Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Polymer 47 (2006) 7670–7679
polymer
www.elsevier.com/locate/polymer

# Polymerization of acrylonitrile in supercritical carbon dioxide

Zi Wang [a], Ya Jun Yang [a], Qingzhi Dong [a], Tao Liu [b], Chun Pu Hu [a,*]

[a] *School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China*
[b] *Unilab Research Center of CRE, State Key Lab of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, PR China*

Received 8 May 2006; received in revised form 1 September 2006; accepted 3 September 2006
Available online 25 September 2006

## Abstract

A series of fluorinated diblock copolymers, consisting of styrene (St)–acrylonitrile (AN) copolymer [poly(St-*co*-AN)] and poly-2-[(perfluorononenyl)oxy]ethyl methacrylate, with various compositions as well as with different molecular weights were synthesized by atom transfer radical polymerization and characterized. Dispersion polymerization of acrylonitrile in supercritical carbon dioxide (scCO$_2$) at 30 MPa and at 65 °C with this kind of amphiphilic block copolymer as a stabilizer and 2,2′-azobisisobutyronitrile as an initiator was investigated. The experimental results indicated that, in the presence of a small amount of poly(St-*co*-AN) (5 wt% to AN), spherical particles of polyacrylonitrile (PAN) were prepared with small diameter and narrow polydispersity ($d_n = 153$ nm, $d_w/d_n = 1.12$), resulting from the high stabilizing efficiency of this fluorinated block copolymer. Furthermore, the polymerization of AN in scCO$_2$ under different initial pressures especially under low pressure (<14 MPa) was studied. When the polymerization was carried out around the critical pressure of CO$_2$ (7.7–7.8 MPa), the PANs with high molecular weight ($M_v \approx 130{,}000$–$194{,}000$) were synthesized at high monomer conversion (>90%) no matter whether the stabilizer was added, compared to those synthesized by dispersion polymerization at 30 MPa. It was also found that the crystallinity of PAN synthesized at 7.7–7.8 MPa was somewhat higher than that synthesized at 30 MPa, while its crystallite size did not change.

*Keywords:* Supercritical carbon dioxide; Acrylonitrile; Polymerization

## 1. Introduction

As an environmental-friendly polymerization media, carbon dioxide (CO$_2$) has become favorable in polymerization industry, because it is nonflammable, nontoxic and inexpensive, and also features excellent mass and heat transferring abilities [1]. Most of the vinyl polymers show poor solubility in supercritical carbon dioxide (scCO$_2$), thus heterogeneous polymerizations especially dispersion polymerization and precipitation polymerization have been studied in recent years. The dispersion polymerizations of various vinyl monomers such as styrene (St) [2], glycidyl methacrylate [3], 2-hydroxyl methacrylate [4], methyl methacrylate (MMA) [5] and vinylidene fluoride [6] have been reported, but the addition of some amphiphilic fluorinated polymers or PDMS-based polymers as the stabilizers as well as quite high pressure (20–46 MPa) to enhance the solubility of these stabilizers in scCO$_2$ is generally required. Although spherical polymer particles can be prepared by dispersion polymerization, the stabilizers involved were usually difficult to be separated from final products, so as to alter the performance of polymer materials, especially the surface properties, resulting in limiting their application in industry. Therefore it is significant to further synthesize new stabilizers with enhanced stabilizing efficiency, thus to relieve their influence on the properties of the polymer products by reducing the stabilizer concentration used. Meanwhile, the precipitation polymerization was also studied due to its capability of producing stabilizer-free polymers, but quite high pressure (usually more than 15 MPa) was still adopted extensively such as in precipitation polymerizations of acrylic acid [7], divinylbenzene [8], divinylbiphenyl [9] and vinylidene fluoride [10].

---

[*] Corresponding author. Tel.: +86 21 64253037; fax: +86 21 64253539.
*E-mail address:* cphu@guomai.sh.cn (C.P. Hu).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.09.011

Polyacrylonitrile (PAN) is one of the most important polymer materials for the production of synthetic fibers, which are traditionally produced by solution polymerization or precipitation polymerization of acrylonitrile (AN) in water [11]. Both the polymerization procedures involve costly purification and drying process, and will cause serious pollution. Therefore, it is of great importance to study how to produce the PAN in $scCO_2$. Shiho and DeSimone [12] pioneered research on the dispersion polymerization of AN in $scCO_2$, in which a block copolymer of St and 1,1-dihydroperfluorooctyl acrylate [poly(St-*b*-FOA)] were used as stabilizers. They prepared well-dispersed spherical PAN particles under 20–46 MPa at 65 °C with 2,2′-azobisisobutyronitrile (AIBN) as an initiator, whereas at least 15 wt% poly(St-*b*-FOA) based on AN was needed to prevent the agglomeration of PAN particles at 10 wt/volume (w/v)% AN concentration. Okubo et al. [13] carried out the precipitation polymerization of AN in $scCO_2$ at 30 MPa and at 65 °C with AIBN as the initiator, in which some micron-sized and well-dispersed PAN particles were prepared. Teng [11] investigated the molecular weight and spinnability of PAN produced by precipitation polymerization of AN in $scCO_2$ under 14–28 MPa from 50 °C to 65 °C with AIBN as the initiator. It is well-known that the pressure for the polymerization of vinyl monomer in $scCO_2$ should be controlled as low as possible, if one considers performing it easily in industry. However, either the dispersion polymerization or the precipitation polymerization of AN in $scCO_2$ under pressure below 14 MPa has not been reported yet.

In this article, a bromine-ended copolymer of St and AN [poly(St-*co*-AN), abbreviated as SAN-Br] was synthesized first by atom transfer radical polymerization (ATRP), then it was used as a macroinitiator to initiate the ATRP of 2-[(perfluorononenyl)oxy]ethyl methacrylate (FNEMA) thus to form a series of well-defined fluorinated diblock copolymers, i.e. poly[(St-*co*-AN)-*b*-FNEMA] [abbreviated as poly(SAN-*b*-FNEMA)]. The dispersion polymerization of AN in $scCO_2$ with this kind of amphiphilic block copolymer as the stabilizer and AIBN as the initiator was investigated (30 MPa/65 °C/18 h). The experimental results indicated that the well-dispersed spherical PAN particles could be prepared at a stabilizer concentration as low as 5 wt%, resulting from the high stabilizing efficiency of this novel block copolymer. Furthermore, the effect of pressure on polymerization of AN in $scCO_2$ with or without adding such a stabilizer was studied. It was found that the PANs with high molecular weight ($M_v \approx$ 130,000–194,000) and a bit high crystallinity were synthesized around the critical pressure of $CO_2$ (7.7–7.8 MPa) and at high monomer conversion (>90%), compared to those synthesized by dispersion polymerization at 30 MPa.

