NOTE

Molecular Weight and Spinnability of Polyacrylonitrile Produced by Precipitation Polymerization in Supercritical CO$_2$

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INTRODUCTION

Polyacrylonitrile (PAN) is traditionally made by precipitation polymerization in water or solution polymerization in different organic or inorganic solvents. Both of these processes have some shortcomings: the former's is the high cost in purification and the requirement of a drying process, and the latter's is the influence on environment pollution due to the solvent used. Supercritical CO$_2$ has been broadly applied as a solvent to produce industrial polymers including PAN,[1–14] because it provides intense advantages as an environmentally friendly, inexpensive, and nonflammable alternative to the aqueous and organic solvents. As reported, supercritical CO$_2$ can play a role similar to a hydrocarbon solvent—hence it is a benefit for dissolving small molecules including monomers.[15] Among the various applications,[1–14] it is noted that the dispersion polymerization in supercritical CO$_2$ have been successfully applied to the polymerization of methyl methacrylate,[2–7] styrene,[8–10] vinyl acelate,[11,12] acrylonitrile,[1] etc. However, this method strongly relies on the special stabilizers used. Compared with dispersion polymerization, precipitation polymerization in supercritical CO$_2$ can ignore the presence of special stabilizers and it is more easy to carry out.

So here we studied the precipitation polymerization of acrylonitrile in supercritical CO$_2$. The polymerization of acrylonitrile (AN) in the supercritical CO$_2$ has been reported by some researchers.[1,14] Shiho and DeSimone[1] have conducted both precipitation and dispersion polymerizations of AN in the supercritical CO$_2$. They mainly discussed the particles of PAN in dispersion polymerization. Though much valuable information in relation to various properties of PAN produced in supercritical CO$_2$ has been reported, the molecular weight and processability of PAN produced in supercritical CO$_2$ did not appear in these articles. And the information is absolutely important for further study of the polymerization in supercritical CO$_2$. In particular, studying the processability of PAN produced in supercritical CO$_2$ will have a great significance on the application of this novelty supercritical fluid technology to the field of applied polymer science. Therefore, in this article, the aims of the work include the following: (1) to investigate the effects of the concentration of either monomer or initiator, total reaction time, temperature, and CO$_2$ pressure on molecular weight of PAN created by precipitation polymerization in supercritical CO$_2$; (2) to investigate the processability of polyacrylonitrile created by precipitation polymerization in supercritical CO$_2$.

EXPERIMENTAL

Materials

AN was purified via reduced pressure distillation.

2,2′-Azo(bisisobutyronitrile) (AIBN) was used as initiator and was recrystallized from methanol.

N,N-dimethylformamide (DMF) was used as solvent for dissolving PAN.

Carbon dioxide was provided by a local air products company, which was used as received.

Precipitation polymerization

The polymerization was carried out using a 500 mL autoclave; the whole system is outlined in Figure 1.

After adding AN and AIBN, the autoclave was covered to start the polymerization. Initially, a short time flow of CO$_2$ prior to the rising of the temperature was done to make the autoclave filled with only the employed CO$_2$. With the temperature increasing, the piston pump was started to fit the need of CO$_2$ flowing into the autoclave continuously to raise the pressure to predesired level. Once the predesired temperature and pressure approached, the reaction was allowed to stir for several hours. During the reaction, a cooling water circulator, attached to an internal coil, was used to control
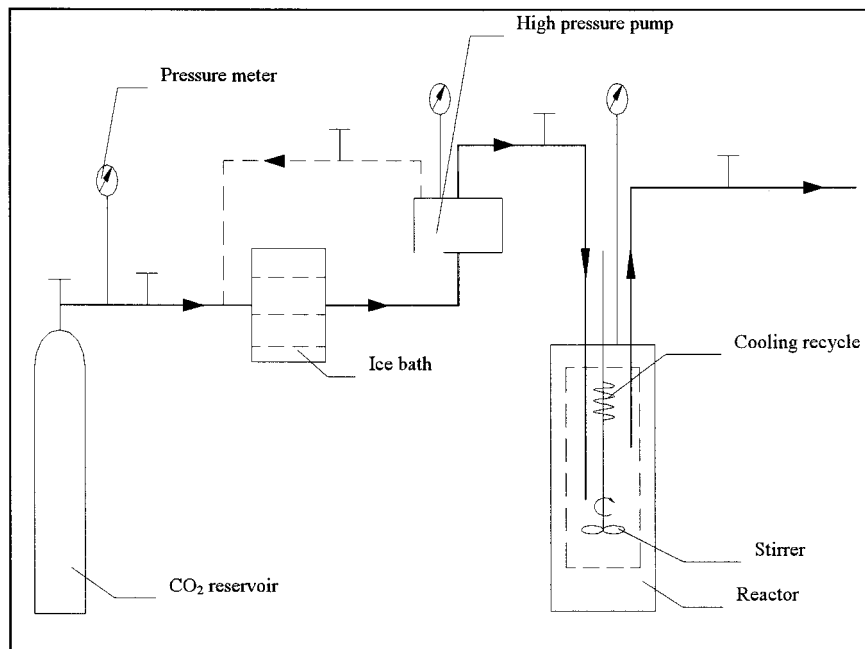
Figure 1 Supercritical CO_2 polymerization system.

