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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Devasia, Renjith , Nair, C. P. Reghunadhan and Ninan, K. N.(2008) 'Rheological Behavior of Dope Solutions of Poly(acrylonitrile-co-itaconic acid) in *N,N*-dimethylformamide: Effect of Polymer Molar Mass', Journal of Macromolecular Science, Part A, 45: 3, 248 – 254

**To link to this Article:** DOI: 10.1080/10601320701842233

**URL:** <http://dx.doi.org/10.1080/10601320701842233>

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# Rheological Behavior of Dope Solutions of Poly(acrylonitrile-*co*-itaconic acid) in *N,N*-dimethylformamide: Effect of Polymer Molar Mass

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Received June, 2007, Accepted September, 2007

The rheological behavior of dope solutions of poly(acrylonitrile-*co*-itaconic acid) or poly(AN-*co*-IA) is important from the point of view of deriving the spinning conditions for good quality special acrylic fibers. The viscosity of the resin dope is dictated by the polymer concentration, molar mass, temperature and shear force. The dynamic shear rheology of concentrated poly(AN-*co*-IA) polymer dope solutions in *N,N*-dimethylformamide, in the molar mass ( $\bar{M}_v$ ) range of  $1 \times 10^5$  to  $1 \times 10^6$  g/mol, was investigated in the shear rate ( $\dot{\gamma}$ ) range of  $1 \times 10^1$  to  $5 \times 10^4$  min<sup>-1</sup>. An empirical relation between  $\eta$  and  $\bar{M}_v$  was found to exist at constant shear rate. The dope viscosity was dependent on the molar mass and the shear rate at a given temperature (T) and concentration. The polymer molar mass index of dope viscosity ( $m$ ) was calculated as functions of concentration (c), shear rate and temperature. The  $m$  values increased with shear rate and temperature. A master equation relating  $m$ , with shear rate and temperature was derived for a given dope concentration. At higher shear rates,  $m$  tends to the value of 3.4, which is close to the molar mass index of viscosity reported for molten thermoplastics.  $m$  increased significantly with shear rate and nominally with temperature, while an increase in concentration decreased it. The onset of shear thinning of the dope shifted to a lower shear rate regime with an increase in polymer concentration and the molar mass. For a given value of molar mass, the increase in viscosity of the dope solution with polymer concentration was dependent on the shear rate.

**Keywords:** polyacrylonitrile; rheology; polymer dope; carbon fiber precursor; shear thinning

## 1 Introduction

Poly(acrylonitrile-*co*-itaconic acid) or poly(AN-*co*-IA) is a well known precursor for carbon fiber production (1–11). The precursor polymer is dissolved in a suitable solvent like *N,N*-dimethylformamide (DMF) to produce the dope and fibers are produced with dry, wet and dry-jet wet spinning methods (8–15). Better quality fibers are derived from high molar mass polyacrylonitrile (PAN) copolymer precursors (15, 16). However, high molar masses impede high solid loading, which could adversely affect fiber properties. An ideal situation demands high solid loaded dope of high molar mass polymer with manageable viscosities. As these are contradicting requirements, alternate methods are to be evolved for viscosity management. In this perspective, we have investigated the dynamic shear rheology of dope

solutions of poly(AN-*co*-IA) in DMF, using polymer samples of varying molar masses. The effects of temperature and shear rate on polymer dope viscosity were also investigated (17).

This paper examines the effect of polymer molecular weight and shear force on the rheology of the polymer dope. Empirical models relating the rheological characteristics with polymer molar mass, temperature and shear rate have been established.

## 2 Experimental

### 2.1 Polymer Synthesis and Characterization

The poly(AN-*co*-IA) samples were prepared by the free radical polymerization of acrylonitrile and itaconic acid in DMF using  $\alpha$   $\alpha'$ -azobisisobutyronitrile (AIBN) as the initiator at 60°C as reported earlier by our group (6, 7). In this work, the polymerization conditions were regulated to get high molecular weight poly(AN-*co*-IA) polymers. The resulting samples were purified by Soxhlet extraction for 8 h using methanol, powdered and dried under vacuum at 50°C for

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8 h. The intrinsic viscosity,  $[\eta]$  was obtained by the method of ‘Huggin’ and is denoted as  $[\eta]_H$  using the data in the concentration range 0.3–0.6 g/dL as reported earlier by our group (8). The viscosity average molecular weight ( $\bar{M}_v$ ) was calculated from the Mark-Houwink-Sakurada equation as follows:

$$[\eta] = K\bar{M}_v^\alpha$$

where  $K = 2.86 \times 10^{-4}$  and  $\alpha = 0.733$  (18).

