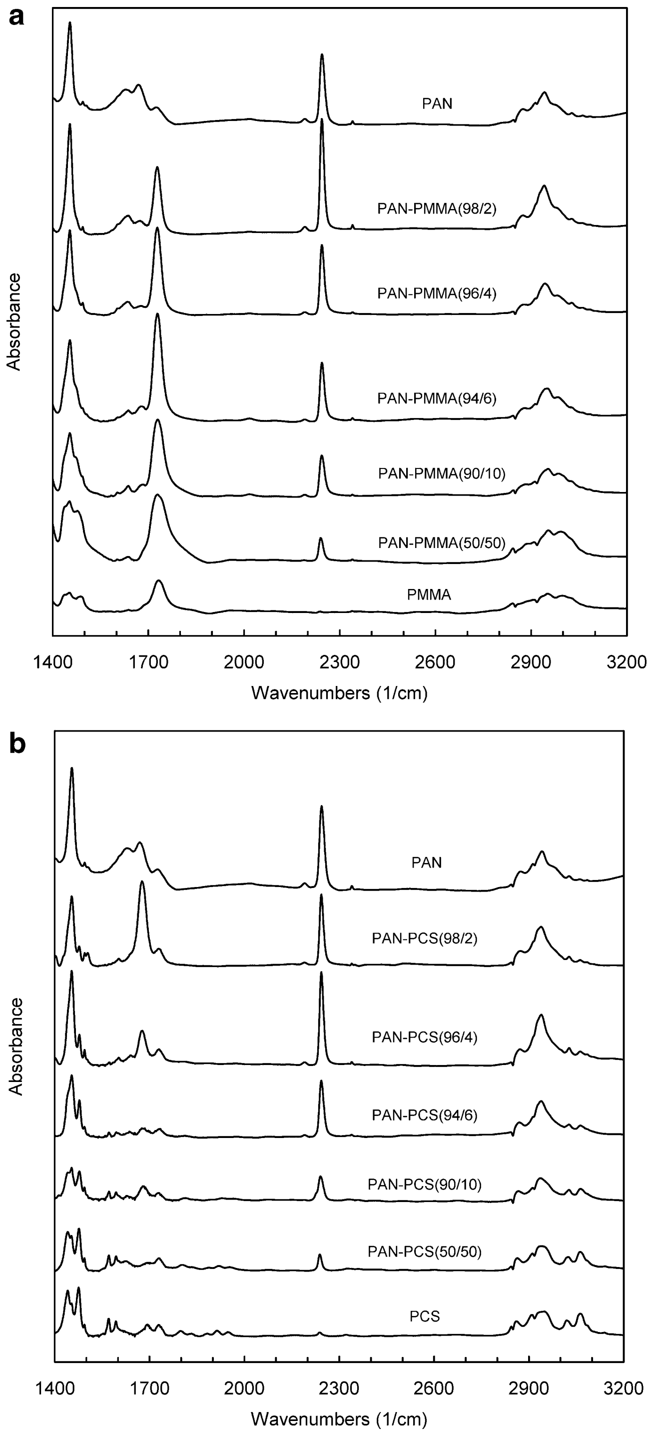

Figure 2. FTIR spectra of homopolymers of acrylonitrile (PAN), methyl methacrylate (PMMA), and 2-chlorostyrene (PCS) and their copolymers AN−MMA (a) and AN−CS (b) synthesized in the present study. For copolymers the mole ratio designations represent the initial feed ratios.

