

Effects of Physical Association Through Nitrile Groups on the MWD-Dependent Viscosity Behavior of Polyacrylonitrile Solutions

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Abstract: The dipole-dipole interactions between polar nitrile groups of polyacrylonitrile (PAN) affected the molecular weight distribution (MWD)-dependent viscosity behavior of the solutions in *N,N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). In both solvents, the 16 wt% PAN solutions of broader MWD but same weight average molecular weight (MW_w) of 150,000 showed more prominent shear-thinning behavior, agreeing qualitatively with the theoretical prediction by Middleman. The dependence of the thinning behavior on the MWD was more pronounced with DMSO. The decrease of the power-law index by broadening of the MWD was more noticeable in DMSO than in DMF. The UV/vis and FTIR spectra confirmed that DMF produced stronger intra- and intermolecular dipole-dipole pairs between nitrile groups of PAN than DMSO. This indicated that physical association between polymer molecules limited the internal plasticizing effect of the low MW_w molecules by disturbing the chain interdiffusion and shear-induced disentanglement. Over the whole range of frequency measured, the higher content of the higher MW_w molecules in the broader MWD solutions resulted in the increase of dynamic viscosity and relaxation time but decrease of loss tangent.

Keywords: polyacrylonitrile solution, physical association, molecular weight distribution, shear-thinning behavior.

Introduction

The processability of polymeric materials and performance of their final products are significantly dependent on the material parameters such as molecular weight (MW), molecular weight distribution (MWD), degree of branching, and chain rigidity and polarity.¹⁻¹⁰ Hence, a lot of attempts have been made to systematically establish the correlations between the material functions and physical properties of polymers. In particular, nonpolar polymers including polyethylene and polypropylene have accumulated an extensive database for the effects of the material characters on their physical properties on the basis of theoretical backgrounds.¹¹⁻²¹ Among the material parameters, the MWD is closely related to the practical processing of polymeric materials because its broadening effectively improves the processability with little reduction of the performance of the resultant products.²²⁻²⁴ For a long time, many engineers have achieved the improvement of the productivity for some industrial polymers based on this principle.

Middleman suggested theoretical prediction for the effect of the MWD on the shear dependence of the viscosity for polymeric materials in 1960s.²⁵ Subsequently, lots of studies on the applicability of the theory on various polymeric systems

have been carried out.²⁶⁻³⁸ With broadening of the MWD, a number of polymeric materials showed greater shear dependence of the viscosity together with lower viscosity values under shear, corresponding to the Middleman's prediction. However, most of studies for the MWD effects have focused on the nonpolar polymeric systems because Middleman did not consider the polymer-polymer and polymer-solvent interactions.

The effects of the MWD on the physical properties of the polar polymers would be different from the nonpolar polymers due to the existence of strong intermolecular interactions. In particular, although polyacrylonitrile (PAN) is still one of the most widely studied polymers in the academic and industrial fields, little study on the MWD effects on its solution properties is available because the highly polar functional groups produce strong intermolecular interactions even in the solutions.³⁹⁻⁴¹ Hence, we investigated the applicability of Middleman's theory on the analysis of the relationship between the MWD and viscosity behavior of PAN solutions. Moreover, the MWD-dependent rheological behavior of the solutions was discussed based on the solubility of PAN in *N,N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) because the extent of physical associations through dipole-dipole interactions between nitrile groups of PAN is dominantly affected by the dissolved state in the solvents.

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Experimental

Materials. PAN of weight average molecular weight (MW_w) 150,000 was purchased from Sigma-Aldrich (USA) and that of MW_w 80,000 and 200,000 was purchased from Polyscience (USA), respectively. The MW_w 80,000 sample was copolymer of acrylonitrile and methacrylic acid (94/6 by mol%). Our previous study verified that abundant nitrile groups ruled over the physical properties of PAN solutions via dipole-dipole interactions although the polymer contains a little copolymer segment.³⁹ EP grades of DMF and DMSO were purchased from Duksan Co. (Korea) and Junsei Co. (Japan), respectively. PAN, DMF, and DMSO were used without further purification.

To evaluate the effects of the MWD, three samples of MW_w 150,000 but different MWD were obtained by mixing the homolog polymers. The polydispersity index (PDI) of the homolog samples was determined by gel permeation chromatography (GPC) with a Dionex Ultimate-3000 GPC system (Thermo scientific, USA) at 30 °C using DMF as eluent. The MWD of the mixed samples was estimated by calculating the PDI of the mixed ones based on the values of the neat samples. The mixing recipes to produce the MW_w 150,000 samples with different MWD are given in Table I. Sample codes are also listed in the table.