## 2. Experimental section

### 2.1. Materials

Ethyl-2-bromoisobutyrate (98%, Aldrich), benzotrifluoride (BTF) (99%, Lancaster) and $CO_2$ (99.5%, Shanghai Wugang Co.) were used as received. FNEMA was synthesized by the reaction of hexafluoropropylene trimer (kindly supplied by Shanghai Institute of Organo-fluorine Materials) and 2-hydroxyethyl methacrylate (98%, Fluka) [14]. $^1$H NMR (Bruker, 500 MHz, with deuterated chloroform as solvent) of FNEMA: 1.92 ppm (3H, $CH_3-$), 4.42 ppm (4H, $CH_2CH_2OCO$), 5.69 ppm (1H, $CH_2=$), 6.10 ppm (1H, $-CH=$). Elemental analysis of FNEMA: C, 32.23 wt%; H, 1.68 wt%; F, 58.64 wt% (theoretical values: C, 32.14 wt%; H, 1.6 wt%, F, 57.67 wt%).

All other materials used in this research were standard laboratory reagents provided by Shanghai Chemical Reagent Plant. Styrene and acrylonitrile were purified by passing through a column filled with neutral alumina to remove the inhibitor. Cuprous bromide (CuBr) was purified according to the procedure reported by Keller and Wycoff [15]. α,α′-Bispyridine (bpy) was recrystallized from *n*-hexane. AIBN was recrystallized from hot methanol.

### 2.2. Synthesis of SAN-Br

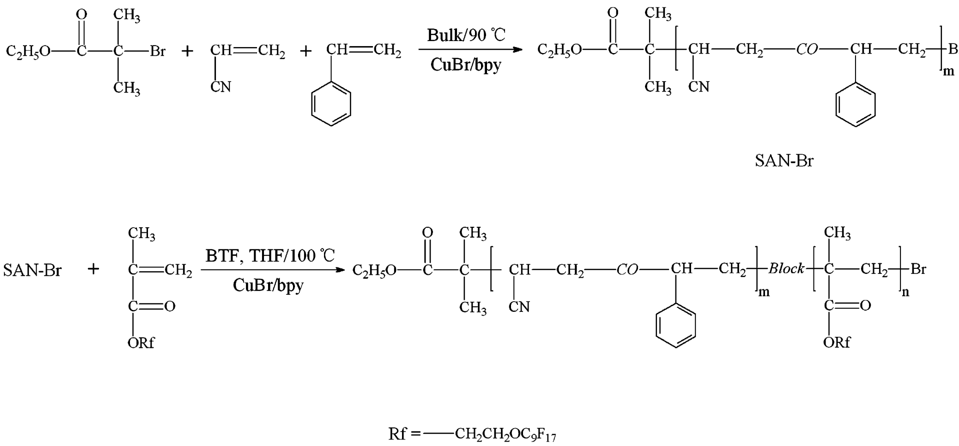
A dry reaction flask with a magnetic stir bar was charged with CuBr and bpy. The flask was sealed with a rubber septum, degassed and back-filled with nitrogen three times. The deoxygenated St, AN and ethyl-2-bromoisobutyrate were introduced into the flask by a syringe. The flask was then heated at 90 °C under stirring. The copolymer product was precipitated in *n*-hexane after passing through a column filled with neutral alumina to remove the copper complex, and dried at 30 °C under vacuum.

### 2.3. Synthesis of poly(SAN-b-FNEMA)

SAN-Br synthesized above was used as the macroinitiator to initiate the ATRP of FNEMA using BTF and tetrahydrofuran (THF) as a mixed solvent. The SAN-Br, CuBr and bpy were charged into a dry reaction flask with a magnetic stir bar. The flask was sealed with a rubber septum, degassed and back-filled with nitrogen three times. The deoxygenated BTF and THF were introduced into the system by a syringe. After the SAN-Br was dissolved, FNEMA was charged. The flask was then heated at 100 °C under stirring. The block copolymer was isolated by precipitation in methanol after passing through a column filled with neutral alumina to remove the copper complex, and dried at 30 °C under vacuum. All synthetic procedures of SAN-Br and poly(SAN-*b*-FNEMA) are listed in Scheme 1.

### 2.4. Dispersion polymerization of acrylonitrile in $scCO_2$

A 20-ml stainless steel high-pressure reactor equipped with a magnetic stir bar was charged with AIBN, AN and poly(SAN-*b*-FNEMA) (for studying the effect of pressure on polymerization, sometimes this block copolymer was not added), and then the reactor was purged with a flow of $CO_2$ to remove the oxygen prior to the start of polymerization. After a desired amount of $CO_2$ was charged, the reactor was placed in a water bath heated to 65 °C. Then, additional $CO_2$ was charged to this



Scheme 1. Synthetic reactions of SAN-Br and poly(SAN-*b*-FNEMA).

system if necessary, until the desired reaction condition was reached. Once the preset temperature and pressure were reached, the reaction mixture was stirred for 18 h. At the end of the polymerization, the reactor was cooled and the $CO_2$ was slowly vented to recover the product. Finally, the reactor was rinsed with *N*,*N′*-dimethylformamide (DMF) to collect residue product for calculation of monomer conversion. The product was extracted with THF before measuring its viscosity average molecular weight.

### 2.5. Characterization

$^1$H NMR spectra of macroinitiator and block copolymer were recorded using a Bruker 500 MHz spectrometer with deuterated chloroform ($CDCl_3$) as solvent. Gel permeation chromatography (GPC) was used to determine the molecular weight averages and the polydispersity index of the SAN-Br and the block copolymers using a Shimadzu SCL-10A and LC-8A system equipped with a Shimadzu RID-10A refractive index detector. DMF was used as an eluent at 40 °C and polystyrene (PS) with a narrow molecular weight distribution (Showa Denko Co.) was used as a standard. Wide angle X-ray diffractogram (WAXD) measurements of specimens were performed on a *D*/max 2550VB/PCX diffractometer with Cu K$\alpha$ radiation ($\lambda = 1.542$ Å) at an operational voltage of 40 kV and the WAXD data were analyzed using Microcal Origin 7.0 software. The viscosity average molecular weight ($M_v$) of PAN was determined with an Ubbelohde viscometer at 30 °C using DMF as solvent. $M_v$ was calculated by $[\eta] = KM_v^{\alpha}$, where values of $K$ and $\alpha$ are $20.9 \times 10^{-3}$ ml/g and 0.75, respectively [16]. The appearance of the PAN particles was observed using a JEOL JSM-6360 scanning electron microscope (SEM). The number-average particle diameter ($d_n$) and particle diameter distribution ($d_w/d_n$) were estimated by measuring 100 individual particles randomly with Adobe Photoshop 7.0 software and calculated using the following equations [2]:

$$d_n = \frac{\sum_{i=1}^{N} d_i}{N} \quad (1)$$

$$d_w = \frac{\sum_{i=1}^{N} d_i^4}{\sum_{i=1}^{N} d_i^3} \quad (2)$$

where $d_i$ is the diameter of the particle $i$ and $N$ is the number of particles measured in that sample.