## 2.2 Preparation of Polymer Solution and Viscosity Measurements

Solutions for rheological measurements were prepared by dissolving a weighed amount of dried polymer sample in DMF (which was freshly distilled over  $P_2O_5$ ) in a tightly capped 50 ml conical flask using a magnetic stirrer to speed up dissolution of the polymer. Polymer concentrations are expressed in weight percentage (3.5, 5, 7.5, and 10% by weight).

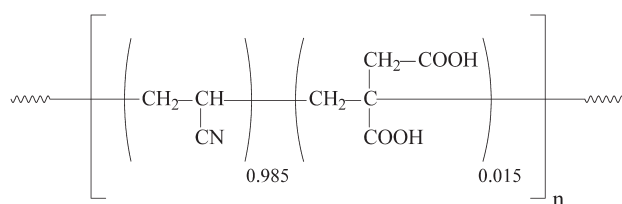
Rheological studies of PAN solutions were carried out in a ‘‘Reologica Viscotech’’ rheometer, working in viscosity mode (cup and bob type) in the temperature range of 30–80°C. Viscosity calibration was done using standard silicon oil samples at different shear rates. For the evaluation of the viscosity, about 15 ml of the solution was taken and transferred to a disposable sample cylinder. Experiments were carried out in the shear rate range  $1 \times 10^1$  to  $5 \times 10^4 \text{ min}^{-1}$ . Values of viscosity ( $\eta$ ), shear stress ( $\tau$ ) and shear rate ( $\dot{\gamma}$ ) were directly obtained from the instrument software.

## 3 Results and Discussion

Four poly(AN-co-IA) copolymers of differing molar masses were used for the studies; their structure is given in Scheme 1 and their details are given in Table 1. In all the cases, the itaconic acid concentration was  $1.5 \pm 0.03 \text{ mol}\%$ .

### 3.1 Rheological Behavior

The viscosities of the polymer dope solutions of varying concentrations in DMF were measured. The viscosity of the polymer dope is dependent on the temperature (T) regime of measurement, dope concentration (c), copolymer molar mass ( $\bar{M}_v$ ) and the shear rate ( $\dot{\gamma}$ ) (17). A typical viscosity dependency on the shear rate (in the shear rate range from



Sch. 1. Typical copolymer of acrylonitrile with itaconic acid.

Table 1.  $[\eta]$  values of polymer samples calculated by the method of ‘Huggin’ and the corresponding  $\bar{M}_v$  values

Sample	$[\eta]_H$ (dL/g)	$\bar{M}_v \times 10^{-5}$ (g/mole)
PI-1	1.83	1.56
PI-2	3.11	3.21
PI-3	5.30	6.65
PI-4	7.21	10.11

$1 \times 10^1$  to  $5 \times 10^4 \text{ min}^{-1}$ ) and temperature for a 10% solution of copolymer sample PI-3 is depicted in Figure 1. The viscosity data for very low shear rates are prone to error and are not considered. Similarly, the viscosity data for shear rate regimes beyond  $5 \times 10^4 \text{ min}^{-1}$  are not of much practical significance and hence, are not of interest.

As expected, the viscosity values were found to decrease with shear rate and temperature. In the lower shear rate regime, the decrease in viscosity with temperature is more drastic in comparison to the higher shear rate regime. Moreover, the ‘Newtonian plateau’ is found to extend to a higher shear rate regime with an increase in temperature (i.e., at higher temperatures, the polymer solutions show a higher tendency towards Newtonian behavior). This is expected, as a rise in temperature causes coiling of the polymer chains in solution, reducing the intermolecular friction and the resistance to flow. The viscosity decreases with both the temperature and shear rate depending on the molar mass and concentrations. This behavior of the polymer solutions has been analyzed and we have established empirical models for the  $\eta$  values relating to these parameters.