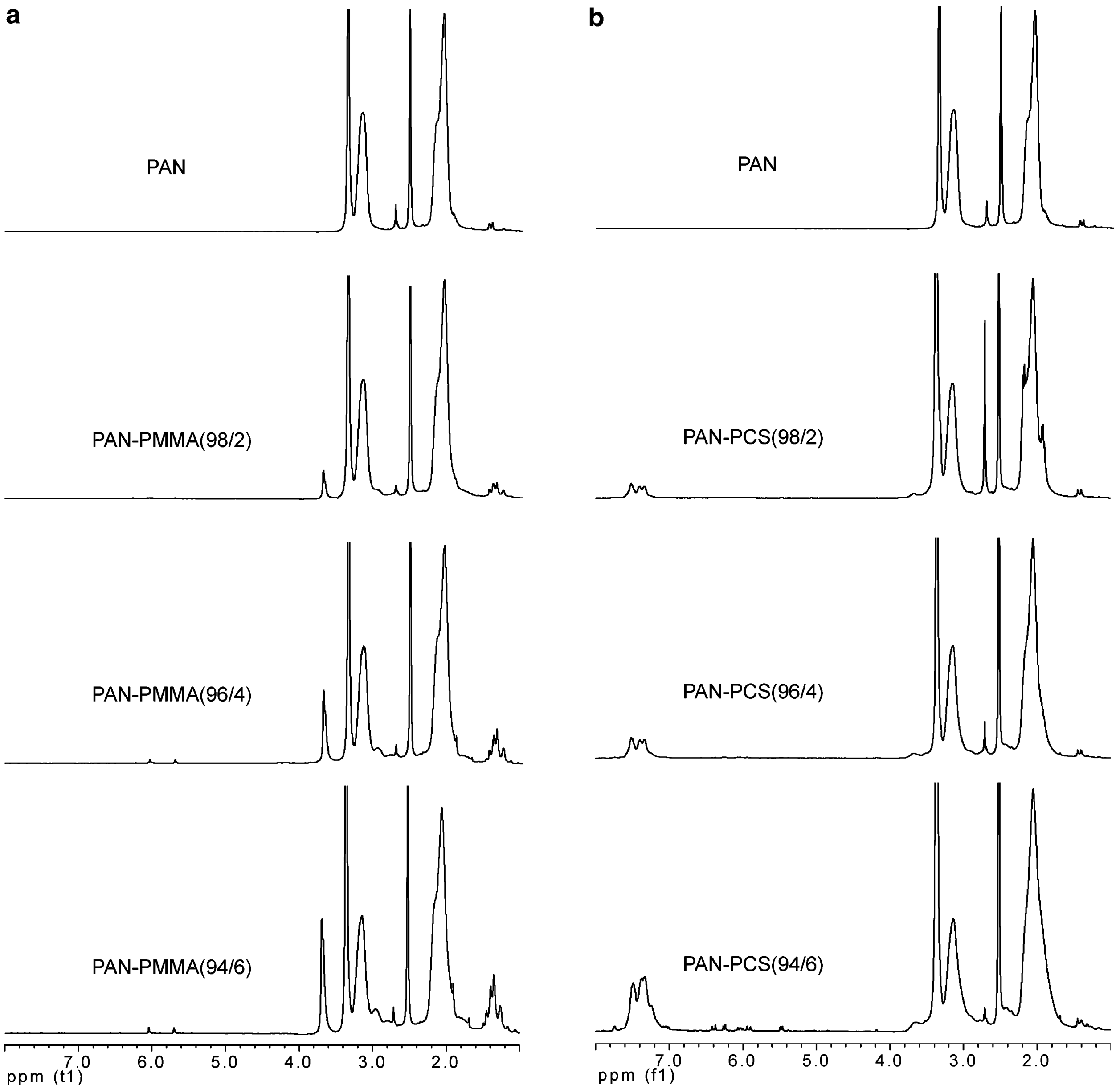

Figure 3. ^{1}H NMR spectra of the acrylonitrile homopolymer (PAN) and its copolymers with methyl methacrylate (a) and 2-chlorostyrene (b). Spectra shown are those of the copolymers produced in powder forms.

of acrylonitrile in the literature[18] under similar temperature and pressure conditions but with 3 times higher AIBN concentrations. The M_n and M_w of PAN were about 20 000 and 70 000, respectively, which can be compared with the results in the present study (M_n = 54 000, M_w = 124 000) since higher initiator concentration is expected to lead to lower chain lengths.

(b) Copolymer Composition and Structure. FTIR spectra were used to identify the chemical components of the copolymers. Figure 2a,b shows the FTIR spectra of PAN, PMMA, and PCS homopolymers and the copolymers of AN with MMA and with CS. In Figure 2a, the stretching vibration peak due to CN groups in AN repeat units appear at 2244 cm^{-1}, and the stretching vibration peak due to CO groups in MMA repeat units is observed at 1729 cm^{-1}. The bending vibration peak due to CH$_2$ and CH$_3$ groups appear at 1454 cm^{-1}. In Figure 2b, the stretching vibration peaks due to aromatic CH and CC groups in CS repeat units are in the ranges of 3019−3063 and 1593−1475 cm^{-1}, respectively.[19] The progression of the characteristic IR absorbance peak in going from PMMA to PAN (Figure 2a) and from PCS to PAN (Figure 2b) for the copolymers is well demonstrated in these spectra.

^{1}H NMR spectra were used to determine the copolymer compositions. Figure 3a,b shows the ^{1}H NMR spectra of PAN homopolymer and the selected AN−MMA and AN−CS copolymers. All the spectra are presented in the same chemical shift range for better visual comparison. For the AN−MMA copolymers (Figure 3a), the ^{1}H chemical shifts due to OCH$_3$, CH, CH$_2$, and CCH$_3$ protons are in the regions of 3.6−3.7, 3.1−3.2, 1.8−2.2, and 1.2−1.4 ppm, respectively. These ^{1}H chemical shift values were consistent with those of AN−MMA copolymers produced by conventional emulsion copolymerization.[20] It was apparent that the relative intensity of resonance peaks corresponding to the OCH$_3$ and CCH$_3$ protons increased with the increased initial monomer concentration of MMA.

The copolymer composition was determined by the stoichiometric calculation based on the integrated area under the peaks of OCH$_3$ and CH$_2$ protons, noting that

Table 3. Composition of the Copolymers As Determined from ^{1}H NMR Spectra[a]

experiment designation	F_{AN}	F_{MMA}	F_{CS}
PAN−PMMA(98/2)	0.975	0.025	
PAN−PMMA(96/4)	0.934	0.066	
PAN−PMMA(94/6)	0.896	0.104	
PAN−PMMA(90/10)	0.826	0.174	
PAN−PMMA(50/50)	0.336	0.664	
PAN−PCS(98/2)	0.966		0.034
PAN−PCS(96/4)	0.944		0.056
PAN−PCS(94/6)	0.869		0.131
PAN−PCS(90/10)	0.736		0.264
PAN−PCS(50/50)	0.407		0.593

[a] Mole fractions of AN (F_{AN}), MMA (F_{MMA}), and CS (F_{CS}) units in AN−MMA and AN−CS copolymers.

