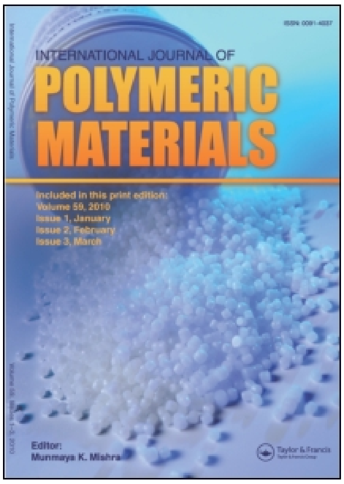

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Effect of Low-Temperature Solution Polymerization Conditions of Acrylonitrile on the Molecular Characteristics of Polyacrylonitrile

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Effect of Low-Temperature Solution Polymerization Conditions of Acrylonitrile on the Molecular Characteristics of Polyacrylonitrile

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Acrylonitrile (AN) was solution-polymerized in dimethyl sulfoxide (DMSO) and tertiary butyl alcohol (TBA) at 30, 40 and 50°C using a low temperature initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN), and effects of polymerization conditions were investigated in terms of molecular structures of polyacrylonitrile (PAN). Low polymerization temperature by adopting ADMVN proved to be successful in obtaining PAN of high molecular weight with smaller temperature rise during polymerization. Through a polymerization of AN in DMSO at 30°C, PAN having weight-average molecular weight (M_w) of 931,000 was obtained, whose polydispersity index of 1.89. For the same polymerization conditions, DMSO was slightly superior to TBA in increasing molecular weight of PAN. In addition, DMSO was superior to TBA in diminishing molecular structural defects such as enaminonitrile structure in PAN polymerized, indicating that differences in polymerization and termination rates due to a different polymerization mechanisms using two polymerization solvents. The M_w, linearity, molecular structural regularity, and whiteness were higher with PAN polymerized at lower temperatures.

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Keywords: Acrylonitrile; low temperature; 2,2′-azobis(2,4-dimethylvaleronitrile); high molecular weight PAN; enaminonitrile

INTRODUCTION

Polyacrylonitrile (PAN) is widely used as a fiber for clothes and industries, as replacement material for carcinogenic asbestos fiber, and as a precursor for carbon fibers [1 – 3]. PAN fibers have high tensile and compressive strengths, tensile modulus, and abrasion resistance. To maximize these physical properties, molecular weight, linearity, and structural regularity of PAN should be increased [4, 5].

In general, it is known that bulk polymerization of acrylonitrile (AN) at polymerization temperature of over 50°C using lower initiator concentration produce high molecular weight (HMW) PAN. However, increased polymerization rate arising from greater rises in temperature causes side reactions. Thus HMW PAN with high linearity and high structural regularity is hardly obtained [6, 7]. To reduce the self heating and the viscosity of the medium, solution polymerization of AN was tried. However, branch formation caused by frequent chain transfer reactions to monomer makes it unfavorable to obtain linear HMW PAN [8, 9]. In contrast, this solution polymerization method has advantages of easy control of viscosity and of higher conversion than those of bulk polymerization [10]. These polymerizations, however, were conducted at temperatures above 40°C. Moreover, polymerization at temperatures below 40°C was only possible by the use of UV or gamma ray radiation methods using more complicated polymerization apparatus [11].

For preparation methods of high performance PAN fiber, the molecular parameters of PAN such as molecular weight, linearity, molecular defect, and stereoregularity influence the physical properties of the fiber in addition to the suprastructures like orientation and crystallization. This implies that polymerization conditions may affect structure and properties of PAN fiber because they determine the molecular structure of PAN. The degree of branching of PAN also has a marked influence. The degree of branching is decreased with lowering polymerization temperature [8, 12]. In addition, it is known that reductions of molecular and structural defects in the PAN are necessary if it is to be used as a precursor for the carbon and graphite fibers. The defects which remain in the form of enaminonitrile and β-ketonitrile groups influence the initiation temperature for the oligomerization reaction of the PAN precursor [5, 13, 14].