## 3. Results and discussion

### 3.1. Synthesis of poly(SAN-b-FNEMA)

The experimental results of SAN-Br macroinitiator and poly(SAN-*b*-FNEMA) with various compositions synthesized by ATRP are summarized in Table 1, where F stands for the PFNEMA block and the subscripts equal to $M_n$ of the blocks measured by $^1$H NMR. Fig. 1 shows the $^1$H NMR spectrum of SAN-Br. The peaks at 6.7 ppm and 7.1 ppm correspond to the aromatic protons in St units. Since the multiple peaks in the range of 1.2–2.5 ppm are assigned to the methylenes and methylidynes in both St and AN units (noting that the peaks for methyl of the ester group in ethyl-2-bromoisobutyrate are overlapped in this range, which may bring some error), the peak area assigned to AN units can be calculated by subtracting the one assigned to St units. Thus, the composition of SAN-Br was estimated: [St]/[AN] = 61/39, which is

Table 1
Synthesis of SAN-Br and poly(SAN-*b*-FNEMA) by ATRP[a]

| Samples | Monomer conversion (%) | $M_{n,th}$[d] (kg/mol) | $M_{n,NMR}$ (kg/mol) | $M_{n,GPC}$ (kg/mol) | PDI |
|---|---|---|---|---|---|
| SAN-Br | 76[b] | 5.8 | 5.3 | 43 | 1.04 |
| $SAN_{5.3K}$-$F_{10K}$ | 70[c] | 16.7 | 15 | 69 | 1.05 |
| $SAN_{5.3K}$-$F_{16K}$ | 56[c] | 24.4 | 21 | 48 | 1.05 |
| $SAN_{5.3K}$-$F_{19K}$ | 46[c] | 27.8 | 24 | 46 | 1.04 |

[a] For SAN-Br, monomer feed [St]/[AN] = 63/37 and [I]/[CuBr]/[Bpy] = 1/0.5/1.5; for block copolymers, $1.0 \times 10^{-4}$ mol SAN-Br and [I]/[CuBr]/[Bpy] = 1/1/3 used for all entries.

[b] Conversion of St and AN.

[c] Conversion of FNEMA.

[d] $M_{n,th} = [M]_0/[I] \times (M_w)_0 \times \text{conv.} + M_I$.

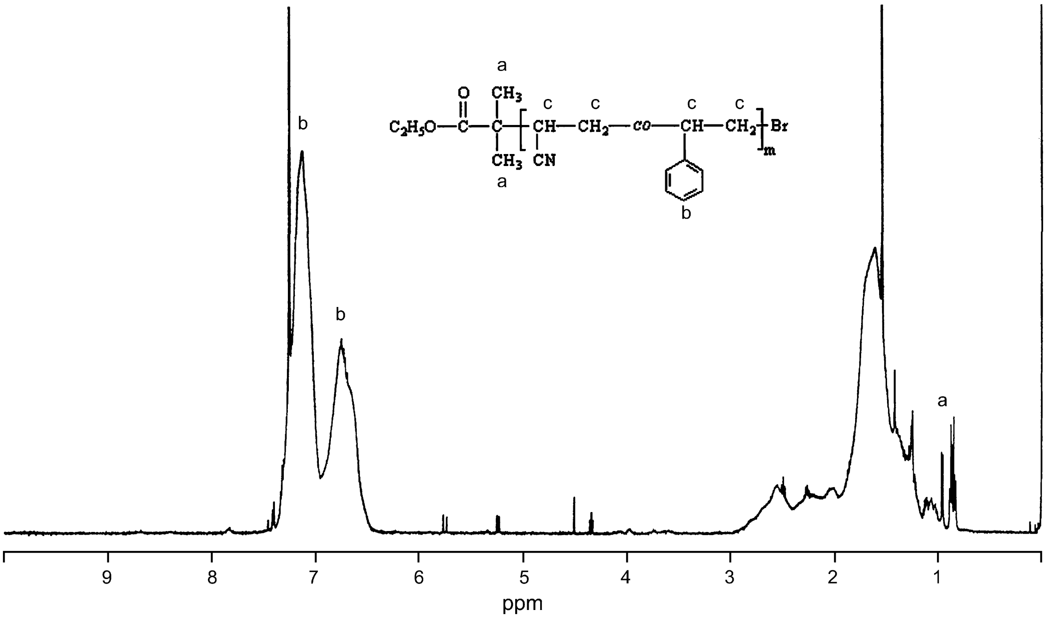


Fig. 1. $^1$H NMR spectra of SAN-Br.

in reasonable agreement with the monomer feed. The possible reason is that the copolymerization of St and AN in this system was carried out under an azeotropic condition (63 mol% St and 37 mol% AN) [17]; furthermore, the composition of copolymer should approach monomer feed due to the high monomer conversion. The narrow molecular weight distribution of SAN-Br in Table 1 suggests that all macromolecular chains propagate at a constant rate throughout the copolymerization, resulting from the inherence of the living polymerization. However, the average molecular weight of SAN-Br tested by GPC ($M_{n,GPC}$) is much higher than the calculated ones ($M_{n,th}$). Thus, it is necessary to check the average molecular weight of SAN-Br by $^1$H NMR ($M_{n,NMR}$) further. As shown in Fig. 1, the peaks in the range of 0.8–0.9 ppm correspond to the protons of the methyl group in ethyl-2-bromoisobutyrate. Recalling that the peak area of aromatic protons in styrene units (6.7 ppm and 7.1 ppm) is already known, $M_{n,NMR}$ of SAN-Br can be calculated on the basis of the area ratio of the two peaks, since this well-defined SAN-Br was characterized. The result ($M_{n,NMR} = 5300$) is in good agreement with $M_{n,th}$, indicating that the deviation between the $M_{n,GPC}$ and $M_{n,th}$ is attributed to the discrepancy between the hydrodynamic volume of SAN-Br and PS standard in DMF.

As listed in Table 1, all block copolymers exhibited narrow molecular weight distribution (PDI $\leq$ 1.05), although the deviation between $M_{n,GPC}$ and $M_{n,th}$ was observed as in the case of SAN-Br. Fig. 2 shows the GPC traces of SAN-Br and the resulting block copolymer (SAN$_{5.3K}$-F$_{10K}$). The monomodal shape of the GPC trace for SAN$_{5.3K}$-F$_{10K}$ suggests the complete initiation of SAN-Br macroinitiator during the ATRP process. Fig. 3 shows the $^1$H NMR spectrum of SAN$_{5.3K}$-F$_{10K}$. The peaks at 4.1 ppm are assigned to two methylenes of ester group in PFNEMA block, and the peaks at 6.6 ppm and 7.1 ppm correspond to the aromatic protons in SAN block. Since this well-defined block copolymer was characterized, based on $M_{n,NMR}$ of SAN-Br and the area ratio of the peaks for the aromatic protons in SAN block and the peaks of two methylenes of ester group in PFNEMA block, $M_{n,NMR}$ of SAN$_{5.3K}$-F$_{10K}$ was calculated as 15,000, also approaching its $M_{n,th}$. Therefore, it can be concluded that the discrepancy in hydrodynamic volume between the block copolymers and PS standard led to the magnification of $M_{n,GPC}$.

The block copolymer with longer PFNEMA block ($M_{n,th}$ = 33,000) was also synthesized by ATRP with SAN-Br as the initiator, but it was found to be difficult to dissolve in DMF, THF or CDCl$_3$, resulting in some problems of characterization. In this case, such a block copolymer was not studied further.