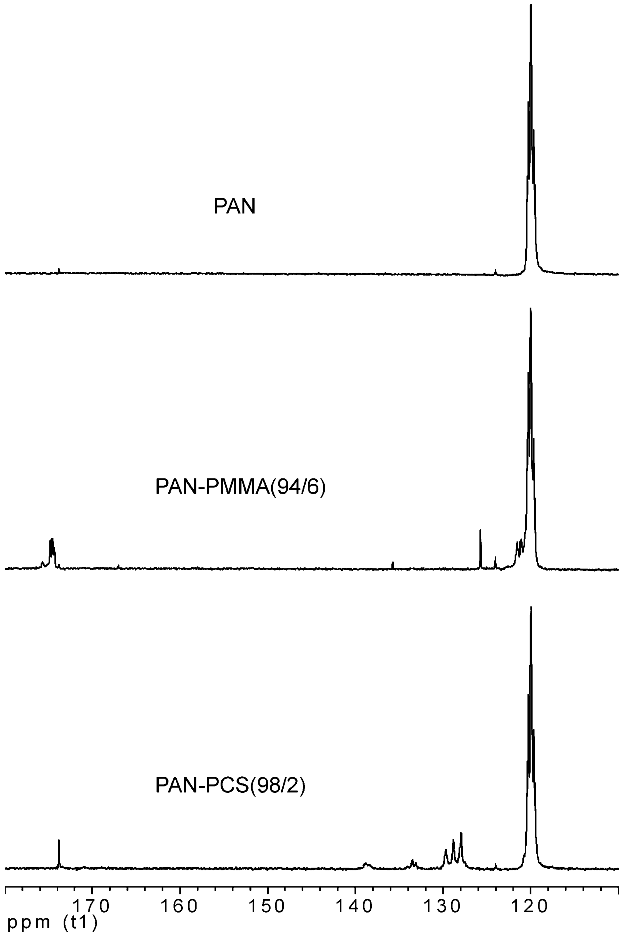

Figure 4. ^{13}C NMR spectra of the acrylonitrile homopolymer (PAN) and two selected copolymers produced in experiments PAN−PMMA(94/6) and PAN−PCS(98/2) displayed in the chemical shift regions of 110−180 ppm.

the methoxy group is on the MMA structure and the methylene group is on both the AN and MMA monomer units that are incorporated into the copolymer. For the AN−CS copolymers (Figure 3b), the ^{1}H chemical shifts due to aromatic, CH, and the CH_2 protons were in the regions of 7.3−7.5, 3.1−3.2, and 1.8−2.2 ppm, respectively. Here, the peak areas of the aromatic protons and methylene protons were utilized in the compositional analysis.

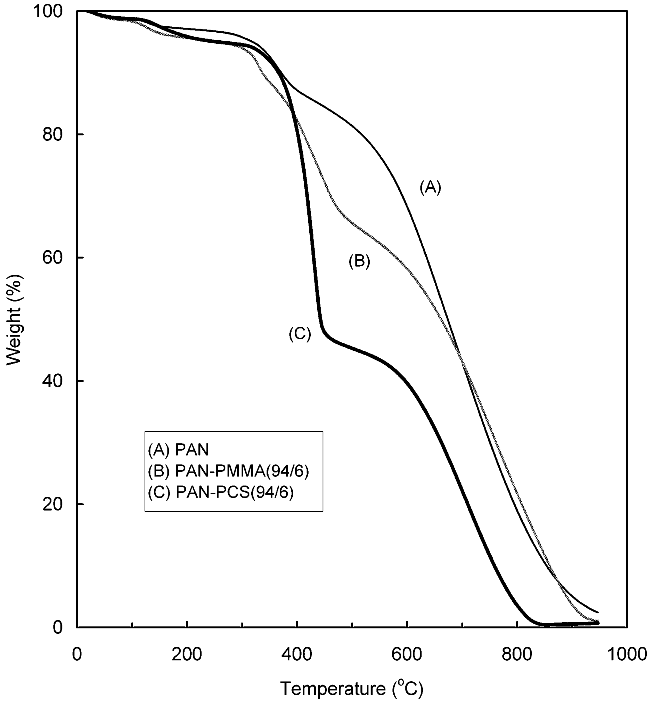

Figure 5. TGA thermograms of the acrylonitrile homopolymer (PAN) and the acrylonitrile−methyl methacrylate and acrylonitrile−2-cholostyrene copolymers produced from a feed molar ratio of 94:6 AN:MMA or CS.