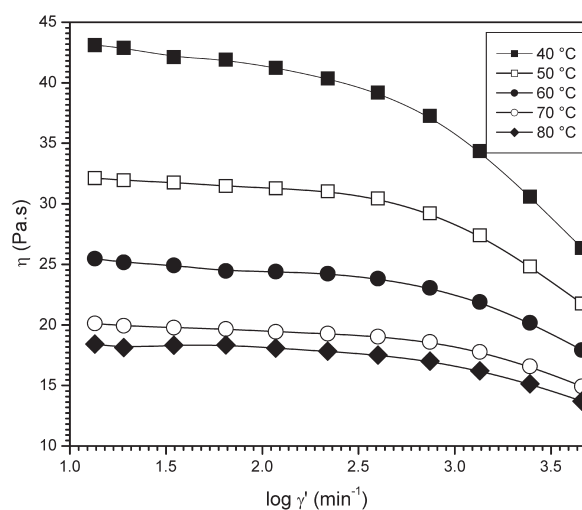


Fig. 1. Dependency of  $\eta$  on the  $\dot{\gamma}$  for polymer sample, PI-3 (10% solution) at different temperatures.

### 3.2 Effect of Concentration and Molar Mass on Viscosity

An increase in the concentration of the dope solution decreases the inter-particle distances and consequently leads to considerable changes in the flow properties of the concentrated polymer solutions. The shear rate dependence of viscosity becomes more pronounced as the molecular weight increases. In other words, the propensity for shear thinning is more for high molar mass polymers. For the same solid content, the dope viscosity shows an upward trend when the molar mass increases as is evident from Figure 2.

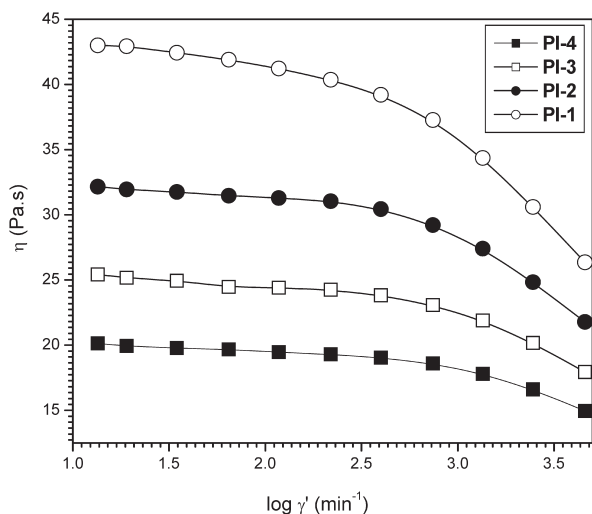
At constant concentration, shear rate and temperature, an empirical relationship exists between viscosity and molar mass as given below:

$$\eta = k \bar{M}_v^m \quad (1)$$

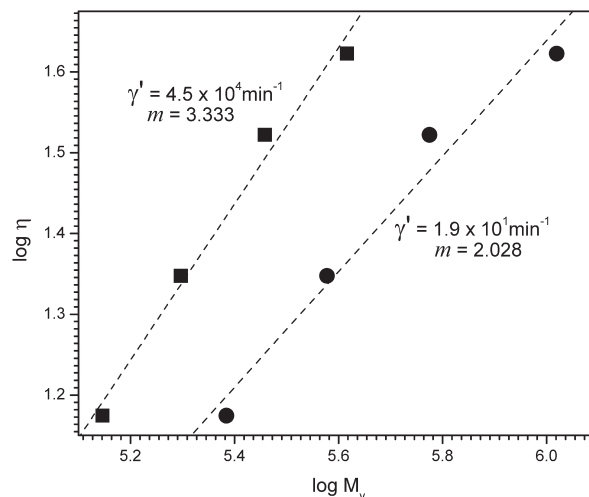
Where,  $k$  is a proportionality constant and  $m$  is the molar mass index of viscosity.

For the calculation of  $m$ , the  $\eta$  values in the shear regime of  $1 \times 10^1$  to  $5 \times 10^4 \text{ min}^{-1}$  was considered (Figure 2). A plot of  $\log \eta$  against  $\log \bar{M}_v$  at a given concentration and shear rate gives the slope as  $m$ . Typical plots for calculation of  $m$  are shown in Figure 3.