### 3.2. Dispersion polymerization of AN in scCO$_2$

Table 2 and Fig. 4 show the effect of poly(SAN-*b*-FNEMA) on the polymerization of AN in scCO$_2$ at high pressure

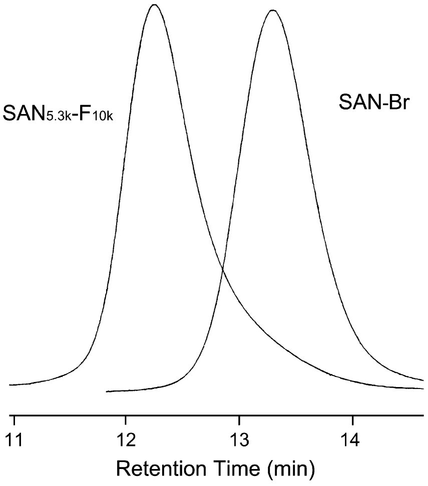


Fig. 2. GPC traces of SAN-Br and SAN$_{5.3K}$-F$_{10K}$.

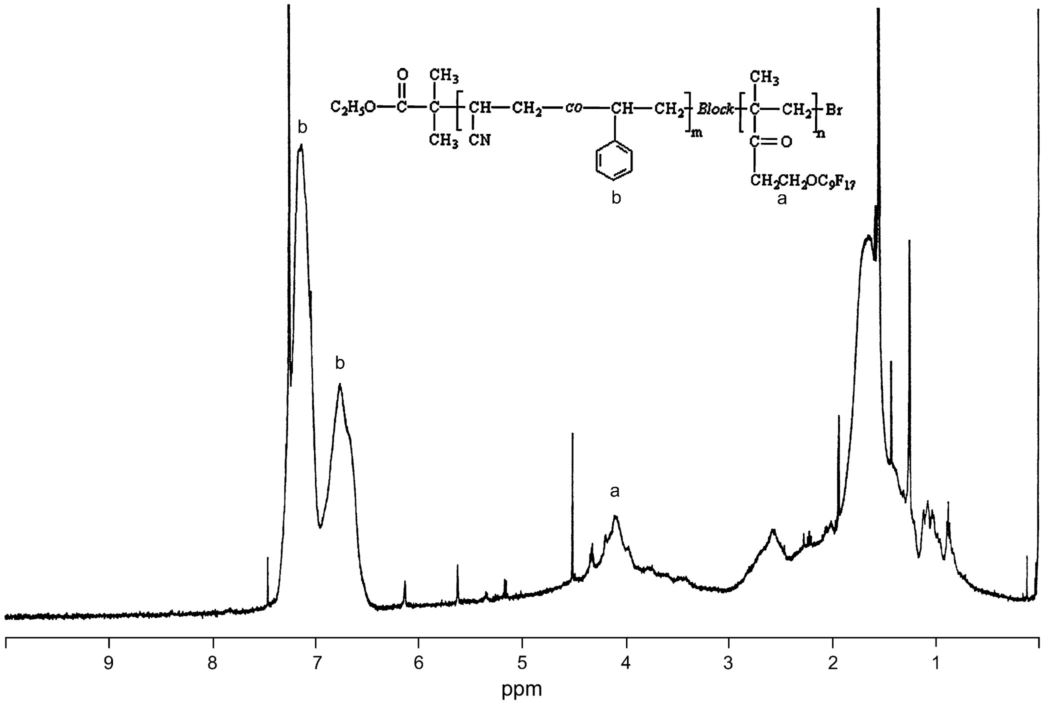


Fig. 3. $^1$H NMR spectra of $SAN_{5.3K}$-$F_{10K}$.

(30 MPa). The precipitation polymerization in the absence of poly(SAN-*b*-FNEMA) (entry 1 in Table 2) was observed and led to some large aggregates of the irregular PAN particles (Fig. 4a) with low monomer conversion and low molecular weight. When 10 wt% $SAN_{5.3K}$-$F_{10K}$ was added to the system, the AN conversion and the molecular weight of PAN remained nearly the same as those found for the precipitation polymerization (entry 2 in Table 2), as well as the coagulated appearance of the irregular particles (Fig. 4b) was observed. Thus, the $SAN_{5.3K}$-$F_{10K}$ with a quite short fluorinated block was proved to be incapable of stabilization in $scCO_2$ for the polymerization of AN. In the case of using 10 wt% $SAN_{5.3K}$-$F_{16K}$, higher monomer conversion and molecular weight of PAN than those performed in the precipitation polymerization were observed (entry 3 in Table 2), but the highly agglomerated PAN particles were still produced (Fig. 4c). Obviously, the $SAN_{5.3K}$-$F_{16K}$ failed to prevent the PAN particles from agglomeration due to its relatively short fluorinated block. When 10 wt% $SAN_{5.3K}$-$F_{19K}$ with a relatively long fluorinated block was employed (entry 4 in Table 2), well-dispersed spherical particles of PAN were produced under 30 MPa (Fig. 4d), suggesting that the $SAN_{5.3K}$-$F_{19K}$ could form stable micelle phase in $scCO_2$ so as to prevent the agglomeration of PAN particles. By decreasing the content of block copolymer to 5 wt% (entry 5 in Table 2), it was still able to yield the discrete spherical particles of PAN (Fig. 4e). The particle diameter and its distribution of PAN prepared in the presence of different concentrations of $SAN_{5.3K}$-$F_{19K}$ were also measured, as shown in Fig. 5. When the concentration of $SAN_{5.3K}$-$F_{19K}$ was decreased by half, i.e. from 10 to 5 wt%, the PAN particles showed an increase in diameter only from 139 to 153 nm as well as in diameter distribution only from 1.04 to 1.12. The surface coverage per $SAN_{5.3K}$-$F_{19K}$ molecule in the polymerization system can be estimated using following equation [3]:

$$S = \frac{6(V_{\mathrm{PAN}} + V_{\mathrm{Stab}})}{d_{\mathrm{n}} n_{\mathrm{Stab}}} \tag{3}$$

Table 2
Effect of poly(SAN-*b*-FNEMA) on dispersion polymerization of acrylonitrile in $scCO_2$[a]

| Entry | Stabilizer | [M][b] (w/v%) | [S][c] (wt%) | Monomer conversion (%) | $d_n$ (nm) | $d_w/d_n$ | $M_v$[d] (kg/mol) | Appearance |
|---|---|---|---|---|---|---|---|---|
| 1 | None | 10 | 0 | 56 | – | – | 46 | Coagulated |
| 2 | $SAN_{5.3K}$-$F_{10K}$ | 10 | 10 | 55 | – | – | 49 | Coagulated |
| 3 | $SAN_{5.3K}$-$F_{16K}$ | 10 | 10 | 70 | 100–400 | – | 67 | Particles (agglomerated) |
| 4 | $SAN_{5.3K}$-$F_{19K}$ | 10 | 10 | 72 | 139 | 1.03 | 79 | Well-defined particles |
| 5 | $SAN_{5.3K}$-$F_{19K}$ | 10 | 5 | 74 | 153 | 1.12 | 75 | Well-defined particles |
| 6 | $SAN_{5.3K}$-$F_{19K}$ | 15 | 15 | 82 | – | – | 115 | Coagulated |

[a] Reaction conditions: AIBN = 1 wt% (based on AN), $P = 30 \pm 1.5$ MPa, $T = 65$ °C and 18 h.
[b] Monomer concentration (w/v%, total volume = 20 ml).
[c] Stabilizer concentration (based on AN).
[d] Viscosity average molecular weight.