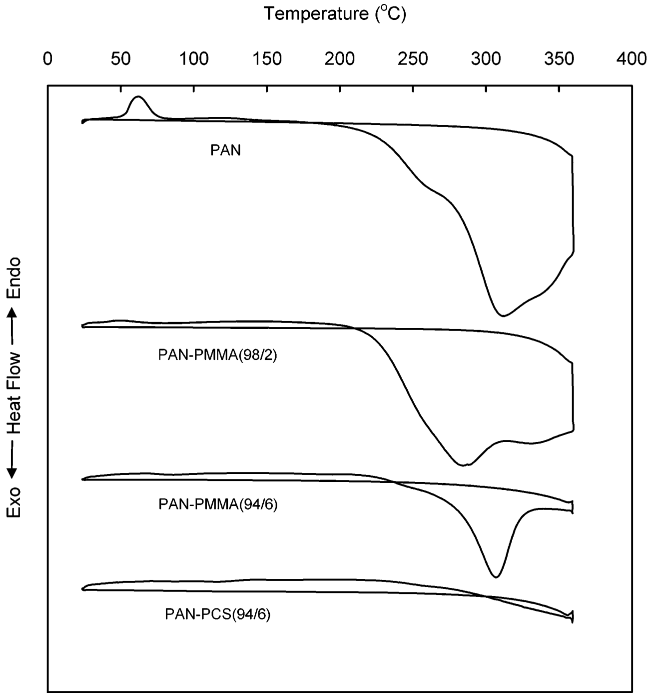

Figure 6. DSC scans of polymer samples produced from the experiments of PAN, PAN−PMMA(98/2), PAN−PMMA(94/6), and PAN−PCS(94/6). The scans represent the first heating to 360 °C and cooling back to 25 °C at 10 °C/min heating/cooling rate in a nitrogen atmosphere.

Table 3 shows the mole fractions of AN (F_{AN}), MMA (F_{MMA}), and CS (F_{CS}) monomer units in the copolymers determined from the ^{1}H NMR spectral data. It was found that the mole fractions of the comonomer (MMA and CS) units in the AN copolymers were greater than those in the feed and this tendency increased with the increasing concentration of the comonomer in the feed. The F_{AN}/F_{MMA} mole ratios in the copolymers were less than the mole ratio f_{AN}/f_{MMA} in the feed, and this decrease was more pronounced in the AN−CS copolymers. The difference between the mole ratios of the comonomers in the copolymers and the feed were observed to become greater for those systems that

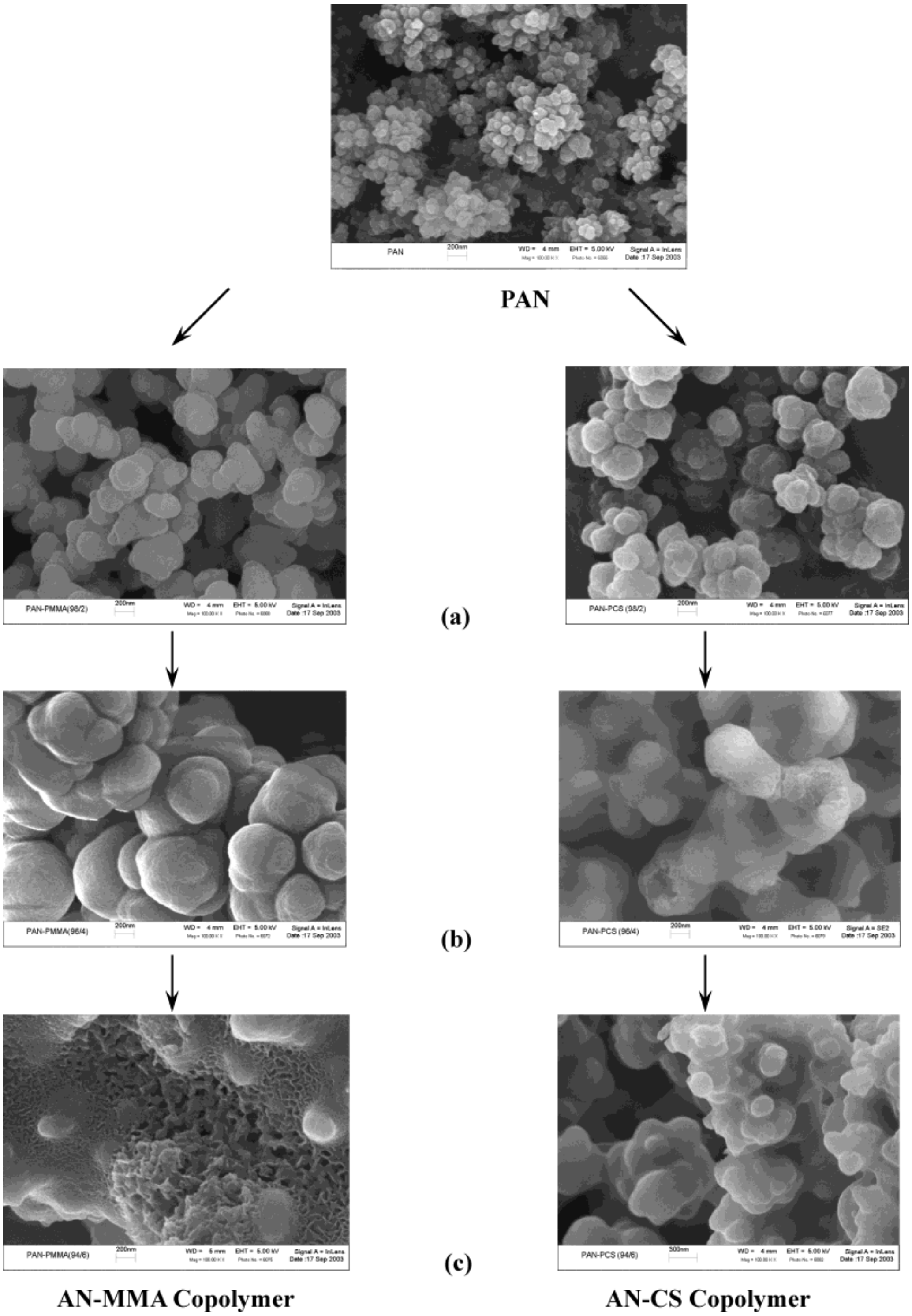

Figure 7. FESEM photomicrographs of acrylonitrile homopolymer (PAN) and AN−MMA and AN−CS copolymers produced from different initial molar feed ratios of comonomers (AN:MMA and AN:CS) at (a) 98:2, (b) 96:4, and (c) 94:6. Magnifications are at ×100 000.

resulted in lower yields (see Table 2). Assessment of reactivity ratios was not done at this time, and this aspect will be explored in the future by carrying out copolymerizations at low conversions.

