Molecular Weight Distribution of Polyacrylonitrile Produced in Supercritical CO$_2$

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ABSTRACT: An effectively linear molecular weight calibration curve of polyacrylonitrile (PAN) was obtained using a copolymer standard with a single broad molecular weight distribution. The molecular weights and molecular weight distributions of PAN obtained from precipitation polymerization of acrylonitrile in supercritical CO$_2$ were quantitated by the calibration curve. The effects of monomer concentration, initiator concentration, the CO$_2$ pressure, and the total reaction time on the molecular weight and molecular weight distribution were studied in detail. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2338–2341, 2002

Key words: supercritical carbon dioxide; polyacrylonitrile; gel permeation chromatography (GPC); molecular weight distribution; yielding

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 involves high-cost purification and the requirement of a drying process, and the latter influences environmental pollution because of the solvent used. Supercritical CO$_2$ has been broadly applied as a solvent to produce industrial polymers including PAN[1–17] because it provides advantages as an environmentally friendly, inexpensive, and nonflammable alternative to the aqueous and organic solvents. As reported, CO$_2$ can play a role similar to a hydrocarbon solvent for dissolving small molecules including monomers.[18] Recently, Shiho and DeSimone conducted both precipitation and dispersion polymerizations of acrylonitrile (AN) in supercritical CO$_2$.[3] They discussed particles of PAN in dispersion polymerization. Though much valuable information in relation to various properties of PAN produced in supercritical CO$_2$ have been reported, the molecular weight distribution of PAN resulting from supercritical CO$_2$ was not included in these publications.[3,17] Such information is absolutely important for industries because it affects the performance of the polymer in commercial products. For this reason, much attention should be paid to understanding molecular weight distribution of PAN polymerized in supercritical CO$_2$. In our lab, precipitation polymerization of acrylonitrile in super-critical CO$_2$ has been successfully conducted, and we have previously discussed effects on the viscosity-average molecular weight and spinnability of the obtained PAN.[19] In this paper, molecular weight distribution of PAN produced in supercritical CO$_2$ will be discussed in detail.

EXPERIMENTAL

Materials

N,N-Dimethylformamide (DMF) was used as a solvent for dissolving PAN. NaNO$_3$ (C.P.) was used as received. A broad molecular weight distribution (MWD) copolymer of AN and methylacrylate (MA; AN:MA = 94 : 6) was provided by the American Cyanamid Company and was calibrated by Stanford Research Center. PAN was obtained from precipitation polymerization of acrylonitrile in supercritical CO$_2$ in our lab.

Methods

Viscosity measurement

The viscosity-average molecular weight of PAN was determined using viscometry.[20,21] The temperature was controlled by a water bath at 25 ± 0.1°C, and DMF was used as a solvent. The following equation was used to estimate the viscosity-average molecular weight, M_v:

$$M\nu = \eta_{sp}/K \times C \qquad (1)$$

where η_{sp} represents the specific viscosity, K is a constant (usually $\sim 1.5 \times 10^{-4}$), and C is the concentration in mol/dm^3 (here, C = 2 g/53 dm^3).[21]
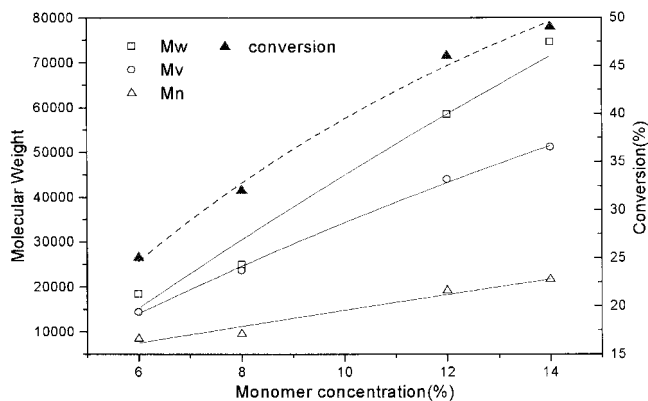
Figure 1 Effect of monomer concentration on the molecular weight and conversion of PAN.