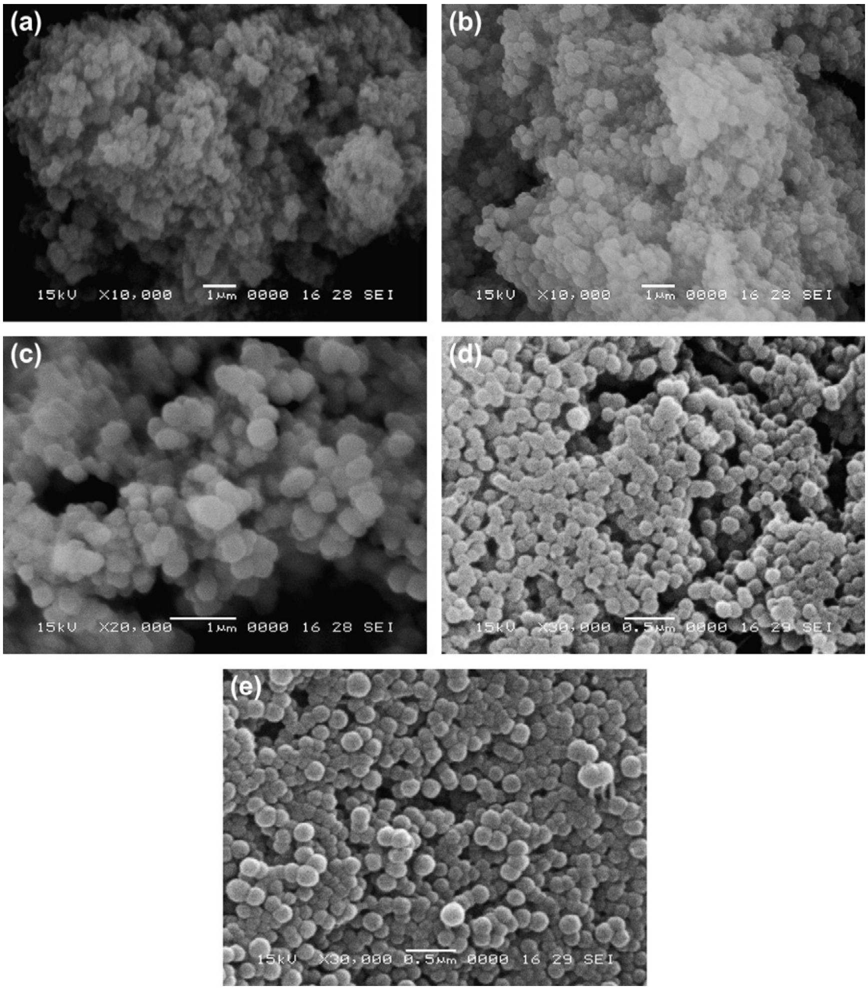


Fig. 4. SEM images of PAN produced by precipitation polymerization (a) and dispersion polymerization with 10 wt% $SAN_{5.3K}$-$F_{10K}$ (b), 10 wt% $SAN_{5.3K}$-$F_{16K}$ (c), 10 wt% (d) and 5 wt% $SAN_{5.3K}$-$F_{19K}$ (e) as stabilizer.

where $V$ stands for volume, and $n_{\mathrm{Stab}}$ is the number of $SAN_{5.3K}$-$F_{19K}$ molecules. As calculated, while the concentration of this block copolymer decreased from 10 to 5 wt%, $S$ increased from 14.2 to 24.8 $nm^2$. Thus, it is clear that the $SAN_{5.3K}$-$F_{19K}$ was still capable of protecting the particles of PAN in the system, although the concentration of $SAN_{5.3K}$-$F_{19K}$ in the polymerization system decreased by half. In other words, the $SAN_{5.3K}$-$F_{19K}$ exhibits high stabilizing efficiency in the polymerization of AN in $scCO_2$.

Shiho and DeSimone [12] reported the effect of poly(St-*b*-FOA) (the values of $M_n$ for PS block and PFOA block are 4.2K and 19.7K, respectively) on the polymerization of AN with AIBN as the initiator in $scCO_2$ and they found that the well-dispersed spherical PAN particles ($d_n = 450$ nm, $d_w/d_n = 1.15$) were produced under the experimental conditions of 10 wt% stabilizer concentration, 8 w/v% AN concentration, 38 MPa and 65 °C. The poly(SAN-*b*-FNEMA) used in this study, however, showed even higher stabilizing efficiency than poly(St-*b*-FOA), since the PAN particles with smaller diameter and narrower distribution were prepared under similar experimental conditions. This enhanced stabilizing efficiency of poly(SAN-*b*-FNEMA) should have been therefore mainly resulted from the good compatibility between the SAN block and PAN synthesized.

The dispersion polymerization of AN at a high monomer concentration (15 w/v%) (entry 6 in Table 2) was also examined. It was found that even if 15 wt% $SAN_{5.3K}$-$F_{19K}$ was added to this system, some coagulated and irregular PAN particles were yielded, which were consistent with the results reported by Shiho and DeSimone [12]. In comparison with the dispersion polymerization of St [2] or MMA [5] in $scCO_2$, the preparation of stable dispersed phase with high PAN content seems difficult. This is probably due to the high polarity of PAN and its insolubility in its own monomer, as well as the strong interaction force between the nitrile groups on the particle surface, which may lead to the aggregation easily. Table 2 indicates that, however, both the monomer conversion and the molecular weight of PAN are all high enough at 15 w/v% AN concentration used. This kind of PAN with high molecular weight ($M_v = 115{,}000$) may have some potential application in industry. For example, the PAN with high molecular weight is somewhat required for the production of carbon fiber [18].

Fig. 6 shows WAXD spectra of the PAN produced by the precipitation polymerization and the dispersion polymerization

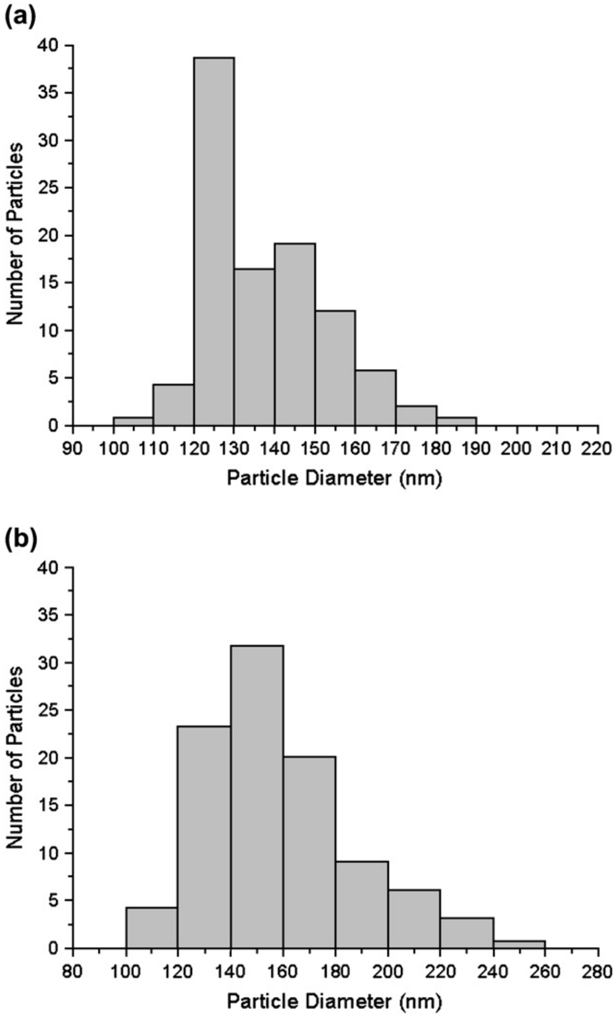


Fig. 5. Particle size distribution of PAN produced with (a) 10 wt% and (b) 5 wt% $SAN_{5.3K}$-$F_{19K}$ as stabilizer.