In this study, a low-temperature initiator, 2,2′-azobis (2,4-dimethylvaleronitrile) (ADMVN), which can reduce the polymerization temperature down to room temperature [15], was selected for solution polymerization of AN to obtain HMW PAN with less branches and molecular defects. Tertiary butyl alcohol (TBA) and dimethyl sulfoxide (DMSO) with low chain transfer constants were used as solvents. The effect of solvent, polymerization temperature, and initiator concentration on the molecular structure of PAN polymerized were examined.

EXPERIMENTAL

Materials

AN (Aldrich Co., 99%) was washed with 5% aqueous solution of NaOH and water, dried over anhydrous $CaCl_2$, and then distilled at 78°C at atmospheric pressure. The initiator ADMVN (Wako Co., 99%) was recrystallized at low temperature twice from absolute methanol. Other extra-pure grade reagents were used without further purification.

Solution Polymerization of AN

AN and solvent (TBA or DMSO) were poured into a three-necked round bottom flask and flushed with nitrogen for 3 h to eliminate oxygen. At the predetermined polymerization temperature, ADMVN was added to the solution. When polymerization had been completed for the ADMVN/DMSO system (homogeneous solution polymerization), the product polymer was precipitated in methanol to eliminate residual monomer and solvent. In contrast, the product polymerized using the ADMVN/TBA system (heterogeneous solution polymerization) was filtered and washed several times with methanol and water. Conversion was calculated by measuring the weight of the polymer. Conversions were averages of five determinations. The detailed polymerization conditions are given in Table I.

TABLE I Parameters for solution polymerization of AN

Type of initiator	ADMVN
Type of solvent	TBA, DMSO
Initiator concentration	0.00005 mol/mol of AN 0.0001 mol/mol of AN 0.0003 mol/mol of AN 0.0005 mol/mol of AN
Monomer concentration	0.6 mol/mol of solvent 1.0 mol/mol of solvent 1.4 mol/mol of solvent
Temperature	30°C, 40°C, 50°C

Characterization

Molecular weight of PAN was calculated by Eq. (1) [16]

$$[\eta] = 3.35 \times 10^{-4}\,[M_w]^{0.72}(\text{in DMF at } 30^\circ\text{C}) \qquad (1)$$

where $[\eta]$ and M_w are intrinsic viscosity and weight-average molecular weight, respectively.

The molecular weight distribution and polydispersity index (M_w/M_n) were obtained by gel permeation chromatography (GPC) using a train of five columns with the following specifications (column 1 = deactivated Porasil, column 2 = deactivated Porasil, column 3 = deactivated Porasil, column 4 = Styragel, and column 5 = Styragel). The carrier solvent was DMF containing 0.05 M lithium bromide with a flow rate of 2.5 ml/min at room temperature.

Infrared spectra (IR) of PAN films were recorded on a Nicolet Magna IR 550 spectrophotometer with 2 cm^{-1} resolution and 30 scans.

A homogeneous 1.0 g/dl solutions of PANs in DMSO which were obtained at polymerization temperatures of 30, 40 and 50°C were poured onto stainless steel tray and dried at room temperature to produce films. The lightness of the PAN film was measured by Color eye (I.D.I., model C).

RESULTS AND DISCUSSION

Molecular Weight and its Distribution of PAN

Generally, in the free radical polymerization, the kinetic chain length, ν, is related to f, and $[I]$ by Eq. (2) [17]

$$\nu = k_p[M]/2(f\,k_d k_t[I])^{0.5} \qquad (2)$$

where f is the initiator efficiency, $[M]$ and $[I]$ are the concentrations of monomer and initiator, and k_d, k_p, and k_t are reaction rate constants of initiator decomposition, propagation and termination, respectively. This equation predicts that the molecular weight of polymer is increased with increasing monomer concentration and/or with decreasing initiator concentration. Figure 1 presents effects of monomer and initiator concentrations on M_w of PAN produced in DMSO and in TBA at 30°C, respectively. PAN was sampled at similar conversions of about 10% to clarify the effects of monomer and initiator concentrations. In accordance with the predictions by Eq. (2), M_w of PAN was increased as monomer concentration was increased or initiator concentration was decreased. Molecular weight of PAN using DMSO was slightly higher than that using TBA at all monomer and ADMVN concentrations. This may be attributed to the early termination reaction of TBA system due to a heterogeneous polymerization