Measurement of Physical Properties. The FTIR spectra of 16 wt% PAN solutions in DMF and DMSO were obtained at 25 °C using Nicolet iS10 spectrometer (Thermo Scientific, USA). The samples were prepared by plating the solution on the top of a KBr pellet. The ultraviolet-visible (UV/vis) spectra of 0.5 g/dL PAN solutions in DMF and DMSO were recorded using UV/vis spectroscopy (Uvicam 8700 series) at 25 °C.

The reduced (η_{red}) and inherent (η_{inh}) viscosities were measured by Ubbelohde viscometer (Schott Co., Germany) over the concentration range from 0.1 to 0.8 g/dL at 30 °C. The intrinsic viscosity ($[\eta]$) of PAN solutions was calculated using the Huggins equation:

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k_H' [\eta]^2 c \quad (1)$$

in which, η_{sp} is specific viscosity, c is concentration, and k_H stands for the Huggins constant, respectively. The $[\eta]$ was obtained

by extrapolating the η_{red} values in the linear concentration range to $c=0$, which assumes no intermolecular interactions.⁴²

The dynamic rheological properties of PAN solutions were measured by Advanced Rheometric Expansion System (ARES, TA Instruments, USA). A parallel-plate geometry with a diameter of 40 mm was adopted. The plate gap and strain level were 0.8 mm and 5%, respectively. In order to prevent the evaporation of the solvent during the measurement, mineral oil (Sigma-Aldrich, USA) was coated to the outer surface of the parallel plates. The dynamic rheological measurement of 16 wt% of PAN solutions was conducted at 30 °C.

Results and Discussion

Physical Association through Nitrile Groups of PAN in DMF and DMSO. The intramolecular interactions between nitrile groups of PAN are profoundly affected by the chain conformation and single molecular behavior in the dilute solutions. Figure 1 shows the η_{red} and η_{inh} of PAN solutions of the homolog M15-1.7 in DMF and DMSO at 30 °C over the concentration range from 0.1 to 0.8 g/dL. PAN solutions

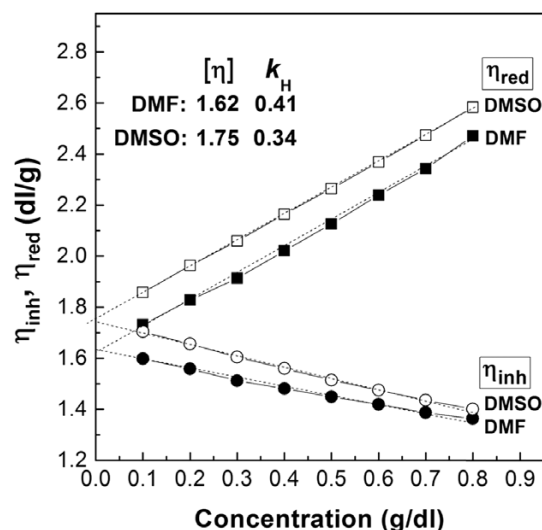


Figure 1. The plots of reduced (η_{red}) and inherent (η_{inh}) viscosities for PAN solutions of the homolog M15-1.7 in DMF and DMSO at 30 °C over the concentration range from 0.1 to 0.8 g/dL.

Table I. The Sample Codes of the Homolog and Mixed PAN Samples and Mixing Recipes to Obtain the MW_w 150,000 Species with Different Polydispersity Index (PDI)