the temperature (Fig. 1). After the reaction, by cooling the reactor to room temperature and venting the CO_2 slowly, the resulting PAN was found not only formed as a polymer powder with a milky white appearance, but also sized on the surface of both the interior wall of autoclave and stir bar. The powdered PAN thus was collected with a glass cell.

Wet spinning

Wet spinning was performed using a laboratory-made small-scale spinning machine as Figure 2 illustrates. To spin the polyacrylonitrile fiber, the obtained PAN was initially dissolved to the dope of $18 \sim 21\%$ by DMF. After swelling and vacuum deaeration, the dope was extruded through spinning head to the coagulating bath, which was made by the solution of DMF/water (1:1 v/v) with a temperature of about 15°C. The fiber was spun using a unique orifice with a diameter of 0.16 mm. After coagulation, the fiber was solidified by a water bath of about 95°C then was drawn with the speed ratio of about 4–5. Finally, the fiber was

cleaned by water, 55°C, and then was dried by oven at 100°C for half an hour.

Characterization

The molecular weight of PAN samples was determined using viscometry.[16,17] The temperature was dominated by a water bath constantly at 25 ± 0.1°C, and DMF was employed as solvent. To estimate the molecular weight, M_V, a literature-introduced equation [17] was applied.

$$M_v = \eta_{sp}/K \times C \tag{1}$$

where η_{sp} represents the specific viscosity, K responds to a constant usually about 1.5×10^{-4}, and C is the mole concentration per dm^3, here $C = 2g/53 \ dm^3$. There were total 18 tested samples, which were measured by two people independently. Every reported value M_v was averaged by at least three measurements, and the standard deviation was
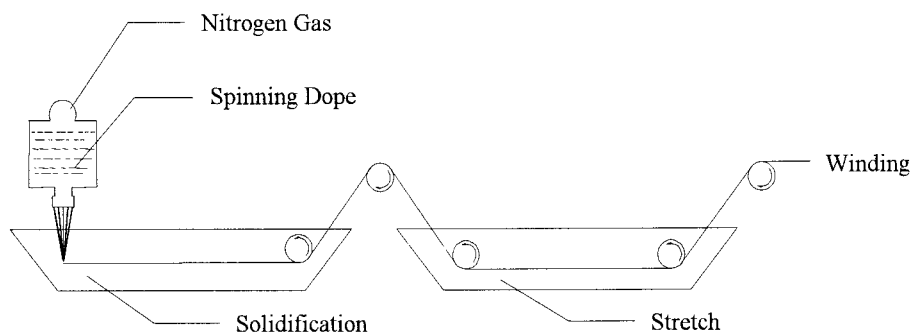

Figure 2 A laboratory wet-spinning system.