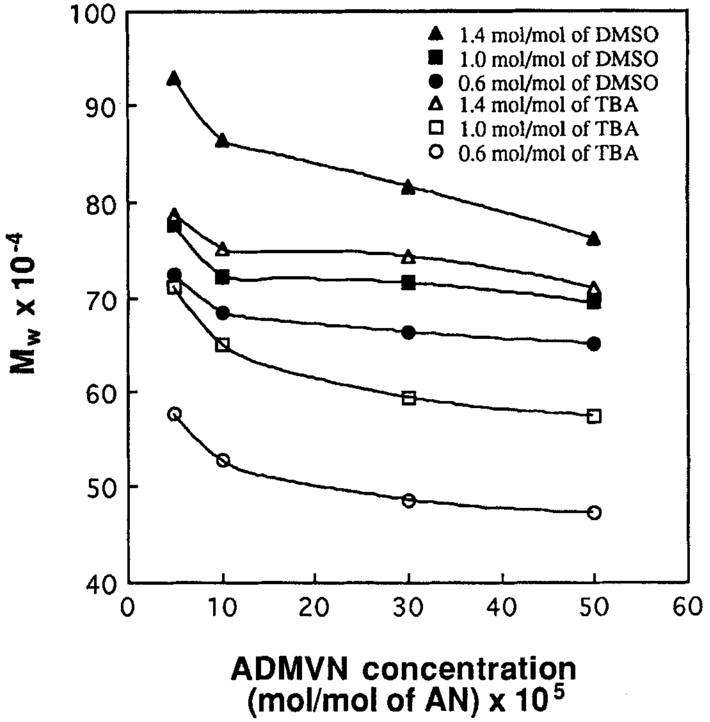

FIGURE 1 Dependence of M_w of PAN obtained at polymerization temperature of 30°C at similar conversion of ca. 10% upon ADMVN concentration.

(monomolecular termination), as proved by activation energy difference [18]. Figure 2 shows effect of polymerization temperature on M_w of PAN produced in DMSO and in TBA using monomer concentration of 1.4 mol/mol of solvent. PAN was sampled at similar conversion of about 10%. Molecular weight increased with a decrease in the polymerization temperature. These results indicate that higher polymerization temperature promotes transfer reactions and decreases molecular weight. DMSO produced higher molecular weight PAN than TBA at all polymerization temperatures.

In this study, to identify the effects of solvent, polymerization temperature, and conversion of AN into PAN on the linearity and molecular weight distribution of the resulting PAN molecules, the

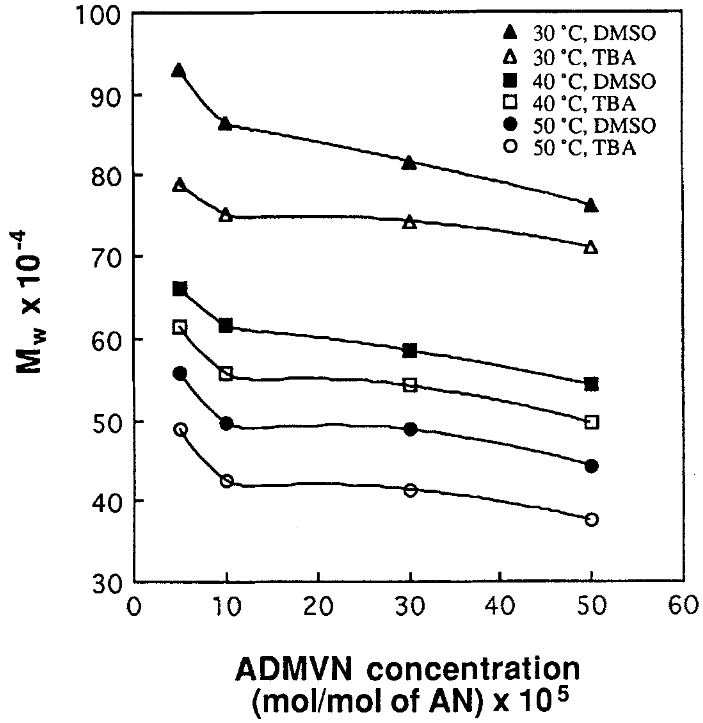

FIGURE 2 Dependence of M_w of PAN obtained at similar conversion of ca. 10% using AN concentration of 1.4 mol/mol of solvent upon ADMVN concentration.