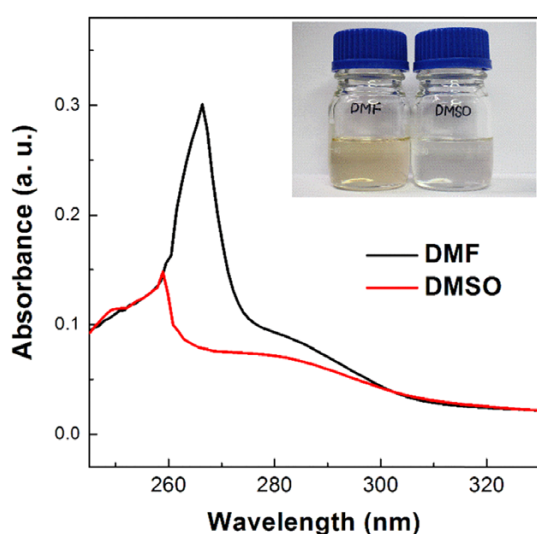
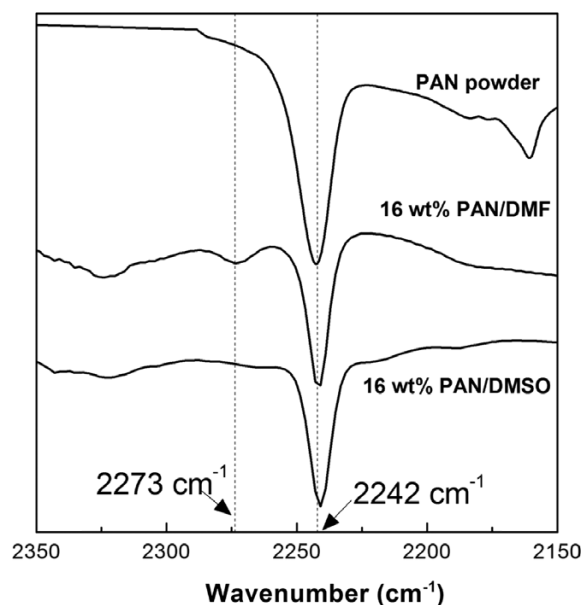
Sample Codes	Composition			MW_w ($\times 10^{-3}$)	PDI
	MW_w 80,000 (ratio by wt)	MW_w 150,000 (ratio by wt)	MW_w 200,000 (ratio by wt)		
M8	1	-	-	80	1.615
M15-1.7	-	1	-	150	1.717
M15-1.9	0.256	0.385	0.359	150	1.950
M15-2.1	0.416	-	0.584	150	2.095
M20	-	-	1	200	1.805

Table II. Overall and Hansen Solubility Parameters of PAN, DMF, and DMSO at 25 °C⁴⁴

	Solubility Parameter (MPa ^{1/2})			
	δ	δ_d	δ_p	δ_h
PAN	25.3	18.2	16.2	6.8
DMF	24.8	17.4	13.7	11.3
DMSO	26.6	18.4	16.4	10.2

give the greater values of the η_{red} and η_{inh} in DMSO than in DMF. Based on these plots, the $[\eta]$ and k_H are obtained and indicated in the figure. The $[\eta]$ and k_H are parameters of a coil dimension of a polymer in a solvent and the interaction strength between polymer and solvent, respectively. As a rule, the decrease of the k_H indicates the increase of the interaction strength between polymer and solvent.⁴³ As shown in Figure 1, DMSO gives the greater $[\eta]$ but lower k_H of the solutions than DMF. This indicates that DMSO expands a single PAN coil greater than DMF by breaking up of the intramolecular interactions between polymer molecules.

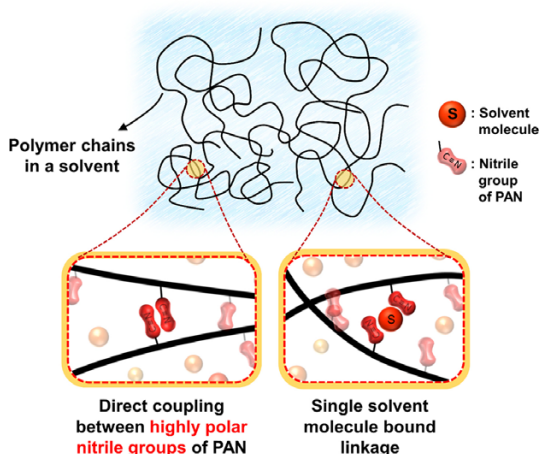
The interaction strength between polymer and solvent can be theoretically estimated by the overall and Hansen solubility parameters of PAN, DMF, and DMSO in Table II. The overall solubility parameter (δ) is given by the sum of the dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) contributions ($\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$), which represents the strength of physical bonding of a material.⁴⁴ DMF has the overall solubility parameter closer to PAN than DMSO. In case of the δ_p term, however, DMSO is much closer to PAN than DMF. This confirms that DMSO produces stronger dipole-dipole interactions with polar nitrile groups of PAN than DMF, agreeing with the k_H analysis.

**Figure 2.** The UV/vis absorption spectra of 0.5 g/dL PAN solutions of the homolog M15-1.7 in DMF and DMSO at 25 °C.**Figure 3.** The FTIR spectra of PAN powder and 16 wt% solutions of the homolog M15-1.7 in DMF and DMSO.