For practical applications, shear rates beyond  $10^4 \text{ min}^{-1}$  are seldom considered and hence, a value of  $5 \times 10^4 \text{ min}^{-1}$  was kept as the upper limit for the shear rate in this study. Generally, the value of  $m$  lies between 2 and 3.5 depending on molecular weight wherein the polymer entanglements become serious enough to contribute to the viscosity (19–21). It is seen that the value of  $m$  increases with an increase in shear rate and temperature. This behavior for a typical case (7.5% by weight) is shown in Figure 4.



**Fig. 2.** Variation of viscosity with shear rate for polymer samples with different molar mass at 60°C. (Concentration of dope solution is kept constant at 7.5%).

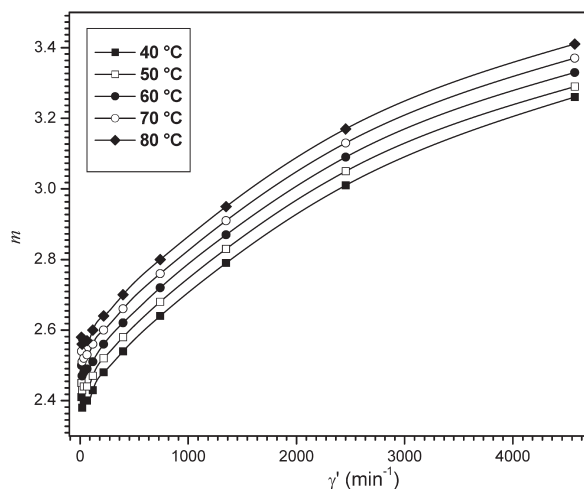


**Fig. 3.** Typical plots for the calculation of  $m$  for the high ( $\gamma' = 4.5 \times 10^4 \text{ min}^{-1}$ ) and low ( $\gamma' = 1.9 \times 10^1 \text{ min}^{-1}$ ) shear rate for a 7.5% solution.

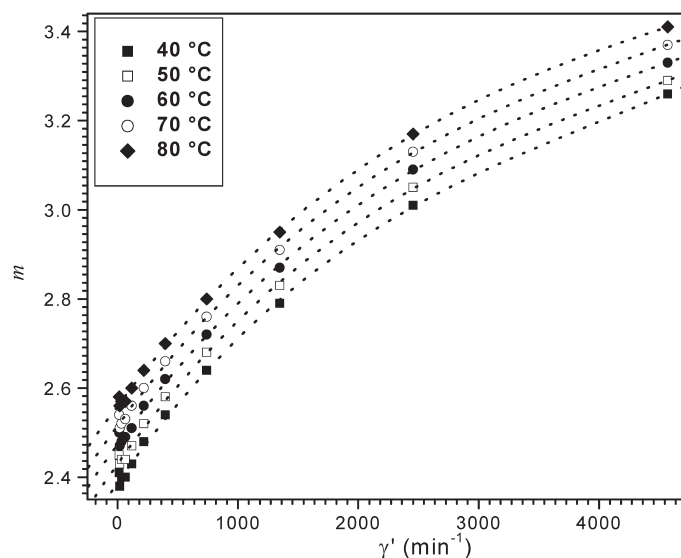
For the concentration regimes studied, the values of  $m$  lie between 2.49 and 3.41. In the present case, the average  $m$  value is 2.66, which is lower than the theoretically expected value of  $3.5 \pm 0.5$  for high molar mass polymers, implying a less severe molar mass dependency for  $\eta$ . At zero shear,  $m = m_0$  and Equation (1) can be rewritten as:

$$\eta_0 = k \bar{M}_v^{m_0} \quad (2)$$

where  $\eta_0$  is the zero shear viscosity.  $m_0$  could be graphically calculated as the  $m$  value extrapolated to zero shear in the  $m$  vs.  $\gamma'$  plot by a non-linear curve fitting (Figure 5). The  $m_0$  values for the polymers at various temperatures and concentrations are given in Table 2.