TABLE I
The Polymerization Conditions and Measuring Results of All the Tested Samples

Entry	Monomer (%)	Initiator (%)	Time (h)	Pressure (±1 MPa)	Temperature (±3°C)	Yield (%)	Molecular weight M_v
1	6	1.25	17	24	65	25	14,409
2	8	1.25	17	24	65	32	23,638
3	12	1.25	17	24	65	46	43,937
4	14	1.25	17	24	65	48	51,145
5	12	1	17	24	65	42	48,036
6	12	2	17	24	65	49	33,266
7	12	2.5	17	24	65	53	27,701
8	12	1.25	5	24	65	8	—
9	12	1.25	12	24	65	28	46,764
10	12	1.25	14	24	65	43	59,130
11	12	1.25	15	24	65	45	79,871
12	12	1.25	22	24	65	51	37,966
13	14	1.25	17	18	65	46	37,373
14	14	1.25	17	20	65	47	43,954
15	14	1.25	17	28	65	47	56,144
16	12	1.25	17	14	50	24	109,392
17	12	1.25	17	14	55	38	108,773
18	12	1.25	17	24	60	38	57,947

about 6% of averaged value. The polymer conversion was determined gravimetrically. The preparation conditions and measuring results of all the tested samples were summarized in Table I.

The morphology of the fibers was identified by a SCAM Scan-4 scanning electron microscope (SEM). The fiber fineness and fiber tensile strength as well as fiber breaking elongation were determined using a XD-1 fiber fineness tester and a XQ-1 fiber strength tester, which were made in China. Each kind of fiber sample was tested at least 15 times, and then the averaged value was taken for this article.

RESULTS AND DISCUSSION

Effect of Monomer Concentration and Initiator Concentration

To investigate the effect of the monomer concentration (w/v %, AN/CO_2) on the molecular weight of PAN, acrylonitrile was added at 6, 8, 12, and 14%, respectively. The pressure of supercritical CO_2 was kept constant at 24±1 MPa, AIBN added was about 1.25% (w/w %, AIBN/AN) of the monomer, the temperature remained at 65 ± 3°C, and the total reaction time was preset as 17 h. Figure 3 shows that as the acrylonitrile concentration increased, both the viscosity average molecular weight, M_v, and the conversion are increased.

To investigate the effect of initiator concentration on molecular weight of PAN, the AIBN/AN (w/w %) ratio was varied from 1.0 to 2.5% while keeping the monomer concentration at 12%. Keeping other reaction conditions the same as above, Figure 4 shows that as the AIBN concentration increased, the yield of PAN is increased, but the viscosity average molecular weight of PAN is reduced.

As we known, for a large number of free radical polymerizations, the polymerization rate is proportional to monomer
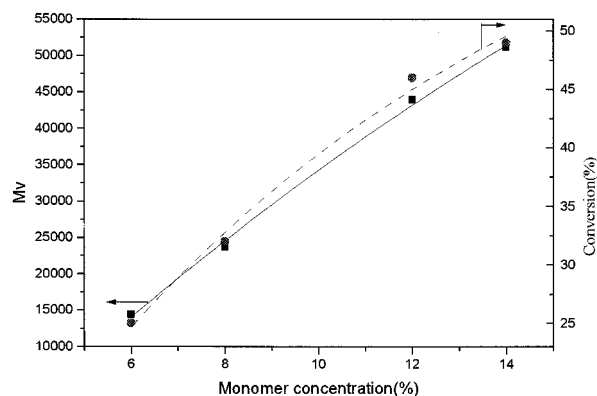

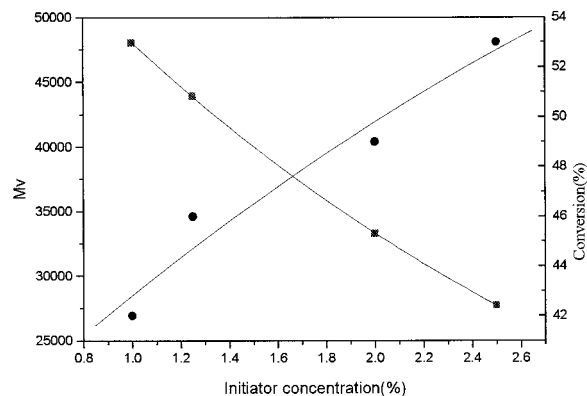**Figure 3** Effect of monomer concentration on the viscosity average molecular weight and conversion of PAN.