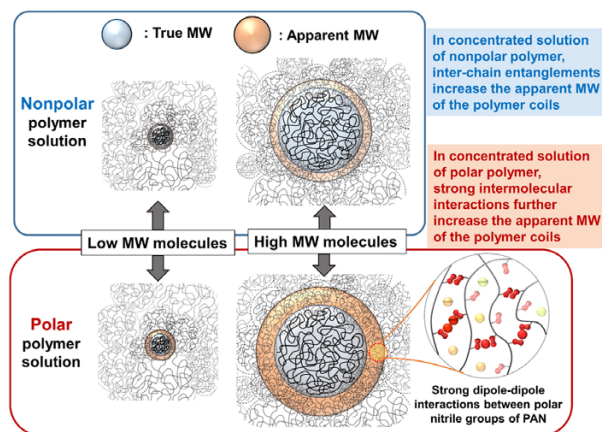
The UV/vis spectra of 0.5 g/dL PAN solutions of the homolog M15-1.7 in DMF and DMSO are shown in Figure 2. The absorption peak in the vicinity of 270 nm is assigned to the π -absorption of the physically associated nitrile groups of PAN, which results in the yellowing of PAN solutions.⁴⁵ In the spectra, PAN solution exhibits much greater absorbance in DMF than in DMSO. The strong absorption peak in DMF confirms the existence of the dipole-dipole pairs of nitrile groups in a single coil.³⁹ That is, the intra-chain association gives rise to the smaller coil dimension of PAN in DMF than in DMSO.

In case of the concentrated solutions, the intermolecular physical bonding between nitrile groups can be identified by the FTIR spectra in Figure 3. The peak at 2242 cm⁻¹ is assigned to nitrile groups of PAN.^{46,47} Another peak in the vicinity of 2273 cm⁻¹ is reported to indicate the complexed nitrile groups between each other or with solvent molecules.⁴⁸ Then, DMF obviously gives the peak at 2273 cm⁻¹ in comparison with DMSO. Consequently, PAN produces the low content of the physical associations through nitrile groups in DMSO due to the strong dipole-dipole interactions between polymer and solvent. In DMF, however, PAN solutions contain numerous intra- and intermolecular complexes between nitrile groups such as direct coupling and single solvent molecule bound linkage as depicted in Scheme I. The strong dipole-dipole interactions between nitrile groups of PAN in DMF would limit the chain dynamics such as disentanglement and interdiffusion.

The MWD Effects on the Viscosity Behavior of PAN Solutions in DMF and DMSO. Figure 4 shows the dynamic viscosity (η') curves of 16 wt% PAN solutions of M8, M20,



Scheme I. The molecular complexes between highly polar nitrile groups of PAN in a solvent.



Scheme II. The schematic presentation of the apparent MW of the low and high MW molecules in nonpolar and polar polymeric systems, respectively.

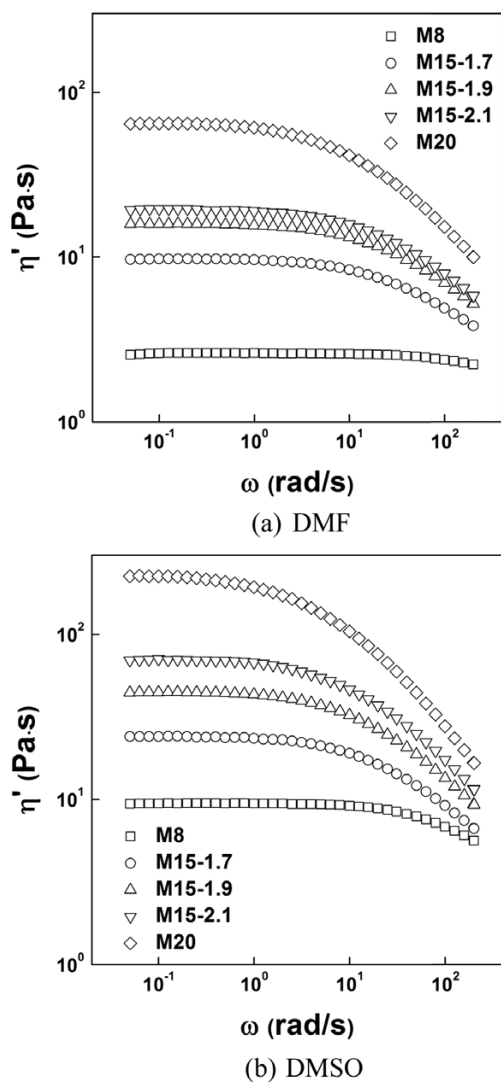
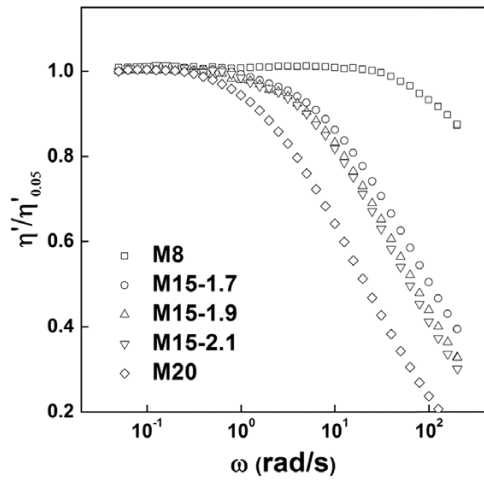