**Fig. 4.** Plot of  $m$  vs.  $\gamma'$  for polymer samples in the temperature range of 40–80°C (Concentration of dope solution kept constant at 7.5%).



**Fig. 5.** Multiple regression curve fitting for calculating  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  for a 7.5% solution.

The  $m_0$  values were found to decrease with an increase in concentration but showed an increase with temperature. It was found that the  $m$  value increases with an increase in shear rate and the relationship between  $m$  and shear rate at a given concentration and temperature was arrived at as follows:

$$m = m_0 + \beta_1 \gamma' + \beta_2 \gamma'^2 + \beta_3 \gamma'^3 \quad (3)$$

Typical curve fitting plots in the temperature regime of 40 to 80°C for a 7.5% solution are shown in Figure 5. The values of the coefficients  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  calculated by fitting the experimental data to Equation (3) for each temperature (for a concentration of 7.5%) are given in Table 3.

Similar acceptable curve fits were obtained for different concentrations and temperatures, and the corresponding coefficients were calculated as per Equation (3).

For a given concentration,  $m_0$ ,  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  are found to vary linearly with temperature (in K scale) and the linear dependences are shown in Figure 6.

**Table 2.**  $m_0$  values for the polymer samples at different dope concentrations and temperatures

Temperature °C	$m_0$ for dope concentration (Weight%)			
	3.5	5	7.5	10
40	2.401	2.397	2.388	2.368
50	2.446	2.437	2.430	2.392
60	2.503	2.480	2.473	2.430
70	2.529	2.524	2.516	2.497
80	2.596	2.585	2.559	2.531

**Table 3.** Values of  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  calculated by multiple regression curve fitting for a 7.5% solution at different temperatures

Temperature (°C)	$m_0$	$\beta_1$	$\beta_2$	$\beta_3$
40	2.388	$3.88 \times 10^{-4}$	$-6.94 \times 10^{-8}$	$5.76 \times 10^{-12}$
50	2.429	$3.82 \times 10^{-4}$	$-6.55 \times 10^{-8}$	$5.08 \times 10^{-12}$
60	2.474	$3.72 \times 10^{-4}$	$-6.07 \times 10^{-8}$	$4.43 \times 10^{-12}$
70	2.516	$3.70 \times 10^{-4}$	$-6.00 \times 10^{-8}$	$4.36 \times 10^{-12}$
80	2.559	$3.60 \times 10^{-4}$	$-5.47 \times 10^{-8}$	$3.62 \times 10^{-12}$

For a 7.5% solution, the various relationships are:

$$m_0 = [0.0043 \times T] + 1.04267 \quad (4)$$

$$\beta_1 = [-6.8 \times 10^{-7} \times T] + 6.0084 \times 10^{-4} \quad (5)$$

$$\beta_2 = [3.49 \times 10^{-10} \times T] - 1.78277 \times 10^{-7} \quad (6)$$

$$\beta_3 = [-5 \times 10^{-14} \times T] + 2.13 \times 10^{-11} \quad (7)$$

Where T is in the Kelvin scale.

Substituting Equations (4), (5), (6), and (7) in Equation (3), we get a master Equation (8) for the molecular weight index of solution viscosity ( $m$ ) in the shear rate regime of  $1 \times 10^1$  to  $5 \times 10^4 \text{ min}^{-1}$  for a concentration of 7.5%, which can be expressed as:

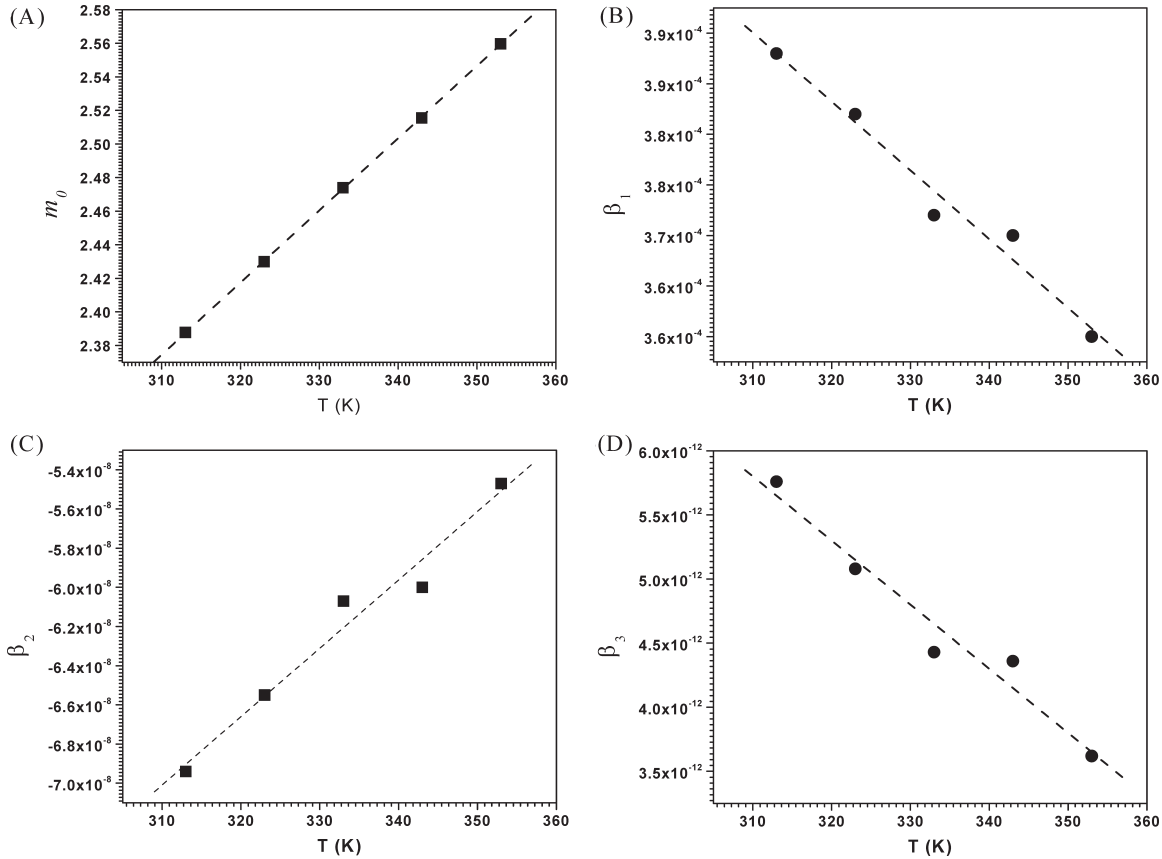
$$m = ([0.0043T] + 1.04267) + (\gamma' \{[-6.8 \times 10^{-7}T] + 6.0084 \times 10^{-4}\}) + (\gamma'^2 \{[3.49 \times 10^{-10}T] - 1.78277 \times 10^{-7}\}) + (\gamma'^3 \{[-5 \times 10^{-14}T] + 2.13 \times 10^{-11}\}) \quad (8)$$

(For  $c = 7.5\%$ ).

Equations were derived similarly for concentrations 3.5, 5 and 10%. The temperature dependency of the parameters  $m_0$ ,  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  for the various concentrations is compiled in Table 4.

Master equations (for deriving  $m$ ) could be created for each concentration by substituting the values of  $m_0$ ,  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  from Table 4 in Equation (3). Using the derived Equation (3),  $m$  could thus be predicted for any temperature and shear rate for a given concentration. Typical plots depicting the variation of  $m$  with temperature and shear rate for two concentrations, i.e., 5% and 10% are shown in Figure 7. At a given temperature and shear rate, the  $m$  values were found to decrease with an increase in concentration. For a given concentration, the  $m$  values show an increasing trend with temperature and shear rate. It can be noted that the variation of  $m$  with shear rate is more significant than its variation with temperature for a given concentration.

As explained earlier, higher molar mass solutions show greater propensity for shear thinning. A greater propensity for shear thinning results in lower  $m$  values. Using the  $m_0$ ,



**Fig. 6.** Plots for calculating the relationship of  $m_0$ ,  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  with temperature for a 7.5% solution.

$\beta_1$ ,  $\beta_2$ , and  $\beta_3$  values from Table 4, the molecular weight index of solution viscosity could be found out for any shear rate, at any given temperature for the four concentrations considered in this work.