with $SAN_{5.3K}$-$F_{19K}$ as the stabilizer. For both PAN samples, a strong peak at $2\theta = 16.6°$ and a weak one at $2\theta = 29.3°$ were observed, corresponding to *d*-spacings of 5.30 and 3.04 Å, assigned to diffractions of (010) and (030) planes, respectively. The crystallinity of the PAN prepared by the precipitation polymerization was 18%, close to that reported by Okubo et al. [13], while the crystallinity of the PAN synthesized by the dispersion polymerization slightly decreased to 17%, which was probably due to the presence of fluorinated block copolymer. The crystallite size can be calculated using Scherrer equation [13]:

$$D = K\lambda/\beta \cos\theta \tag{4}$$

where $K$ is the constant (0.9), $\lambda$ is the wavelength of Cu K$\alpha$ radiation (1.542 Å), $\beta$ is the half width of the peaks at $2\theta = 16.7°$ and $\theta$ is the Bragg's angle. The calculated results indicated that the size of the crystallite for the PAN synthesized either by the precipitation polymerization or by the dispersion polymerization is all the same (76 Å), which is similar to those prepared by slurry polymerization [19] and smaller than those produced by mini-emulsion polymerization [20].

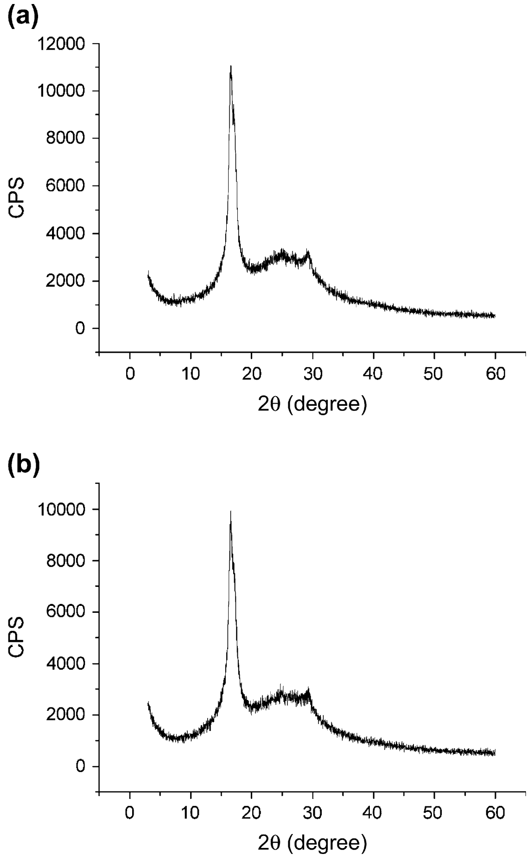


Fig. 6. WAXD of PAN produced by (a) precipitation polymerization (entry 1 in Table 2) and (b) dispersion polymerization (entry 5 in Table 2).

### 3.3. Effect of pressure on polymerization of AN in $scCO_2$

Table 3 lists the effect of initial pressure on polymerization of AN in $scCO_2$. When the initial pressure of dispersion polymerization system in the presence of $SAN_{5.3K}$-$F_{19K}$ was decreased to 20.3 MPa (entry 3 in Table 3), the monomer conversion decreased appreciably, indicating that the stable

Table 3
Effect of initial pressure on polymerization of acrylonitrile in $scCO_2$[a]

| Entry | [S][b] (wt%) | Pressure (MPa) | Monomer conversion (%) | $M_v$[c] (kg/mol) | Appearance[d] |
|---|---|---|---|---|---|
| 1 | 5 | 30.0 | 74 | 75 | Fine powder |
| 2 | 5 | 24.8 | 72 | 72 | Fine powder |
| 3 | 5 | 20.3 | 56 | 71 | Powder |
| 4 | 5 | 15.5 | 59 | 84 | Powder |
| 5 | 5 | 8.5 | 98 | 148 | Powder and bulk |
| 6 | 5 | 7.7 | 91 | 194 | Powder and bulk |
| 7 | 0 | 29.6 | 56 | 46 | Powder |
| 8 | 0 | 19.0 | 55 | 44 | Powder |
| 9 | 0 | 16.2 | 55 | 40 | Powder |
| 10 | 0 | 9.2 | 96 | 92 | Powder |
| 11 | 0 | 7.8 | 99 | 130 | Powder and bulk |

[a] Reaction conditions: [M] = 10 w/v% (total volume = 20 ml), AIBN = 1 wt% (based on AN), $T = 65$ °C and 18 h.
[b] Stabilizer concentration (based on AN).
[c] Viscosity average molecular weight.
[d] By visual observation.

dispersed phase could not form due to the insolubility of $SAN_{5.3K}$-$F_{19K}$ in $scCO_2$ at 20.3 MPa. Although the PAN product was collected as white powder with moderate fluidity compared to the free-flowing fine powder prepared under 30.0 MPa or 24.8 MPa, the molecular weight of this kind of PAN was not affected obviously by decreasing the initial pressure. As the initial pressure was further decreased to 15.5 MPa, both the AN conversion and the molecular weight of PAN increased (entry 4 in Table 3). However, a sudden increase in the monomer conversion (98%) and the molecular weight of PAN ($M_v = 148,000$) was observed at 8.5 MPa (entry 5 in Table 3), which was much higher than those performed at 30 MPa. As shown by SEM photographs (Fig. 7a and b), the large aggregates composed of irregular particles linked by some bridge-like small particles were formed at such a low pressure. Fig. 7c shows a magnified SEM photograph of these bridge-like particles. It reveals that there are many spherical particles with diameter in the range of 100–150 nm, which may be attributed to the $SAN_{5.3K}$-$F_{19K}$ added to the system. It was of interest to find that the molecular weight of PAN even reached as high as 194,000 and the AN conversion was still high enough (91%), when the pressure was further decreased to 7.7 MPa, which came close to the critical pressure of $CO_2$. Except for the high monomer conversion and molecular weight, these two PAN specimens synthesized around the critical pressure (8.5 MPa and 7.7 MPa) appeared as a mixture of powder and bulk, but they could be grinded into powders and could be dissolved in DMF easily. It was also found that some inner parts of the bulk in the PAN synthesized at 7.7 MPa showed dark yellow or black colour due to strong exotherm and were insoluble in DMF, which should have been resulted due to an autoacceleration in the polymerization rate of AN [21]. This phenomenon has been corresponded to the decrease in termination rate of propagating radicals leading to fast polymerization rate for the free radical polymerization of vinyl monomers because of decrease in the diffusion rate of polymer radicals [21,22]. In this case, the high AN conversion and the high molecular weight of PAN found in this polymerization system could be expected.