Figure 4 shows the ^{13}C NMR spectra of PAN homopolymer and the selected AN−MMA and AN−CS copolymers mainly in the CN carbon resonance region. In these spectra, the resonance peaks of CN carbon of PAN unit were in the same range of 119.5−120.4 ppm. The CN carbon peak of the PAN homopolymer consisted of three major envelopes, and each envelope is further divided into three peaks. These peak patterns are consistent with those in the literature in which the PAN was synthesized by the precipitation polymerization in aqueous phase[21,22] and in supercritical CO_2 phase[23] using redox-type initiator and AIBN, respectively. These authors identified that the three envelopes for CN carbon corresponds to the triad tacticity and the split of the envelope into three peaks reflect the pentad tacticity of the polymers. It has been shown that PAN

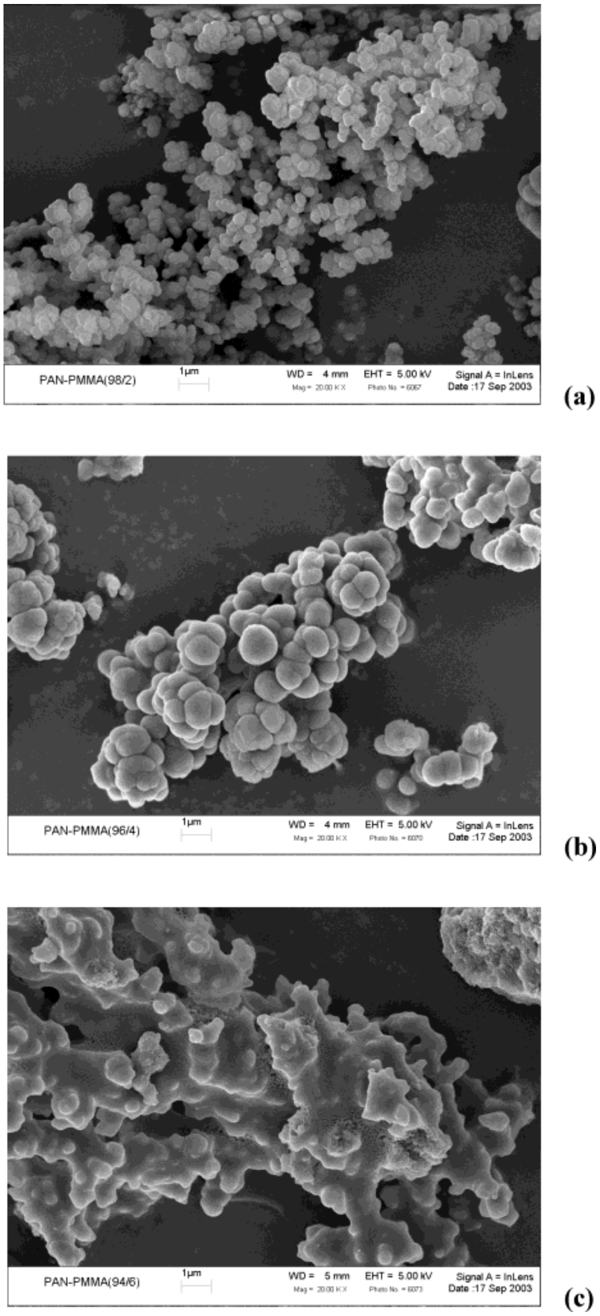

Figure 8. FESEM photomicrographs of AN−MMA copolymers produced from initial molar feed ratios (AN:MMA) of (a) 98:2, (b) 96:4, and (c) 94:6. Magnifications are at ×20 000.