Figure 4. The dynamic viscosity (η') curves of 16 wt% PAN solutions of M8, M15-1.7, 1.9, and 2.1, and M20 in (a) DMF and (b) DMSO at 30 °C, respectively.

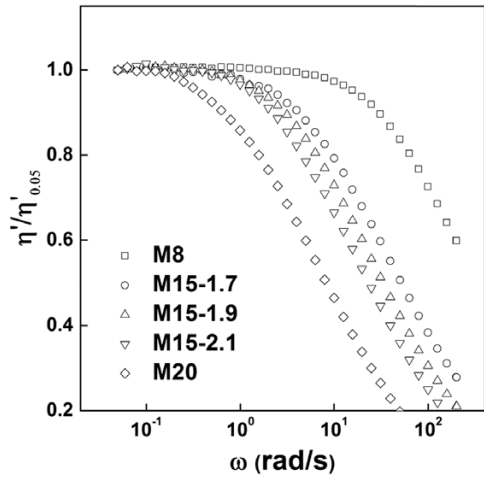
and three M15 samples with different MWD in DMF and DMSO at 30 °C, respectively. The PAN solutions of higher MW_w exhibit more prominent shear-thinning behavior together with the greater values of the viscosity as might be expected. Then, it should be noted that the solutions of the broader MWD give greater values of the η' among the M15 samples. In fact, the viscosity value of polymeric system would be predominantly dependent on the high MW moiety more than low MW one.^{25,49} In the broader MWD, the higher content of the high MW molecules leads to much higher apparent MW and corresponding viscosity due to numerous entanglement points with adjacent chains as illustrated in Scheme II. Particularly, this phenomenon might be noticeable in polar polymeric systems because polar functional groups produce strong intermolecular interactions between chains even in the solutions.³⁹⁻⁴¹ Hence, the greater apparent viscosity of the broader MWD is obtained over the whole frequency range observed in the η' curves of PAN solutions. In addition, all tested PAN solutions give greater η' in DMSO than in DMF. This indicates the higher apparent MW of PAN in DMSO, resulting from the larger coil dimension in DMSO than in DMF.

The effect of the MWD on the shear-thinning behavior of PAN solutions is confirmed by the η' curves normalized with an initial viscosity value at 0.05 rad/s in Figure 5. At 16 wt%, the M15 solutions of the broader MWD exhibit more noticeable shear-thinning behavior, which results from the internal plasticizer effect of the low MW molecules. That is, the shear dependence of the viscosity is considerably affected by the content of the low MW molecules although the apparent η' value is dominantly dependent on the high MW ones. The plasticizing role of the low MW molecules is depicted in Scheme III. Thus, the polar polymeric system follows the theoretical prediction that the broadening of the MWD enhances the shear-thinning behavior, as suggested by Middleman.²⁵