### 3.3 Variation of Viscosity with Concentration

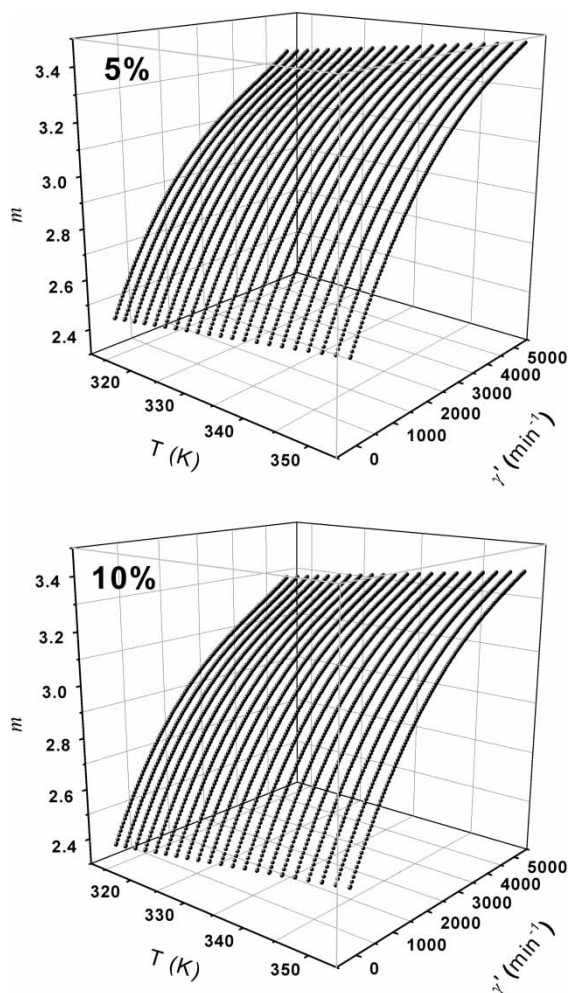
The viscosity increases monotonously with an increase in concentration of the polymer dope for various molar masses, as demonstrated in Figure 8. The  $\eta_0$  or zero shear viscosity could be graphically calculated as the  $\eta$  value extrapolated to zero shear in the  $\eta$  vs.  $\dot{\gamma}$  plot by non-linear curve

fitting. At any given shear rate, the viscosity shows an upward trend with an increase in concentration as seen in Figure 8 for a typical case.

The variation of viscosity with concentration and shear rate is typically shown in Figure 9. At lower concentrations (3.5% and 5%), the Newtonian plateaus are visible after the viscosity measurements are stabilized at relatively higher shear rates. Shear thinning was observed for higher concentrations and a similar behavior was seen in the case of other polymer solutions as well. These data show that solutions of lower concentration tend to show Newtonian behavior at high shear rates in comparison to concentrated solutions.

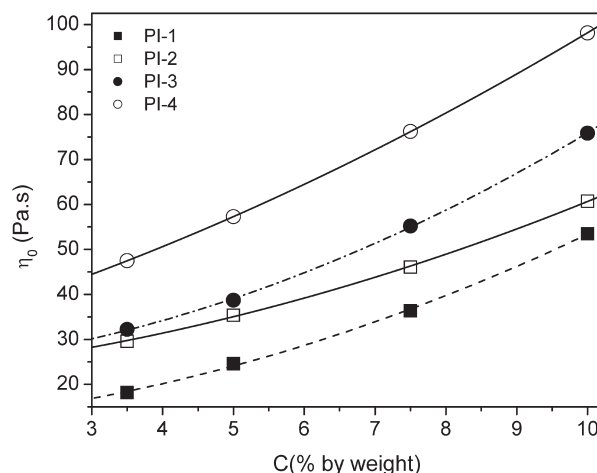
**Table 4.** Concentration and temperature dependencies of  $m_0$ ,  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$