Every reported M_v value was averaged by at least three independent measurements with a standard deviation of ~6%.

Calibration of PAN

Molecular weights and MWDs of the polymer samples were determined with a Waters gel permeation chromatograph (GPC, model 1500) with Ultrastyragel columns (7.8 × 300 mm) of 10^4, 10^5, and 10^6 Å porosities, using $DMF/NaNO_3$ as the eluent. The experiments were carried out at 50°C, with an injection volume of 200 μL and a pumping rate of 1 mL/min.

To eliminate the electrostatic effect,[22] we carried out GPC determinations in 0.065 mol/L $DMF/NaNO_3$. Because the common polystyrene standards were not available for the GPC calibration of PAN, a single broad MWD copolymer standard was used.[23,24]

The conversion of PAN was determined gravimetrically.

RESULTS AND DISCUSSION

Molecular weight and MWD as a function of monomer concentration and initiator concentration

To investigate the effects of monomer concentration (w/v %, AN/CO_2) on molecular weight and MWD, AN was added at 6, 8, 12, and 14%, respectively. The pressure of supercritical CO_2 was kept constant at 24 ± 1 MPa, ~1.25% 2,2'-azo(bisisobutyronitrile) (AIBN) was added (w/w %, AIBN/AN), the temperature was kept at 65 ±3°C, and the total reaction time was preset as 17 h. The relationship between molecular weight and conversion with varied monomer concentration is shown in Figure 1. As the AN concentration increased, both the molecular weight and the conversion increased. As monomer concentration increased, the threshold molecular weight for precipitation was increased because of the presence of large amounts of AN monomer in the continuous phase at low degrees of polymerization. The GPC chromatograms obtained
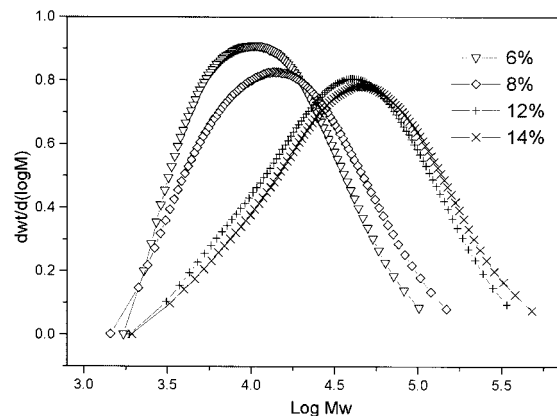

Figure 2 Effect of monomer concentration on the MWD of PAN.

at four different concentrations of AN are shown in Figure 2. As plotted in Figure 2, the polydispersity indexes (M_w/M_n) of MWD of PAN obtained at 6–14% monomer concentration are 2.2, 2.63, 3.12, and 3.44, respectively. These products seem to have slightly broader MWDs.

The AIBN/AN (w/w %) ratio was varied from 1.0 to 2.5% while keeping the monomer concentration at 12%. As the AIBN concentration increased, molecular weight was reduced and the yield of PAN was increased, though the degrees are small. This result is in accord with the reaction principles of free-radical polymerization. The GPC chromatograms obtained at four different concentrations of initiator are shown in Figure 3. The polydispersity indexes of the MWD in Figure 3 are ~3–3.2. It seems that there is no discernible trend observed between the polydispersity and the AIBN concentration. This result may be due to the small variation of AIBN concentrations in this range.
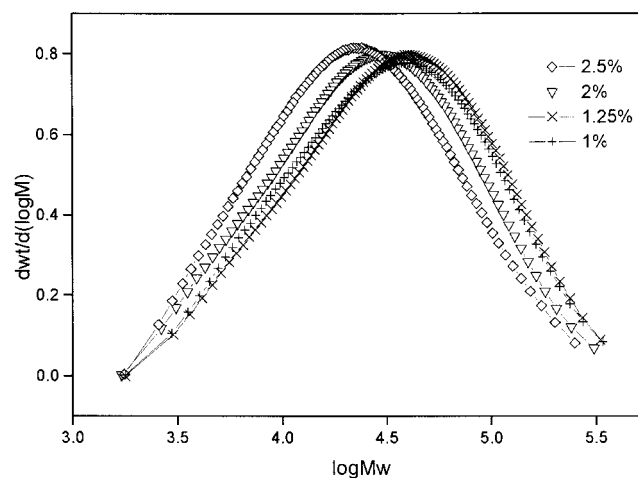