Table 3 also shows the effect of pressure on the polymerization of AN without adding stabilizer. As the initial pressure was decreased from 29.6 MPa to 16.2 MPa, the low AN conversion and the PAN powders with somewhat low molecular weight as well as moderate fluidity similar to those synthesized

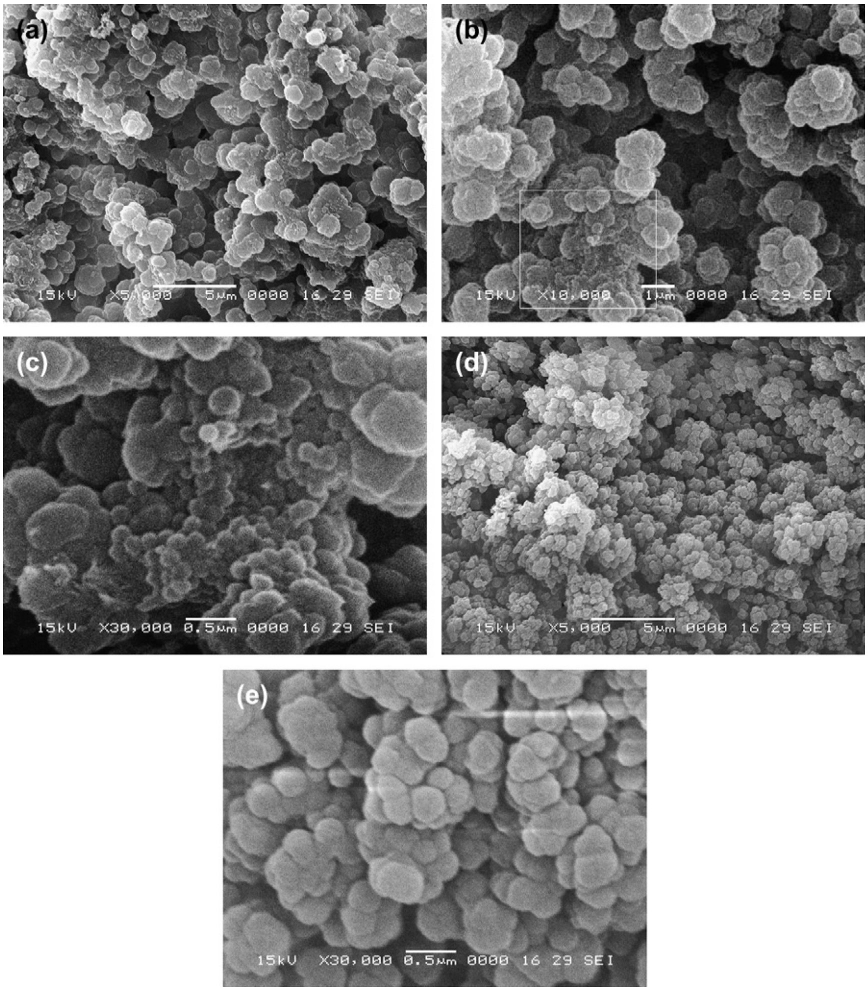


Fig. 7. SEM images of PAN polymerized under low pressure. (a) and (b) polymerized with 5 wt% $SAN_{5.3K}$-$F_{19K}$ under 8.5 MPa (entry 5 in Table 3); (c) the magnification of a local part of (b) shown by white rectangle; (d) and (e) polymerized without stabilizer under 7.8 MPa (entry 11 in Table 3).

by dispersion polymerization at 20.3 MPa were observed. Analogous to that found in the polymerization system with the addition of $SAN_{5.3K}$-$F_{19K}$, a sudden increase in the monomer conversion and the molecular weight of PAN took place under the pressure of 9.2 MPa, but the PAN still retained the same powder like appearance as that formed under higher pressure. When AN was polymerized around the critical pressure of $CO_2$, i.e. 7.8 MPa, the AN conversion and the molecular weight of PAN further increased to a large extent. The appearance of the PAN was a mixture of powder and bulk, and looked quite the same as that synthesized by precipitation polymerization at 30 MPa under SEM (Fig. 7d and e), in which the bridge-like small particles disappeared. All the experimental results indicate that the polymerization rate of AN in $scCO_2$ around the critical pressure suddenly increased resulting in increase of the AN conversion and the molecular weight of PAN appreciably, which is independent of the presence of the stabilizer.

Recently, a detailed mathematical model for the dispersion polymerization of MMA in $scCO_2$ was introduced by Mueller et al. [23], in which there are two phases in the polymerization system, i.e. a continuous phase mainly composed of $scCO_2$, MMA and AIBN, and a dispersed phase that mainly composed of PMMA and PMMA propagating chain. In this case, the significance of the rate of monomer diffusion from continuous phase to dispersed phase should be considered. For the polymerization systems studied here the diffusion coefficient of AN in continuous phase can be estimated by Lusis and Ratcliff's equation [24]:

$$D_{\mathrm{M}} = \frac{8.52 \times 10^{-10} T}{\mu_{\mathrm{CO_2}} v_{\mathrm{CO_2}}^{1/3}} \left[ 1.40 \left( \frac{v_{\mathrm{CO_2}}}{v_{\mathrm{M}}} \right)^{1/3} + \left( \frac{v_{\mathrm{CO_2}}}{v_{\mathrm{M}}} \right) \right] \tag{5}$$

with $D_{\mathrm{M}}$ in $\mathrm{cm}^2/\mathrm{s}$, $T$ in K, $\mu_{\mathrm{CO_2}}$ viscosity of $CO_2$ in poises, $v_{\mathrm{CO_2}}$ molar volume of $CO_2$ in $\mathrm{cm}^3/\mathrm{mol}$ and $v_{\mathrm{M}}$ molar volume of AN in $\mathrm{cm}^3/\mathrm{mol}$. It was calculated that $D_{\mathrm{M}}$ was equal to $2.08 \times 10^{-4}\ \mathrm{cm}^2/\mathrm{s}$ at 30 MPa, whereas it increased to $1.27 \times 10^{-3}\ \mathrm{cm}^2/\mathrm{s}$ at 7.7 MPa. The results show that the diffusion coefficient of AN monomer in the continuous phase goes up for almost one magnitude when the initial pressure decreases from 30 MPa to 7.7 MPa, giving rise to significant impact on the partition of the monomer between the continuous phase and polymer phase. Kazarian et al. [25] investigated the relationship between the pressure and the partition coefficient $K_c$ of various solutes (i.e. some organic compounds, such as deuterated isopropanol, deuterated acetone, and azo-dyes) between the continuous phase and polymer phase (such as PMMA, PDMS-based polymer) in $scCO_2$ under isothermal condition. The $K_c$ was defined as a ratio of $C_{\mathrm{polymer}}/C_{\mathrm{CO_2}}$, where $C_{\mathrm{polymer}}$ and $C_{\mathrm{CO_2}}$ were the concentrations of solute in continuous phase and polymer phase under thermodynamic equilibrium condition, respectively. It was found that while $P > 15$ MPa, the value of $K_c$ only slightly changed with changing pressure and was close to unity. However, while $P < 10$ MPa, it increased rapidly with a decrease in pressure, and the $K_c > 10$, while the pressure was around the critical pressure of $CO_2$. Thus, the concentration of AN in the PAN phase could be much higher than that in the continuous phase under 7.7–7.8 MPa. The high conversion of AN and high molecular weight of PAN synthesized under 7.7–7.8 MPa could be therefore attributed to the strong diffusion ability of AN from continuous phase to polymer phase, making the PAN phase as the main loci of the chain propagating reaction, although the enhancement of agglomeration for the powders in the polymer phase was observed (see Table 3), giving rise to decrease in the total surface area of the PAN phase. All these experimental behaviors are now being studied.