polydispersity index was obtained through GPC experiments. Figure 3 shows results. The higher the polymerization temperature, the larger the polydispersity index. This result can be explained by the fact that matrix effect [7] and chain transfer reaction due to a relatively higher polymerization temperature leads to lowering molecular weight and widening molecular weight distribution. From the fact that in the case of DMSO at 30°C, a lower value of ca. 1.9 was obtained, it was concluded that low temperature solution polymerization of AN in DMSO produced linear HMW PAN. M_w and polydispersity index of PAN formed in DMSO at 30°C using ADMVN concentration of 0.00005 mol/mol of AN were 931,000 and 1.89, respectively.

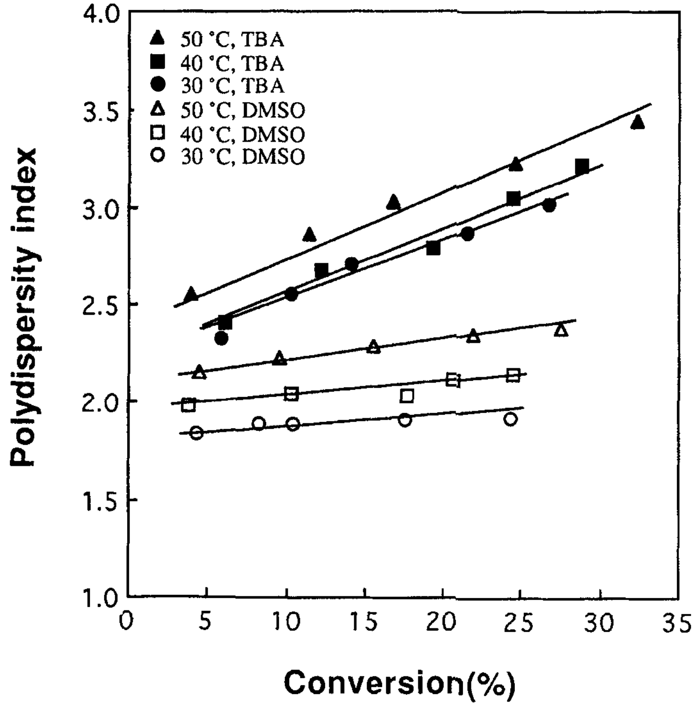

FIGURE 3 Effect of solvent, polymerization temperature, and conversion on the polydispersity index of PAN produced using AN concentration of 1.4 mol/mol of solvent and ADMVN concentration of 0.00005 mol/mol of AN.

Structural Irregularity in PAN

In the polymerization of AN, preparing of PAN with HMW, high linearity, narrow molecular weight distribution, and high structural regularity is hindered by side reactions, which generate molecular structural defect such as enaminonitrile [19, 20]. In this study, to identify the effect of polymerization conditions on the formation of molecular structural defects in PAN polymerized, FT-IR spectroscopic method was used. It has been well known that the characteristic peaks at 2940 cm^{-1} and 1665 cm^{-1} in IR spectra of PAN are, respectively, due to stretching vibration ones of CH_2 and $C = C$ or $C = N$. The peak at 1665 cm^{-1} is assigned to enaminonitrile structure in PAN [21]. A quantitative analysis of enaminonitrile structure formed during polymerization can be done from the absorbance ratios of 1665 cm^{-1} to 2940 cm^{-1}, A_{1665}/A_{2940}.