**Figure 3** Effect of initiator concentration on the MWD of PAN.
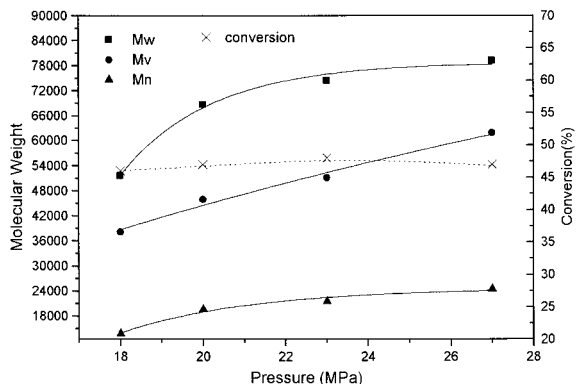
Figure 4 Effect of CO_2 pressure on the molecular weight and conversion of PAN.

Molecular weight and MWD as a function of CO_2 pressure

AN was added at 14%, AIBN was added at ~1.25% of the monomer, the temperature was kept at 65 ± 3°C, and the total reaction time was pre-set as 17 h. Taking the pressure of CO_2 as a variable, the effect on the polymerization of AN is presented in Figure 4. The change of the pressure evidently seems not to affect the PAN yield. The average molecular weight of PAN increased as the pressure is increased. As the pressure changed from 14.5 to 33.1 MPa at 65°C, the density of supercritical CO_2 increased from 0.60 to 0.85 g/mL.[4] The higher density CO_2 at higher pressure should have greater solvency for the growing PAN oligomer radicals. Thus, the chains should grow to a longer length prior to the onset of precipitation. As a result, the resulting molecular weight of PAN increases. In addition, high pressure may plasticize the polymer phase, thus the monomer diffusion within the polymer phase might be enhanced.[25–27] The MWD of PAN under different pressure conditions is shown in Figure 5. The higher pressure seems to be helpful to narrow the MWD, possibly because of the reduced contribution of solution polymerization at higher pressure. The
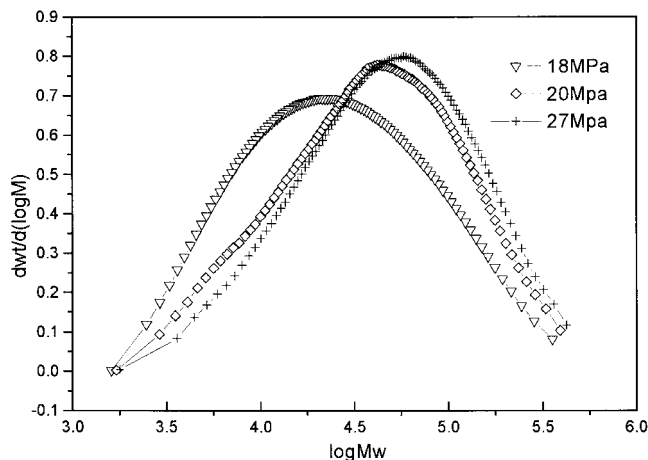
**Figure 5** Effect of CO_2 pressure on the MWD of PAN.
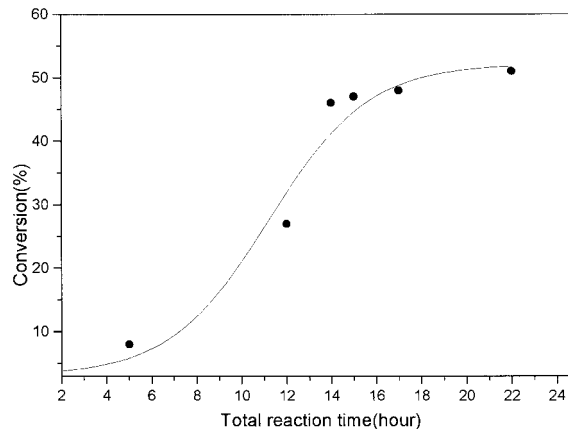
Figure 6 Conversion of PAN as a function of the total reaction time.