Fig. 8 shows the WAXD spectra of PAN synthesized without stabilizer at 7.8 MPa and with the addition of 5 wt% $SAN_{5.3K}$-$F_{19K}$ at 7.7 MPa. For both PAN samples, a strong peak at $2\theta = 16.6°$ and a weak one at $2\theta = 29.3°$ were observed, corresponding to $d$-spacings of 5.30 and 3.04 Å, assigned to diffractions of (010) and (030) planes, respectively. The crystallinity of the PAN synthesized without stabilizer was 24%, while that of the PAN synthesized with 5 wt% $SAN_{5.3K}$-$F_{19K}$ slightly decreased to 22%, all higher than their counterparts produced at 30 MPa. Nevertheless, their crystallite size still remained the same (76 Å).

In conclusion, a series of new fluorinated diblock copolymers, poly(SAN-*b*-FNEMA), with various compositions were synthesized by ATRP and characterized. The effect of their composition and concentration added on the polymerization

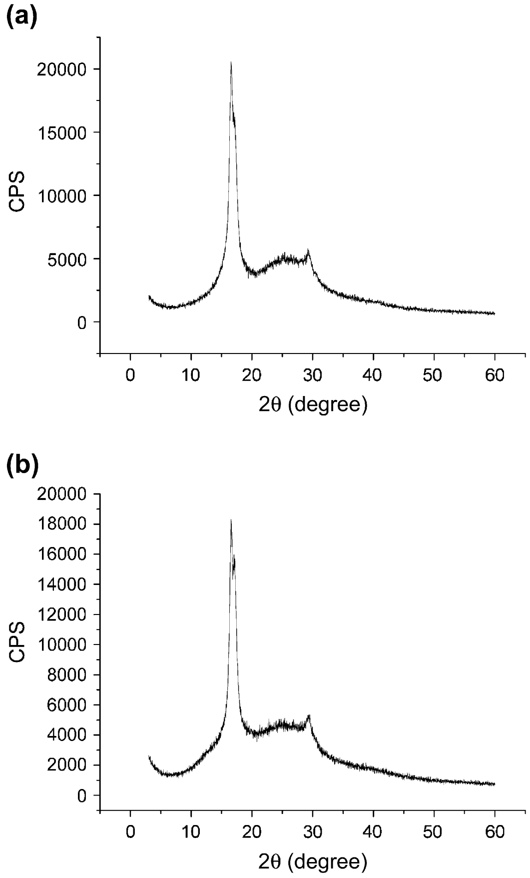


Fig. 8. WAXD of PAN polymerized under low pressure. (a) Polymerized without stabilizer under 7.8 MPa (entry 11 in Table 3); (b) polymerized with 5 wt% $SAN_{5.3K}$-$F_{19K}$ under 7.7 MPa (entry 6 in Table 3).

of AN in $scCO_2$ with AIBN as the initiator at 30 MPa and 65 °C was studied. As shown by the experimental results, well-dispersed spherical PAN particles were prepared in the presence of a small amount of $SAN_{5.3K}$-$F_{19K}$ (5 wt%), indicating the quite high stabilizing efficiency of this block copolymer. Furthermore, the effect of pressure on the polymerization of AN in $scCO_2$ was examined. It was of interest to find that the AN conversion and the molecular weight of PAN increased significantly under the pressure close to the critical one of $CO_2$ (7.7–7.8 MPa), no matter whether the $SAN_{5.3K}$-$F_{19K}$ was used. In other words, the rate of polymerization was very fast under 7.7–7.8 MPa, compared with other systems studied under higher pressure. Finally, it was also found that the crystallinity of the PAN synthesized at 7.7–7.8 MPa was a bit higher than those produced at 30 MPa.

## References

[1] Kendall JL, Canelas DA, Young JL, DeSimone JM. Chem Rev 1999;99:543.
[2] Carnelas DA, DeSimone JM. Macromolecules 1997;30:5673.
[3] Shiho H, DeSimone JM. Macromolecules 2001;34:1198.
[4] Ma Z, Lacroix-Desmazes P. Polymer 2004;45:6789.
[5] Ding L, Olesik SV. Macromolecules 2003;36:4779.
[6] Tai H, Wang W, Howdle SM. Polymer 2005;46:10626.
[7] Romack TJ, DeSimone JM. Macromolecules 1995;28:912.
[8] Cooper AI, Hems WP, Holms AB. Macromol Rapid Commun 1998;19:353.
[9] Okubo M, Fujii S, Maenaka H, Minami H. Colloid Polym Sci 2002;280:1084.
[10] Charpentier PA, DeSimone JM, Roberts GW. Ind Eng Chem Res 2000;39:4588.
[11] Teng XR. J Appl Polym Sci 2003;87:1393.
[12] Shiho H, DeSimone JM. Macromolecules 2000;33:1565.
[13] Okubo M, Fujii S, Maenaka H, Minami H. Colloid Polym Sci 2003;281:964.
[14] Zhang ZB, Ying SK, Shi ZQ, Xu XD. J Polym Sci Part A Polym Chem 2001;39:2670.
[15] Keller RN, Wycoff HD. Inorg Synth 1946;2:1.
[16] Brandrup J, Immergut EH, Grulke EA. Polymer handbook. 4th ed. New York: Wiley; 1999.
[17] Tsarevsky NV, Sarbu T, Gobelt B, Matyjaszewski K. Macromolecules 2002;35:6142.
[18] Bortner MJ, Bhanu V, McGrath JE, Baird DG. J Appl Polym Sci 1991;42:3045.
[19] Bashir Z. Polymer 1992;33:4304.
[20] Landfester K, Antonietti M. Macromol Rapid Commun 2000;21:820.
[21] Hua FJ, Hu CP. Eur Polym J 1999;35:103.
[22] Odian G. Principles of polymerization. 2nd ed. New York: Wiley; 1981. p. 271–6.
[23] Mueller PA, Storti G, Morbidelli M. Chem Eng Sci 2005;60:1911.
[24] Lusis MA, Ratcliff GA. Can J Chem Eng 1968;46:385.
[25] Kazarian SG, Vincent MF, West BL, Eckert CA. J Supercrit Fluids 1998;13:107.