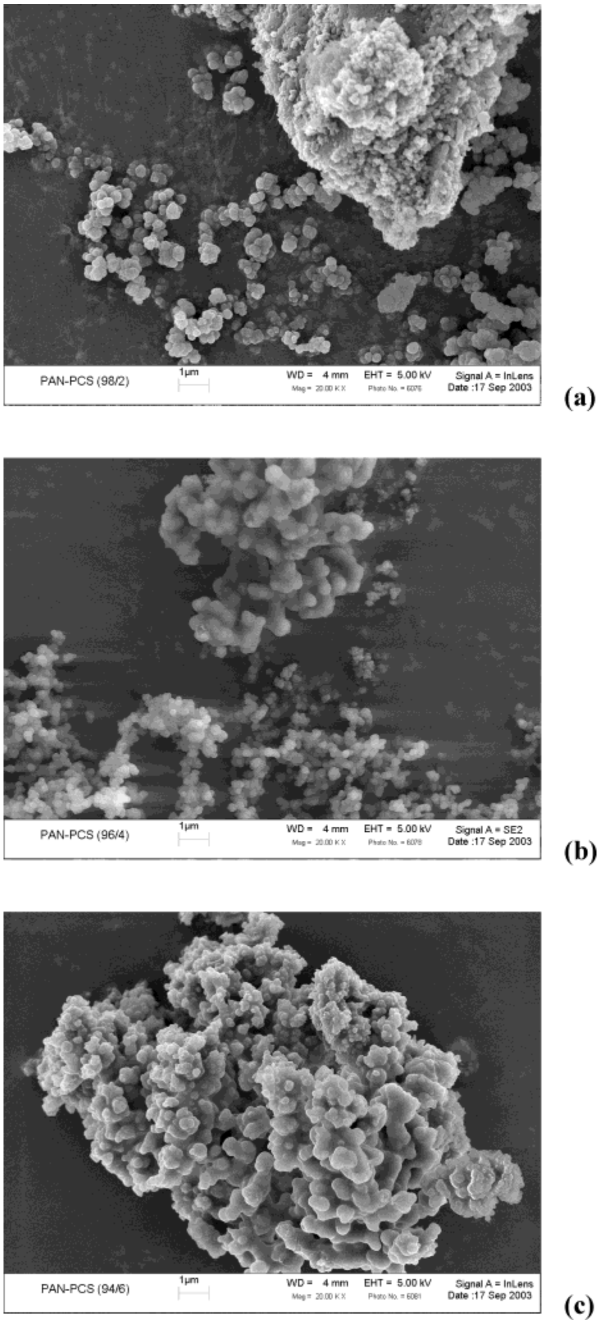

Figure 9. FESEM photomicrographs of AN−CS copolymers produced from initial molar feed ratios (AN:CS) of (a) 98:2, (b) 96:4, and (c) 94:6. Magnifications are at ×20 000.

synthesized in supercritical CO_2 had lower isotacicity than PAN polymerized by other methods, and therefore the PAN homopolymer turned out to be completely random in stereoregularity.[23]

(c) Thermal Charaterization. Figures 5 and 6 show the thermogravimetric (TGA) behavior and differential scanning calorimetry (DSC) results on some of the copolymers. The TGA data show a small ($<5\%$) weight loss at temperatures below 100 °C that can be attributed to evolution of any residual monomer or dissolved CO_2. The primary weight loss starts around 300 °C followed by further essentially complete weight loss above 600 °C. The AN−CS copolymer appears to be initially stable but shows much a higher weight loss at 400 °C compared to that of AN homopolymer or the AN−MMA copolymer.

Figure 6 shows the DSC scans during initial heating to 360 °C followed by cooling back to room temperature. These scans show that PAN and the AN−MMA copolymers undergo exothermic reactions starting around 200 °C. The 94:6 copolymer shows more complete reaction by 350 °C. Acrylonitrile polymers are well-known to undergo cyclization and stabilization reactions.[12,24] The copolymer with CS appears to be more stable at these temperatures as was also noted in the TGA results. However, as shown in the TGA results, once the reactions start at around 400 °C, they lead to nearly 60% loss in weight.

(d) Morphology. Morphology of polymer products varied with the initial molar ratio of comonomers. The physical states of the polymers are summarized in Table 2. Descriptions of the physical state are based on the

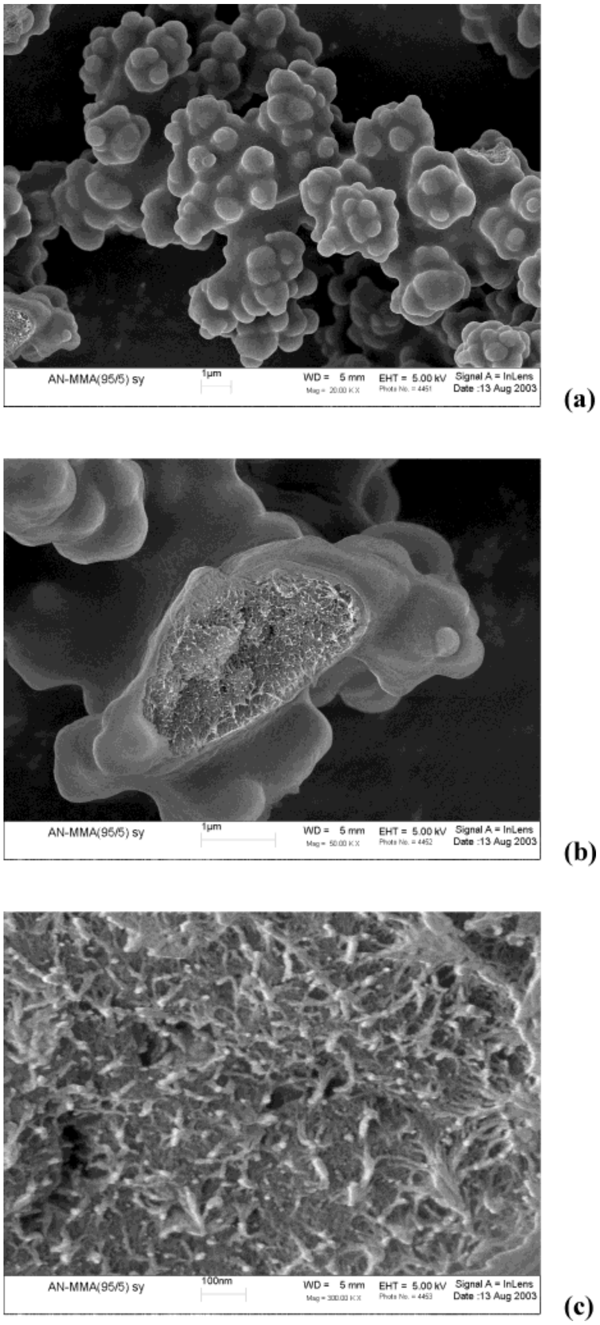

Figure 10. FESEM photomicrographs of AN−MMA copolymers produced from initial molar feed ratio (AN:MMA) of 95:5: (a) magnification at ×20 000; (b) magnification at ×50 000 showing the fractured surface of the lower left region in (a); (c) porous morphology of the region in (b) depicted at a high magnification at ×300 000.