increasing of the polymerization rate within the coagulated particle phase, due to increased monomer diffusion at higher pressure, results in a reduced contribution from polymerization in the solution phase. Similar observations have also been reported by O'Neill et al.[9] On the other hand, different results with the precipitation polymerization of acrylic acid have been reported by Romack et al.[16] These authors showed no appreciable effect of pressure on molecular weight and MWD in the pressure range 12.5–34.5 MPa.

Effect of reaction time

Keeping all other conditions the same as those just presented and taking reaction time as a variable, an increase in the yield of PAN was noted as the time was prolonged (Figure 6). The conversion time curve has a characteristic sigmoidal shape, showing the acceleration of the polymerization rate with conversion. This result is similar to what is typically observed in common solvents where an auto-acceleration effect occurs in polymerization of AN.[28] Once the particles are formed, it is believed that the polymerization takes place primarily in the monomer-swollen particles. Polymerization in precipitated particles results in an auto-acceleration effect, which leads to an increase in the rate of polymerization and an increase in the molecular weight of the polymer. A similar auto-acceleration effect was observed in the dispersion polymerization of MMA in supercritical CO_2.[4] It is believed that because CO_2 can plasticize the polymer,[25–27] polymerizations carried out in CO_2 offer the advantage of increasing the diffusivity of monomers into the growing polymer particles to maintain a sufficient rate of propagation, which in turn effectively facilitates the auto-acceleration effect. The variation of average molecular weight and the polydispersity indexes (PDI) of MWD with reaction time are plotted in Figure 7. A peak corresponding to the reaction time at ~15 h
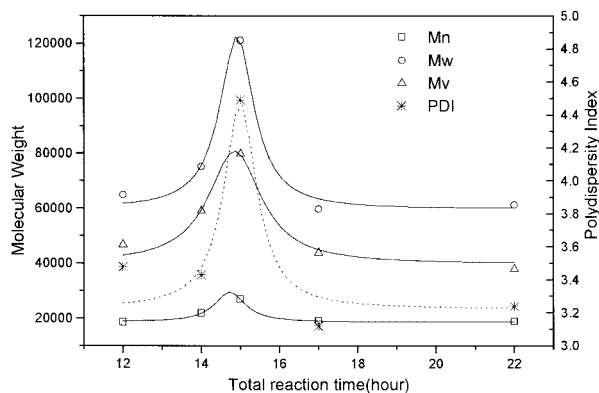
Figure 7 Molecular weight and PDI as a function of the total reaction time.

appears. The peak occurs near the point where the maximum in polymerization rate is reached.[24] Polydispersity is likely to be constant, with molecular weight varying within experimental error.

CONCLUSIONS

Using a single broad MWD copolymer of AN, PAN produced from precipitation polymerization in supercritical CO_2 was calibrated. The MWD became broad as the monomer concentration increased. There was no appreciable effect of initiator concentration on MWD when AIBN concentration ranged from 1.0 to 2.5%. Changing the density of the continuous phase by manipulating the CO_2 pressure had a dramatic effect on the reaction. The molecular weight could be enhanced by high pressure, whereas MWD became narrow. The MWD was probably constant with the molecular weight varying as the reaction time changed.

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