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Influence of temperature on Newtonian viscosity of Nylon-12

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Summary: The intrinsic and zero shear viscosity of Nylon-12 is investigated in a mixture of carbon tetrachloride and phenol (1:1 by weight) and in metacresol at 298-348K temperature range. The variation in viscosity with temperature is explained in terms of entanglement among the polymer molecules and the thermodynamic quality of the solvents. The results so obtained are scaled using a reducing parameter proposed by Baloch. It is found that this parameter works very well over the entire range of concentration and temperature investigated, even in mixed solvents.

Introduction

Theories of the molecular weight and polymer concentration dependence in zero shear viscosity of linear polymers are based on quite different models over dilute and concentrated region (1-6). It is almost established that the zero shear viscosity is equal to 3.4 power of molecular weight of the polymers, if the molecules coil with each other. However, the problem of dependence of zero shear viscosity over concentration is more complicated, except for very dilute solutions. There are two approaches to the analysis of polymer concentration dependence of zero shear viscosity, one from dilute solution and the other polymer melt side. In dilute region, mostly Huggins equation is considered for the purpose and $\eta^{o}_{sp}/C\,[\eta]$ is given as a function of $C\,[\eta]$. Here $\eta^{o}_{sp} = (\eta^{o}-\eta_{s})/\eta_{s}$, η^{o} & η_{s} being the zero shear viscosity and viscosity of the solvent respectively. Whereas C and $[\eta]$ are the concentration and intrinsic viscosity of the polymer respectively. Though $C[\eta]$ is used as a reducing parameter in concentrated solutions but it is not as perfect (7,8). Further the existing gap between various theories for dilute and concentrated region (1,9-11) can be narrowed if the existence of the so-called semidilute concentration is recognized as proposed by de Gennes (12), whereas the coils of the polymers overlap each other while the segment density remains low and the excluded volume works between the segments. Keeping this concept of semidilute region, in view a new reducing parameter (characteristic concentration, C_{ch}) was proposed through which a reduction in viscosity data for a variety of polymer solutions over a wide range of concentration and temperature became possible. The dependence of different parameters with temperature is even more complicated. Though the dilute region is extensively studied but is less conclusive (13-18). Nylon-12 with unique industrial, mechanical applications and thermodynamical properties is very little investigated and is either the determination of molecular weight by light scattering (19-21) or developing a relationship between molecular weight and intrinsic viscosity of the polymer (22-24). This requires further examination.

Keeping these facts in view , the Newtonian viscosity of Nylon-12 in a pure and in a mixed solvent is studied, over a wide range of concentration and temperature. The results so obtained are scaled and discussed according to the model proposed by Baloch (8).

Experimental

The polymer Nylon-12 investigated is an alliphatic polyamide, kindly provided by BASF, Germany. It has molecular weight equal to 4.8×10^4 (as obtained in our laboratory). A mixture of phenol and carbon tetrachloride (1:1 by weight) and metacresol were used as solvents. These chemicals were of E. Merck, German grade.

A sufficient amount of the polymer was placed in a required amount of solvent for at least a week. After complete dissolution of the polymer, solutions at required concentration (0.002-0.09 g cm^{-3}) were prepared by dilution method.

The viscosity measurements were made at different temperatures (298.16 - 348.16± 0.01K) for all the concentrations of the polymer. The viscometers used for the purpose were Ostwarld type (only for dilute systems) and concentric cylinder Haake Rotovisco, RV-12 for the whole range of concentration. The required temperature was attained using Haake thermostat.

Results and discussion

The intrinsic viscosity of Nylon-12 in carbon tetrachloride and phenol (1:1 by weight) as solvent was determined by extrapolation method. The equation used for the purpose was:

$$\eta_{sp}/C = [\eta] + K_1 [\eta] C + ... \qquad (1)$$

Here η_{sp} ($=\eta_r - 1$), η_r and K_1 being the specific viscosity, relative

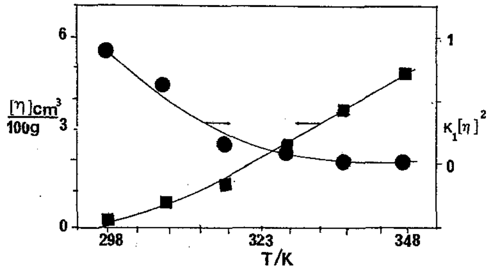

Figure 1.

Temperature dependence of (■) Intrinsic Viscosity and (●) Huggins constant of Nylon-12 in mixed solvents.

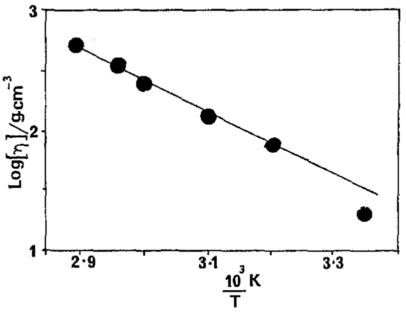

Figure 2.