Figure 4 shows effects of polymerization temperature, solvent type, and conversion on the A_{1665}/A_{2940} value. Three things are worth noting

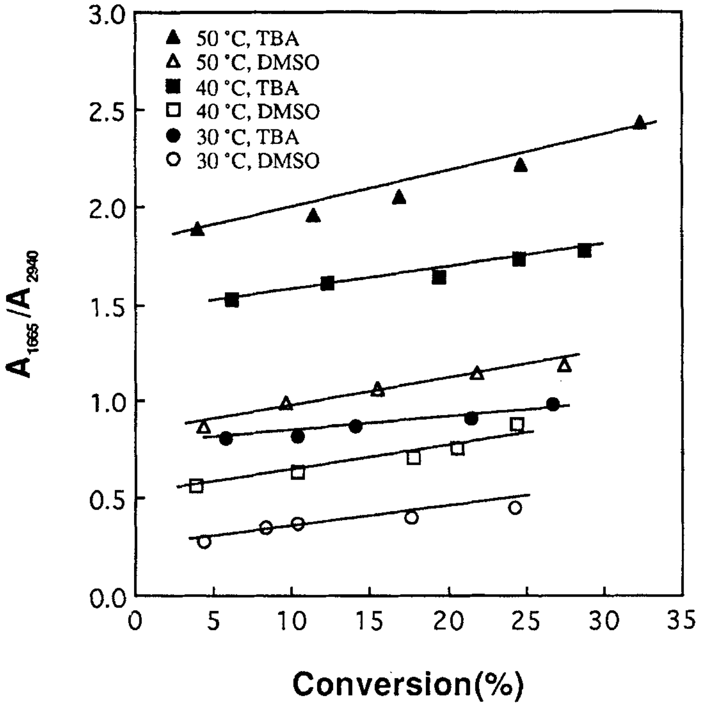

FIGURE 4 A_{1665}/A_{2940} of PAN polymerized in TBA and DMSO at three different polymerization temperatures using AN concentration of 1.4 mol/mol of solvent and ADMVN concentration of 0.00005 mol/mol of AN with conversion.

in this figure. Firstly, the A_{1665}/A_{2940} of TBA system was much higher (nearly twice) than that of DMSO system. This was explained by higher polymerization rate and faster termination rate due to a heterogeneous polymerization of AN in TBA. Secondly, these values were fairly decreased with decreasing polymerization temperature. So, it was identified that decreasing polymerization temperature is an effective way to lower the molecular structural defects in PAN. Thirdly, the A_{1665}/A_{2940} was increased with increasing conversion, indicating that at higher conversions of AN into PAN, the accelerated polymerization reaction may bring about a side reactions like chain transfer reaction more easily.

Figure 5 shows the relationship between the AN and ADMVN concentrations and the A_{1665}/A_{2940}. The A_{1665}/A_{2940} value was decreased with increasing AN concentration and decreasing ADMVN concen-

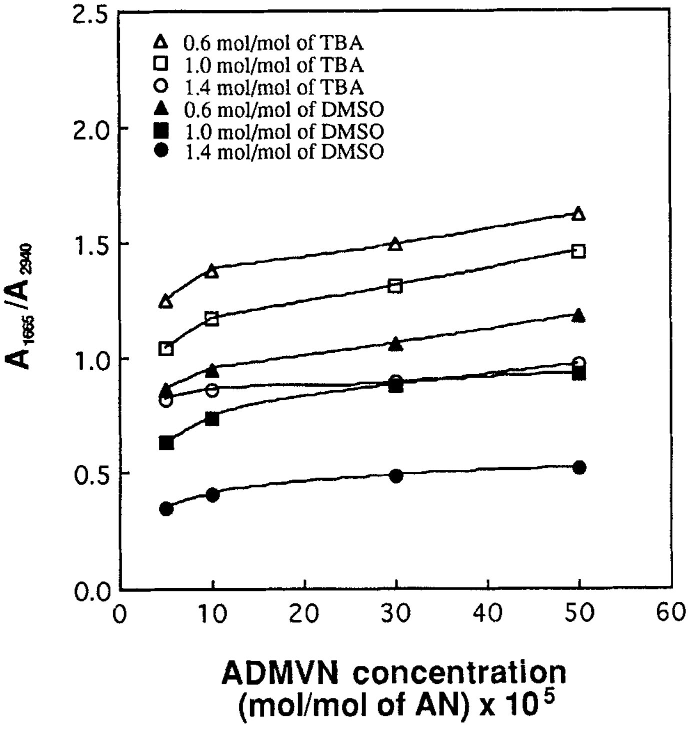

FIGURE 5 A_{1665}/A_{2940} of PAN polymerized in TBA and DMSO at 30°C at three different monomer concentrations using ADMVN concentration of 0.00005 mol/mol of AN with conversion.

tration. This result was well coincident with the fact that under higher monomer and lower initiator concentrations, HMW PAN with lower structural defects can be prepared, which was reported by Patron and Bastianelli [19].