Figure 4 Effect of initiator concentration on the viscosity average molecular weight and conversion of PAN.
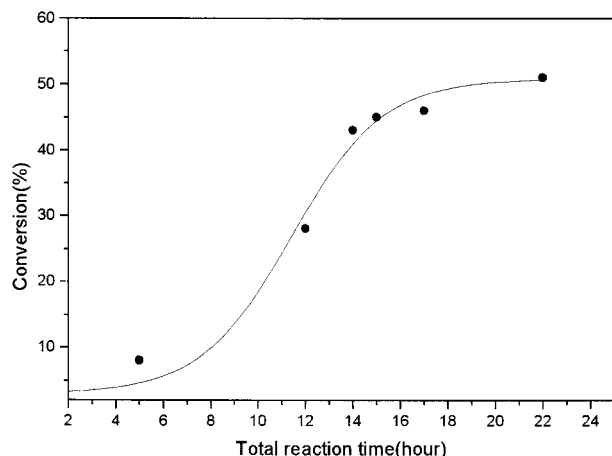
Figure 5 Conversion of PAN as a function of the reaction time.

concentration and to the square root of initiator concentration. And the kinetic chain length is proportional to monomer concentration, but it is inversely proportional to the square root initiator concentration.[18] So the effects of monomer concentration and initiator concentration on the molecular weight and conversion (Fig. 3 and Fig. 4) all conform to the classical reaction principles of free-radical polymerization.

Effect of the Reaction Time

Taking reaction time as a function, the pressure of supercritical CO_2 was kept constant at 24 ± 1 MPa, AIBN was added about 1.25% of the monomer, the temperature remained at $65 \pm 3°C$, and the total reaction time was ended at 5, 12, 14, 15, 17, and 22 h, respectively. Figure 5 shows that as the time prolonged, the yield of PAN increased. The conversion time curve has a characteristic sigmoidal shape showing the acceleration of the polymerization rate with conversion. This is similar to what is typically observed in common solvents where the autoacceleration effect occurs in polymerization of acrylonitrile.[19] Since the polyacrylonitrile does not dissolve in its monomer or supercritical CO_2, polyacrylonitrile precipitated from the monomer solution from
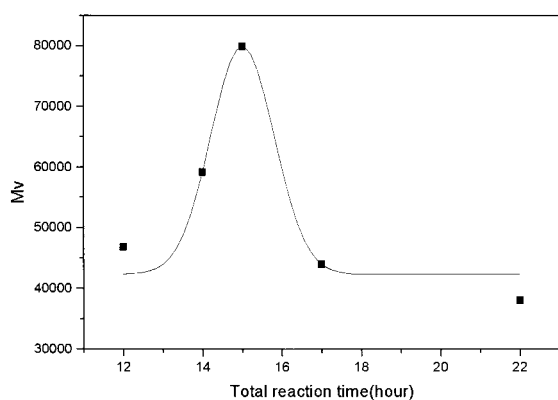

Figure 6 Viscosity average molecular weight of PAN as a function of the total reaction time.

TABLE II
Effect of the CO_2 Pressure on the Viscosity Average Molecular Weight and Conversion of Polyacrylonitrile

Entry	Pressure (± 1 MPa)	Yield (%)	Molecular weight[a] M_v
1	18	46	37,373
2	20	47	43,954
3	24	48	51,145
4	28	47	56,144

[a] Standard deviation about 6%.

the start of the reaction. It is believed that the polymerization takes place primarily in the monomer-swollen particles. Polymerization in precipitated particles results in the autoacceleration effect, which leads to an increase in the rate of polymerization and an increase in the molecular weight of the polymer. The viscosity average molecular weight, M_V, in Figure 6 seems to be varied in response to the reaction time. A peak corresponding to the reaction time at about 15 h is subject to the molecular weight of about 80,000. This peak may be occurring near the point where the maximum in polymerization rate is reached.[20]