The degree of the shear-thinning of the solutions is quanti-

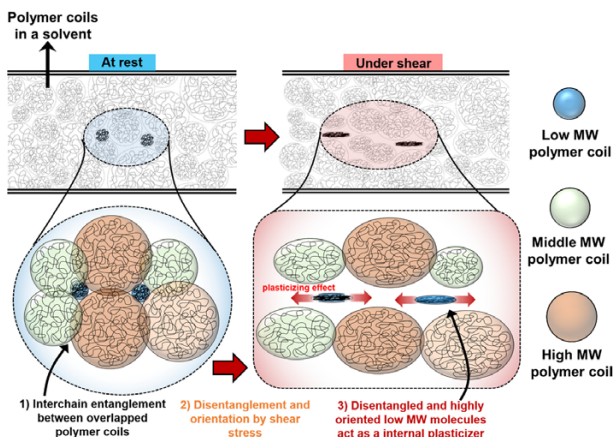


(a) DMF



(b) DMSO

Figure 5. The dynamic viscosity (η') curves normalized with the initial viscosity value at 0.05 rad/s of 16 wt% PAN solutions of M8, M15-1.7, 1.9, and 2.1, and M20 in (a) DMF and (b) DMSO at 30 °C, respectively.



Scheme III. Schematic presentation of the plasticizing role of the low MW molecules in the polymer solutions.

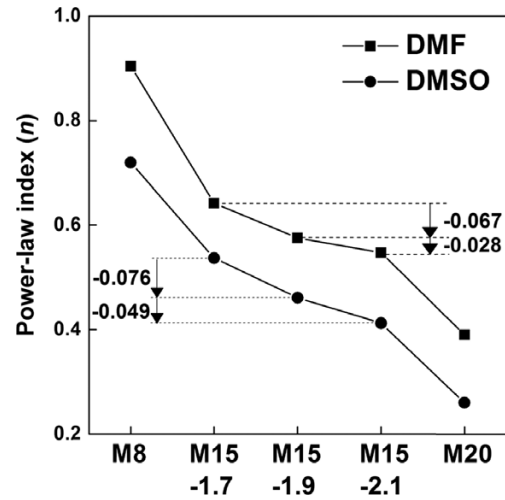
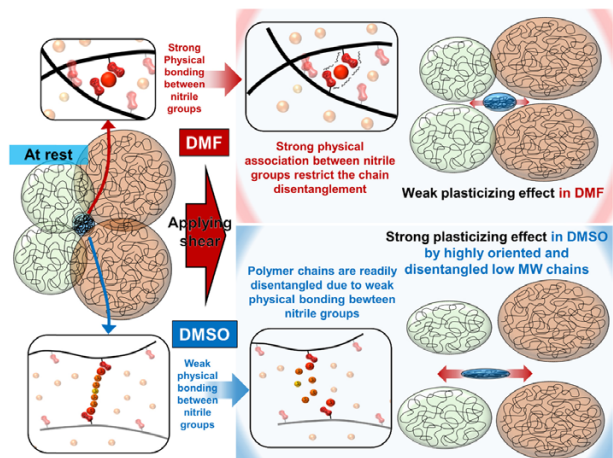


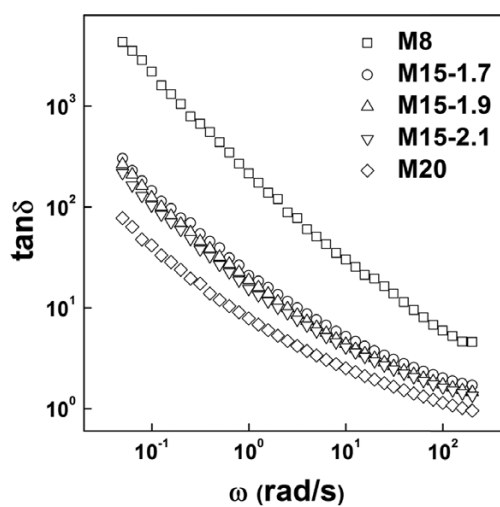
Figure 6. The power-law index (n) of 16 wt% PAN solutions of M8, M15-1.7, 1.9, and 2.1, and M20 in DMF and DMSO at 30 °C, respectively. The n was obtained within relatively narrow frequency range from 120 to 200 rad/s in which the viscosity of the all solutions clearly exhibits shear-thinning behavior.

tatively verified by the power-law index (n) in Figure 6, which is obtained within relatively narrow frequency range from 120 to 200 rad/s in which the viscosity of the all solutions exhibits shear-thinning behavior. The n of 1 indicates Newtonian fluid and the lower value than 1, shear-thinning fluid.⁵⁰⁻⁵² In Figure 6, the M15 solutions in both DMF and DMSO show the decrease of the n with broadening of the MWD as expected. This further supports the plasticizer role of the low MW molecules even in the polar polymeric system.