Concentration ( $c$ )	$m_0$	$\beta_1$	$\beta_2$	$\beta_3$
3.5	$[0.0045 T] + 0.9925$	$[-6.5 \times 10^{-7} T] + 7.632 \times 10^{-4}$	$[10.15 \times 10^{-12} T] - 1.6832 \times 10^{-7}$	$[-2.8 \times 10^{-14} T] + 1.21 \times 10^{-11}$
5.0	$[0.0044 T] + 1.0198$	$[-6.73 \times 10^{-7} T] + 6.830 \times 10^{-4}$	$[7.18 \times 10^{-11} T] - 1.7334 \times 10^{-7}$	$[-4.1 \times 10^{-14} T] + 1.84 \times 10^{-11}$
7.5	$[0.0043 T] + 1.0426$	$[-6.8 \times 10^{-7} T] + 6.008 \times 10^{-4}$	$[3.49 \times 10^{-10} T] - 1.7827 \times 10^{-7}$	$[-5.0 \times 10^{-14} T] + 2.13 \times 10^{-11}$
10.0	$[0.0042 T] + 1.0534$	$[-7.3 \times 10^{-7} T] + 5.276 \times 10^{-4}$	$[1.31 \times 10^{-9} T] - 1.8321 \times 10^{-7}$	$[-6.3 \times 10^{-14} T] + 2.63 \times 10^{-11}$

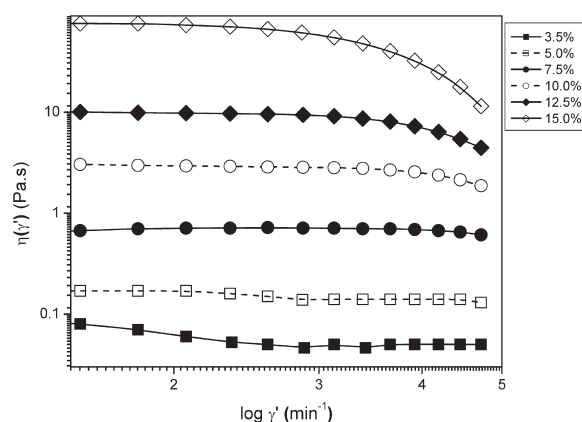


**Fig. 7.** Variation of  $m$  with temperature and shear rate for dope concentrations of 5% and 10%.

It can be found in Figure 9 that at higher shear rates, more concentrated solutions show greater shear thinning behavior. It is reported that concentrated polyacrylonitrile solutions show pseudoplastic behavior like liquid crystalline polymers (22). Moreover, the flexibility of the C-C bond of the poly(AN-co-IA) main chain is less than that of the C=O bond and C≡N bond, and it further decreases due to the strong polarity of the -C≡N. The poly(AN-co-IA) chain segments cannot be reoriented under constant shear because of the lack of rigid chain segments (22, 23). So, higher concentrations mean more entanglements, which indicate that only low shear rates are needed to orient the macromolecules. As the amount of entanglements is higher, there is not enough time for the chains to slip and disengage. With the increase of the shear rate, the number of the oriented segments also increases. So, the more concentrated dope solutions show greater tendency for shear thinning behavior. There is also a shift of the onset of shear thinning behavior to a lower shear regime as the concentration increases.



**Fig. 8.** Variation of  $\eta_0$  with a concentration at 60°C for dope solutions of different polymer samples.



**Fig. 9.** Dependency of viscosity of dope solutions of PI-2 on concentration and shear rate.

#### 4 Conclusions

The viscosity of the dope solution of the PAN copolymer showed a systematic increase with an increase in molar mass. The molecular weight index of viscosity ( $m$ ) increased with shear rate and approached the value for molten polymers. The  $m$  value increased significantly with the increase in the shear rate and marginally with a rise in temperature. A relationship was established to find the  $m$  value at any given temperature and shear rate for a given concentration. The  $m$  tends to increase significantly with shear rate and nominally with temperature. However, higher concentrations tend to decrease  $m$ . At higher concentrations and molar mass, the increased viscosity due to polymer entanglements resulted in the shifting of the shear thinning behaviour to a lower shear rate regime. The polymer solution viscosity increased significantly with concentration. The rheological behavior of poly(AN-co-IA) solutions in DMF demonstrated that the polymer concentration,

molecular weight, temperature and shear rate played a key role in determining the polymer-polymer interactions and the dope viscosities.

## 5 Acknowledgements

The permission granted by Director, VSSC to publish the paper is gratefully acknowledged.

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