visual observation of the products immediately after the recovery of polymers from the reactor. Three types of end products were obtained depending on the copolymer compositions. The homopolymerization of AN and copolymerization with a high AN content led to free-flowing powders as end products. As the concentrations of MMA and CS were increased in the feed mixture, the products tended to become more gellike materials or soft solids. The formation of gellike polymers is attributed to the combined effect of the presence of carbon dioxide and the unreacted monomer that lower the glass transition temperature. The formation of gellike PMMA in the present study can be compared with other observations reported in the literature[25,26] in which spherical PMMA particles were obtained using stabilizers. All the gel-type polymers turned to hard glassy solids after the drying step in a vacuum chamber.

The significance of the copolymer glass transition temperature in the morphology has been noted in the literature with other systems as well.[27,28] In dispersion copolymerization of functionalized methacrylate monomers such as methyl methacrylate and (ethylene glycol) methacrylate, the copolymers produced with comonomer feed ratios of 50:50, 75:25, 90:10, 95:5, and 98:2 MMA:EGMA resulted in copolymers with glass transition temperatures of −15, 10, 31, 52, and 68 °C.[27] Morphologically, because of the low glass transition of these copolymers, sticky gels and sticky white solids were obtained as the end products. In dispersion copolymerization of 2-(dimethylamino)ethyl methacrylate (DMA) with methyl methacrylate in supercritical CO_2, while the copolymer formed from 50:50 MMA:DMA feed comonomer composition resulted in a viscous liquid or bulk solid, the copolymers formed from feed comonomer ratios of 90:10 and 95:5 were observed to lead to the formation of fine powders.[28]

Morphological variations of PAN polymer caused by the copolymerization with the guest monomers (MMA and CS) are illustrated in Figure 7 at a magnification of 100 000. The PAN homopolymer was produced in a free-flowing spherical powder form with some degree of irregularity in shape and low degree of aggregation. Mean diameters of the individual particles were around 100 nm, which is comparable to the PAN particles produced from previous studies reported in the literature for the dispersion polymerization using stabilizers[6] and the precipitation polymerization without using stabilizers.[11]

The microscopic results show that the morphology of PAN polymer was modified by copolymerizing AN monomer with guest monomers where the concentrations of the guest monomers are very low. The images in Figure 7 correspond to the copolymers of AN with MMA and CS produced from the comonomer mixtures with the initial molar ratios (AN:MMA or AN:CS) of 98:2 (a), 96:4 (b), and 94:6 (c), respectively. These copolymers mainly consist of AN segments with small portions of MMA or CS (see Table 3). It was found that the morphology of PAN was significantly altered by these minor compositional modifications. In the case of the AN−MMA copolymer, the particle size increased significantly with the increase of MMA portion in copolymer, and finally the sphericity of particle disappeared at high MMA insertions. At higher MMA contents, a porous morphology for the copolymer was obtained (Figure 7c). For the AN−CS copolymer, a similar trend was observed with the merging of enlarged particles, finally forming a glassy texture. With copolymerization there is a decrease, if not elimination, of the crystallinity of PAN and formation of basically glassy copolymers. It is important to note that even low levels of comonomer insertions lead to significant changes.

Figures 8 and 9 show these copolymers at a lower magnification to demonstrate the progression of morphology from powders with minor agglomeration to highly glassy bulk solids. Figure 10 is another set of FESEM pictures for AN−MMA copolymer produced from an initial feed mixture with a molar comonomer ratio of 95:5 AN:MMA. With this system, also glassy structures are shown to dominate. Parts b and c of Figure 10 are the enlargements of a section on the lower left corner in Figure 10a which demonstrates the porous nature of the inner portions of these end products.

In addition to the morphological variation, a color change of PAN polymer was observed so that almost white color of PAN homopolymer changed to yellowish when the copolymers were formed, and the color became denser with increasing comonomer insertion in both systems.

Conclusions

The present study has shown that homopolymers and copolymers of acrylonitrile with methyl methacrylate and 2-chlorostyrene can be formed by free-radical precipitation polymerization in supercritical carbon dioxide. Depending upon the copolymer composition, morphologies ranging from free-flowing powders to soft solids and gels are obtained. Morphology of acrylonitrile homopolymer is significantly altered upon copolymerization and by the insertion of small portions of methyl methacrylate or 2-chlorostyrene into the chain. The acrylonitrile copolymers could be obtained in powder forms when the molar concentrations of the comonomer methyl methacrylate or 2-chlorostyrene were less then 10% in the feed mixture. The degree of agglomeration showed an increase with increasing comonomer insertion into the chain. With the change of the crystalline nature of the acrylonitrile homopolymer to glassy copolymers, the extent of swelling and/or the reduction in T_g in the presence of carbon dioxide appear instrumental in leading to soft solids and gellike morphologies. The number-average molecular weight of the copolymers ranged from 40 000 to 300 000, and the polydispersity index was between 1.4 and 4.8. Copolymer compositions determined from ^{1}H NMR spectra show that the AN/MMA or AN/CS mole ratios in the copolymers were lower then the respective ratios in the feed mixtures.