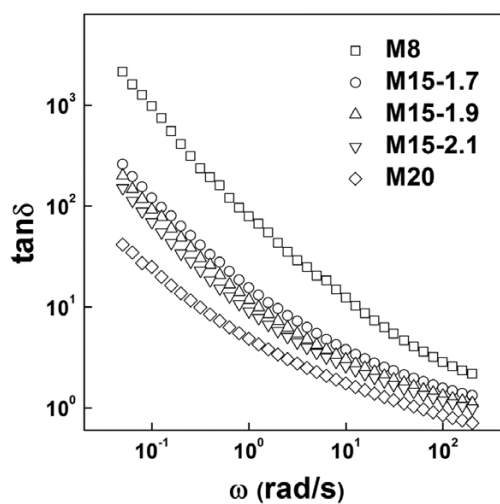
It is worth mentioning that the extent of the decrease of the n is greater in DMSO than in DMF. That is, the MWD dependence is more pronounced with DMSO. This result reveals that the MWD effect is dictated by the degree of the



Scheme IV. The effect of physical association through polar nitrile groups on the plasticizing role of the low MW molecules in DMF and DMSO.



(a) DMF

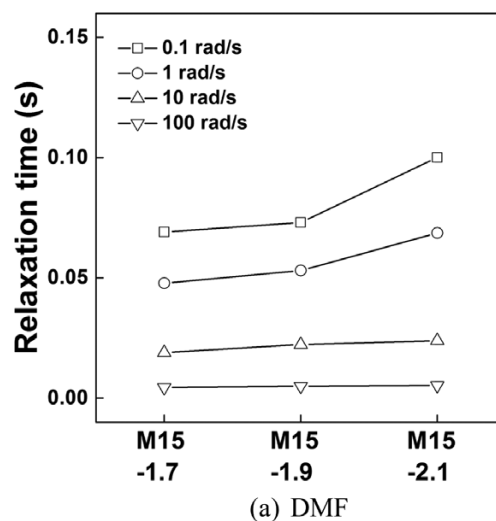


(b) DMSO

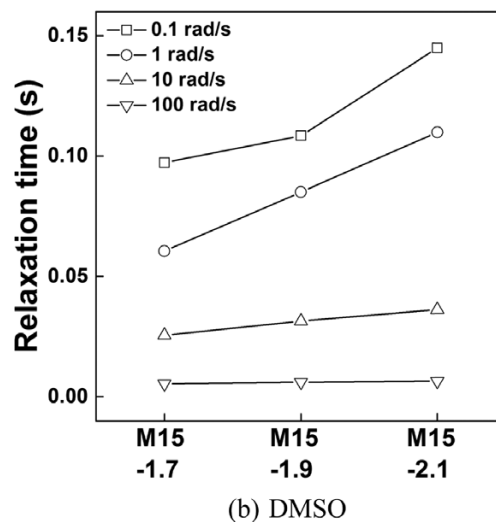
Figure 7. The loss tangent ($\tan\delta$) curves of 16 wt% PAN solutions of M8, M15-1.7, 1.9, and 2.1, and M20 in (a) DMF and (b) DMSO at 30 °C, respectively.

intermolecular interactions between nitrile groups in a given solvent. Thus, strong dipole-dipole interactions and resultant physical associations of PAN in DMF disturb the plasticizing role of the low MW molecules. As shown in Scheme IV, strong physical bonding between nitrile groups in DMF restricts the shear-induced chain disentanglement and interdiffusion. In DMSO, however, the low MW moiety is readily disentangled and oriented due to the low content of the physical association between nitrile groups at rest.

Figure 7 shows the loss tangent ($\tan\delta$) curves of 16 wt% PAN solutions in DMF and DMSO, respectively. The $\tan\delta$ offers an information on the phase change of the systems under shear. In principle, the liquid-like character is dominant when $\tan\delta > 1$, whereas solid-like character is dominant when $\tan\delta < 1$.⁵³⁻⁵⁵ The $\tan\delta$ value decreases with broadening of the MWD.



(a) DMF



(b) DMSO

Figure 8. The relaxation time (λ) of 16 wt% PAN solutions of three M15 samples with different MWD at various frequencies in (a) DMF and (b) DMSO at 30 °C, respectively.

The increase of the solid-like character indicates that the phase character of the solutions is predominantly affected by the high MW molecules. In fact, the increase of the liquid-like character by increasing the low MW content may be insignificant in the solution system because of the presence of numerous solvent molecules. In addition, the shear dependence of the $\tan\delta$ of PAN solutions depends dominantly on the MW rather than MWD. That is, the broadening of the MWD hardly causes the phase change of PAN solutions.