The molecular structural defects in PAN molecule seriously influence the color of the polymer, which are incorporated during polymerization by one of the following reactions: chain transfer, initiation, or termination [19, 22]. Figure 6 presents effects of polymerization tem- perature, type of solvent and conversion on the degree of lightness of PAN film. The lightness of the PAN film polymerized at lower temperature and at lower conversion was higher than that at higher ones. This may be explained by the fact that the amount of side reactions were diminished by the polymerization of AN at lower temperature. In addition, the

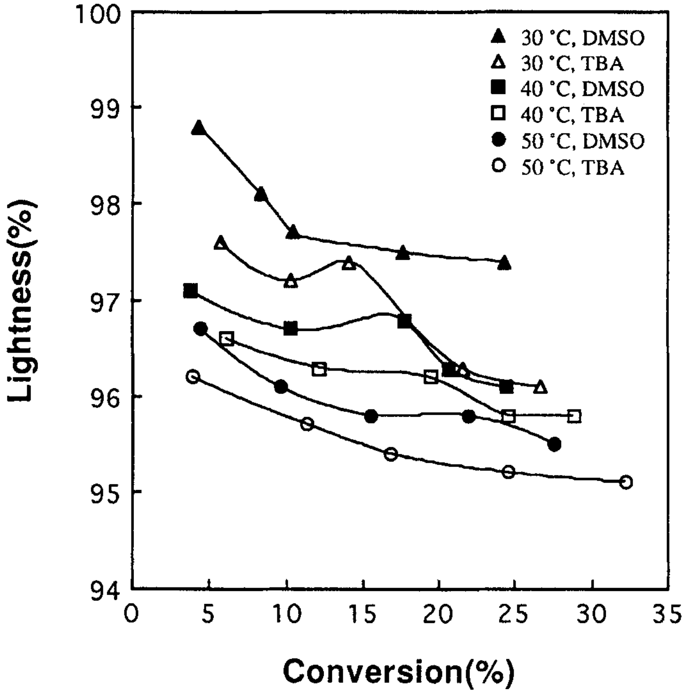

FIGURE 6 Lightness of the films of PAN polymerized in TBA and DMSO at three different polymerization temperatures using AN concentration of 1.4 mol/mol of solvent and ADMVN concentration of 0.00005 mol/mol of AN with conversion.

lightness of DMSO system was lower than that of TBA system. This was explained by higher polymerization rate and faster termination rate due to a heterogeneous polymerization of AN in TBA, which well agreed with the result presented in Figure 4.

CONCLUSIONS

As is well known [6, 7], it is not easy to obtain linear HMW PAN with high conversion by free radical polymerization initiated with azobisisobutyronitrile because of the polymerization exotherm and chain branching during polymerization. However, in solution polymerization of AN using solvent with lower chain transfer constant, a low-temperature initiator, ADMVN seemed to be advantageous in suppressing chain transfer (branching) reaction because it could lower polymerization temperature down to ca. 30°C. Hence, ADMVN was more effective in preparing HMW PAN with less branches. Initiation of AN in DMSO by using ADMVN concentration of 0.00005 mol/mol of AN produced PAN with M_w of 931,000 and polydispersity index of 1.89. For the same polymerization conditions, DMSO was slightly superior to TBA in increasing molecular weight of PAN. Moreover, DMSO was superior to TBA in diminishing molecular structural defects such as enaminonitrile structure in PAN polymerized, indicating that differences in polymerization and termination rates due to a different polymerization mechanisms using two polymerization solvents. The molecular weight, linearity, molecular structural regularity, and whiteness were higher with PAN polymerized at lower temperatures.

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