Acknowledgment. We thank Todd Pechar for his help with obtaining the FTIR spectra, Hailing Yang for her help in generating the TGA and DSC scans, and the staff in the Macro program for their help with the GPC tests.

References and Notes

(1) Kiran, E. In *Supercritical Fluids*; Kiran, E., Debenedetti, P. G., Peters, C. J., Eds.; Kluwer Academic Publishers: Boston, 2000; p 253.
(2) Kiran, E. In *Supercritical Fluids*; Kiran, E., Debenedetti, P. G., Peters, C. J., Eds.; Kluwer Academic Publishers: Boston, 2000; p 167.
(3) Cooper, A. I. *J. Mater. Chem.* **2000**, *10*, 207−234.
(4) Canelas, D. A.; DeSimone, J. M. *Adv. Polym. Sci.* **1997**, *133*, 103−140.
(5) Wang, M. X.; Griffith, R. M. T.; Giles, M. R.; Williams, P.; Howdle, S. M. *Eur. Polym. J.* **2003**, *39*, 423−428.
(6) Shiho, H.; DeSimone, J. M. *Macromolecules* **2000**, *33*, 1565−1569.
(7) Ding, L.; Olesik, S. V. *Macromolecules* **2003**, *36*, 4779−4785.
(8) Coote, M. L.; Davis, T. P.; Klumperman, B.; Montero, M. J. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1998**, *C38*, 567−593.
(9) Byun, H.-S.; Kim, Y.-S.; Im, J.-K. *J. Korean. Ind. Eng. Chem.* **1998**, *9*, 924−929.
(10) Teng, X.-R. *J. Appl. Polym. Sci.* **2003**, *87*, 1393−1398.
(11) Okuba, M.; Fujii, S.; Maenaka, H.; Minami, H. *Colloid Polym. Sci.* **2003**, *281*, 964−972.
(12) Godshall, D.; Rangarajan, P.; Baird, D. G.; Wilkes, G. L.; Bhanu, V. A.; McGrath, J. E. *Polymer* **2003**, *44*, 4221−4228.
(13) Leiberich, R.; Dohrn, R.; Waldmann, H.; Alberts, H. German Patent DE 19618832, 1997 (Chem. Abstr. No: 128:13533).
(14) Leiberich, R.; Dummersdorf, H.-U.; Waldmann, H.; Gasche, H.-E.; Kricsfalussy, Z. Europ. Patent, EP 684264 1995; (Chem. Abstr. No: 124:118314).
(15) Zhang, W.; Dindar, C.; Bayraktar, Z.; Kiran, E. *J. Appl. Polym. Sci.* **2003**, *89*, 2201−2209.
(16) Sufi, B. A.; Bates, R. B.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **2001**, *34*, 9205−9207.
(17) Mark, J. E. *Polymer Data Handbook*; Oxford Press: New York, 1999; p 255.
(18) Teng, X.-R.; Shao, H.-L.; Hu, X.-C. *J. Appl. Polym. Sci.* **2002**, *86*, 2338−2341.
(19) Ribeiro-Claro, P. J. A.; Teixeira-Dias, J. J. C. *J. Raman Spectrosc.* **1994**, *25*, 353−357.
(20) Reddy, G. V. R.; Babu, Y. P. P.; Reddy, N. S. R. *J. Appl. Polym. Sci.* **2002**, *85*, 1503−1510.
(21) Kamide, K.; Yamazaki, H.; Okajima, K.; Hikichi, K. *Polym. J.* **1985**, *17*, 1233−1239.
(22) Schaefer, J. *Macromolecules* **1971**, *4*, 105−110.
(23) Teng, X.-R.; Hu, X.-C.; Shao, H.-L. *Polym. J.* **2002**, *34*, 534−538.
(24) Bhanu, V. A.; Rangarajan, P.; Wiles, K.; Bortner, M.; Sankarpandian, M.; Godshall, D.; Glass, T. E.; Banthia, A. K.; Yang, J.; Wilkes, G.; Baird, D.; McGrath, J. E. *Polymer* **2002**, *43*, 4841−4850.
(25) Lepilleur, C.; Beckman, E. J. *Macromolecules* **1997**, *30*, 745−756.
(26) Christian, P.; Giles, M. R.; Griffiths, R. M. T.; Irvine, D. J.; Major, R. C.; Howdle, S. M. *Macromolecules* **2000**, *33*, 9222−9227.
(27) Giles, M. R.; Griffiths, R. M. T.; Irvine, D. J.; Howdle, S. M. *Eur. Polym. J.* **2003**, *39*, 1785−1790.
(28) Wang, W.; Giles, M. R.; Bratton, D.; Irvine, D. J.; Armes, S. P.; Weaver, J. V. W.; Howdle, S. M. *Polymer* **2003**, *44*, 3803−3809.

MA040030C