Unlike the phase character of the solutions, the molecular relaxation behavior would be considerably affected by the MWD. Figure 8 shows the relaxation time (λ) of 16 wt% PAN solutions of the three M15 samples in DMF and DMSO at several frequencies, respectively. The λ under dynamic shear can be calculated by Eq. (1).⁵⁶

$$J' = G'/([\eta^*]\omega)^2 = \lambda/[\eta^*] \quad (2)$$

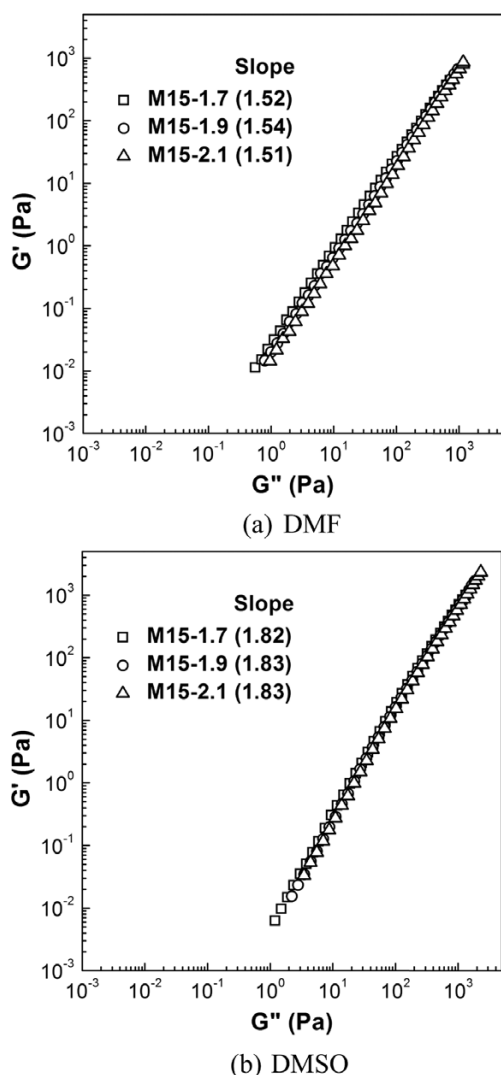


Figure 9. The logarithmic Cole-Cole plot of storage modulus (G') versus loss modulus (G'') for 16 wt% PAN solutions of three M15 samples with different MWD in (a) DMF and (b) DMSO at 30 °C, respectively. Numbers on the graph are the slope of the curves.

in which, J' is compliance, G' is storage modulus, and η^* stands for complex viscosity, respectively. The M15 solutions in the both solvents exhibit the increase of the λ with broadening of the MWD at the lower shear rate. This result originates from the slower relaxation of the high MW molecules than low MW ones. However, the difference in the λ with the MWD gets faint with increasing frequency, then becomes negligible at 100 rad/s. This supports that the effects of the high MW molecules become insignificant but plasticizing effects of the low MW moiety become noticeable.

Figure 9 exhibits a logarithmic plot of G' versus loss modulus (G'') of 16 wt% PAN solutions with different MWD, the so-called Cole-Cole plot. The slope of 2 on the Cole-Cole plot is empirically encountered with absolutely homogeneous

polymer solutions without any physical structure. Thus, the deviation of slope from 2 is a measure of the heterogeneity of the polymer solutions.⁵⁷ In the figure, three M15 solutions show an almost single master curve irrespective of the MWD in both DMF and DMSO. It is because the heterogeneity of the polar polymer solutions is dominantly determined by the strong dipole-dipole interactions. This suggestion can be further supported by the little deviation of the slopes with the MWD. Then, the greater slopes in DMSO further confirms the weak intermolecular interactions in the solutions than in DMF.

Conclusions

The MWD-dependent viscosity behavior of PAN solutions in the polar solvents was qualitatively in line with the athermal system-based prediction as suggested by Middleman. However, the MWD effects on the shear-thinning behavior were more noticeable in DMSO than in DMF. That is, the internal plasticizing role of the low MW molecules was restricted in DMF because of the strong physical associations through highly polar nitrile groups of PAN. In other words, the strong dipole-dipole interactions between polymer molecules interrupted the shear-induced chain disentanglement and interdiffusion. Hence, it is prerequisite to understand the intermolecular interactions of polar polymers in the MWD control for improving the processability.

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