Effect of The Pressure of Supercritical CO_2

Taking the pressure of CO_2 as a function, the monomer concentration was kept at 147, the effects of CO_2 pressure on the molecular weight of PAN is presented in Table II. It is found, though, that the change of the pressure seems not to affect evidently the PAN yield; the molecular weight of PAN is increased as the pressure increased. This means the increase of the pressure causing the growing polymer chains increases—hence resulting in the increase of the molecular weight for precipitation. In addition, another possible reason is that the high pressure may plasticize the polymer phase—thus the monomer diffusion within the polymer phase might be enhanced.[21–23] These observations have also been reported by Romack et al.[13]

Effect of the Reaction Temperature

Taking the temperature as a function and each 5°C as a step, the reaction was desired to vary from 50 to 65°C, respectively. Table III presented the result of the M_V responding to each desired temperature condition. According to Table III,

TABLE III
Effect of the Temperature on the Viscosity Average Molecular Weight and Conversion of Polyacrylonitrile

Entry	Temperature (°C)	Pressure (± 1 MPa)	Yield (%)	Molecular weight[a] M_v
1	50	14	24	109,392
2	55	14	38	108,773
3	60	24	38	57,947
4	65	24	46	43,937

[a] Standard deviation about 6%.

TABLE IV
Fiber Properties of PAN Produced in Supercritical CO_2

Entry	Molecular weight M_v	Drawing rate	Titer (dtex)	Standard deviation σ	Tenacity (cN/dtex)	Standard deviation σ	Breaking elongation (%)	Standard deviation σ
1	56,144	4.33	3.61	0.14	3.75	0.39	9.0	0.38
2	56,144	4.75	3.39	0.15	3.81	0.19	8.6	0.46
3	56,144	5.08	2.76	0.19	3.23	0.22	6.8	0.59
4	Reference PAN	—	3.17 ~ 3.5	—	2.65 ~ 3.53	—	30~42	—

the higher the reaction temperature, the smaller is the molecular weight. And the yield is increased at higher temperature. Temperature effects are usually complex because the polymerization rate depends on a combination of three rate constants: decomposition, propagation, and termination. For initiator-induced polymerization, generally, the overall rate of polymerization is increased as temperature increases. Consequently, the yield can be improved at higher temperature. But a very high temperature may cause an increase of the chain termination rate, the chain transfer rate, etc. [18]
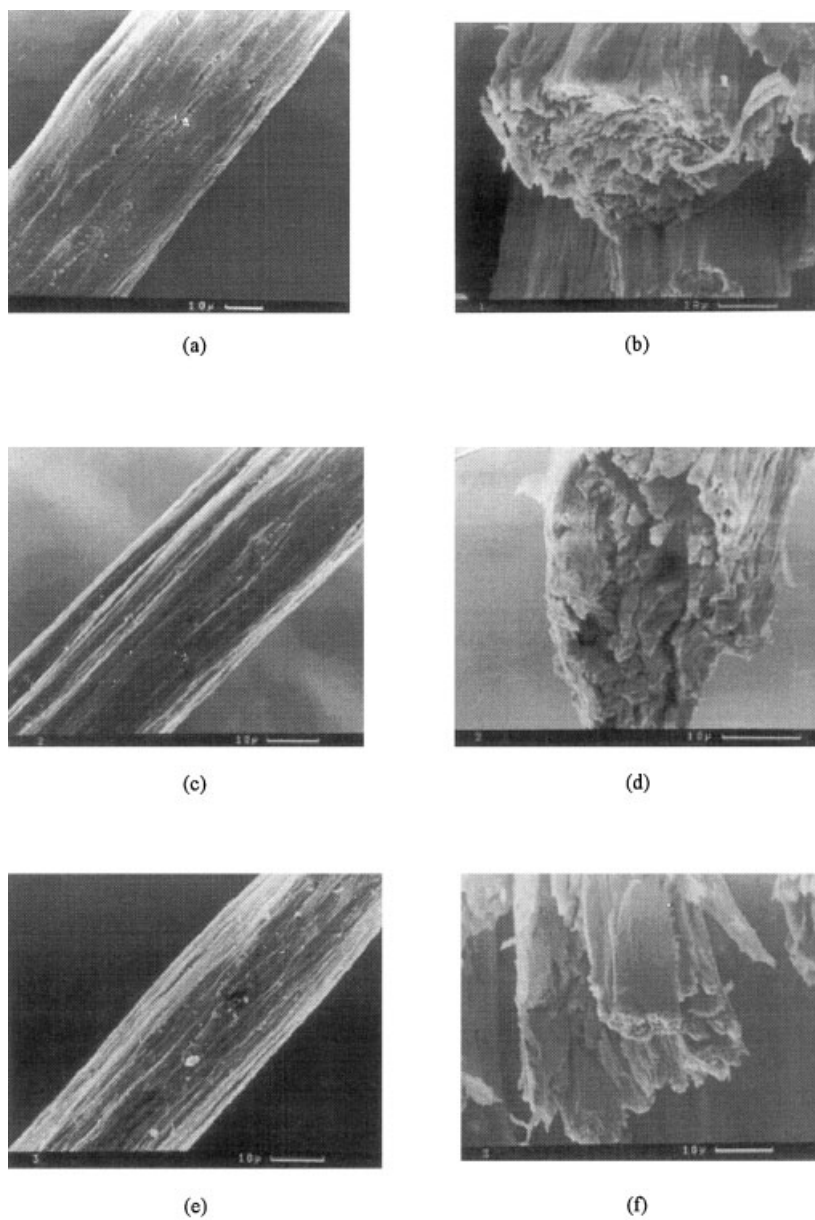

(a)

(b)

(c)

(d)

(e)

(f)

Figure 7 SEM photograph of PAN fibers.

Hence, the decrease of the molecular weight due to the temperature rising is understandable.

Spinnability of Polyacrylonitrile Produced in Supercritical CO_2

Prior to spinning, the solubility of PAN was estimated using DMF as solvent. Taking two PAN samples, one having a higher molecular weight, e.g., about 80,000, and another having a lower M_v, e.g., about 56,000, to dissolve in DMF solvent, respectively, the observation was that the former is poorly dissolved and the later was easily dissolved. Then, the later was employed to spin into fiber according to the spin condition as Table IV presents. The SEM pictures of PAN fibers resulting in supercritical CO_2 are shown in Figure 7(a)–(f), where (a), (c), and (e) represent the surface of fiber with the titer of 3.61 dtex, 3.39 dtex, and 2.76 dtex (dtex = the fiber fineness unit; 1 dtex = 0.1 tex); and (b), (d), and (f) respond to the cross section, respectively. Figure 7(a)–(f) shows that the PAN fibers are made of many microfibrils, and the microfibrils lie roughly parallel to the fiber axis. This structure conforms to the commercial PAN fiber stucture.[24] Figure 7(a), (c), and (e) show there are some defects and flaws on the surface of the PAN fiber and the fiber cross-sections [Fig. 7(b), (d), and (f)] shows many voids present in the fiber. The certain degree of structural imperfection creates internal stress in the fibers and affects their technical properties. And the solvent residues or impurities may cause these flaws and voids in PAN fibers at the stage of coagulation or further handling of the fiber. A comparison of the referenced PAN fiber offered by a local company, Table IV shows that the PAN fibers produced by supercritical CO_2 have similar tenacities as the commercial PAN fibers. However, the breaking elongation is very small, which can be explained by the poor spinnability of PAN homopolymer at least in part. (Note: commercial PAN fibers are usually made by copolymers[25]). Though the mechanical properties of fiber presented here are not as good as the commercial fiber, this work proves that the PAN produced in supercritical CO_2 is capable of being processed. Without a doubt, this study will be very helpful for using the new supercritical fluid technology in the field of polymer engineering.

CONCLUSIONS

Using AIBN as initiator and supercritical CO_2 as a solvent, the precipitation polymerization of acrylonitrile was studied. It was found that the effects of monomer concentration, initiator concentration, reaction time, as well as reaction temperature on the viscosity average molecular weight and conversion of polyacrylonitrile were basically in accordance with the classical reaction principles of free-radical polymerization. The higher pressure seemed helpful in increasing the molecular weight of the product due to higher solvency of supercritical CO_2 at higher pressure. In addition, using DMF as solvent, the spinnability of PAN produced by precipitation polymerization in supercritical CO_2 was also proved in this work.

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