Logarithm of Intrinsic Viscosity as it varies with the reciprocal of temperature.

viscosity and Huggins constant respectively. The data for specific viscosity using both types of viscometers were found to be the same, within the experimental error. The plots of η_{sp}/C versus C were linear in dilute (0.002 - 0.01 g cm^{-3}) region for every temperature. The results obtained for intrinsic viscosity are plotted against temperature in figure 1. The figure shows the intrinsic viscosity increases linearly with temperature except for the lowest one. This increase may be due to an improvement in quality of the solvent with temperature and the polymer molecules expand, resulting in an increase in intrinsic viscosity (16,18,25,28). Such trend was also observed by other investigators for different polymers (16-18,27,28). However these observations are contrary to the ones reported by us, in case of metacresol as a solvent for the same polymer (24). This shows that the solvent quality of metacresol for Nylon-12 deteriorates with temperature. The Huggins constants obtained in this case are in decreasing order with temperature (Fig.1), whereas in metacresol the other way round (24). This observation support the explanation given for variation in intrinsic viscosity with temperature. The Huggins constants measured in mixed solvents are in the range of 24-0.001. These are according to the reported values, which vary from negative to as high as 24 (15, 25, 28) for such polmer solvent systems. As the polymer associates very much at low temperature the viscosity increases sharply with the rise in concentration. However on the improvement of the solvent quality the extent of expected increase in viscosity with concentration diminishes regularly, and hence K_1 decreases.

The logarithm of the intrinsic viscosity is plotted versus 1/T in figure 2. All the data lie on the straight line except for at the lowest temperature (298.2K), which is near to T_g and hence the system does not follow the Arrhenius equation (5). Zero shear viscosity is also plotted versus 1/T for different concentrations in figure 3.It is observed that the viscosity decreases with increase in temperature for all the concentrations and give a positive slope as observed by others (17,30,31). Further, the slope increases linearly with concentration (Fig.4). This can be explained in terms of increase in entanglement with concentration and hence requires more energy to flow. This statement is also supported by the equation given by Budtov (32),which states that the activation energy decreases when the quality of the solvent or expansion coefficient increases. It further says that the activation energy also depends upon the thermodynamic properties of solvent and solute. However the plots of log η_r versus 1/T show negative slopes as observed in case of intrinsic viscosity. The diviation from lineaarity becomes pronounced at lower temperature and for higher concentration (Fig.5).The magnitude of the slopes increases with conc-

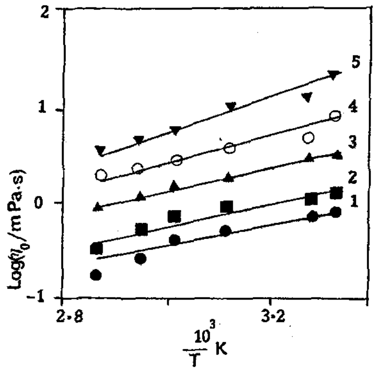

Figure 3. Zero shear viscosity of Nylon-12 in mixed solvents as a function of temperature. The polymer concentration is (1) 0.01 (2) 0.02 (3) 0.04 (4) 0.06 (5) 0.08 g cm^{-3}

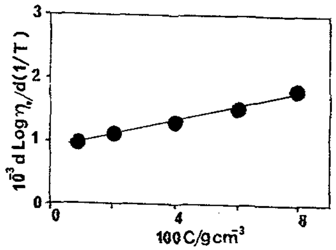

Figure 4. Slopes of logarithm of zero shear viscosity versus reciprocal of Temperature as a function of polymer concentration .

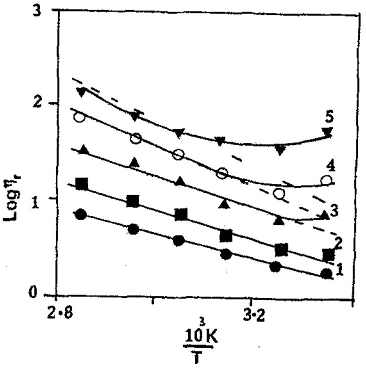

Figure 5. Relative viscosity versus temperature. The symbols and the numbers on the plots have the same meanings as in case of Fig.3. The dotted lines are the forced straight lines drawn through the data points.

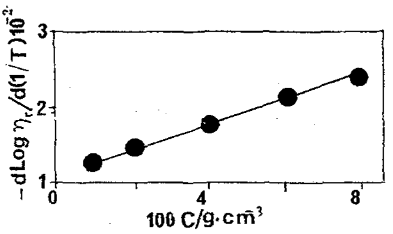

Figure 6. The slopes of log η_r versus 1/T as a function of concentration of Nylon-12 in mixed solvents.

entration as in case of zero shear viscosity. These slopes are plotted versus concentration in figure 6. The zero shear viscosity obtained in metacresol and in mixed solvents, and measured at 308.2K is plotted in figure 7. The result show that the viscosity is less in metacresol throughout the concentration range investigated as compared to the one in mixed solvents. This is what one expects, as metacresol is less viscous and is better solvent than the mixed ones (33,34).

Baloch (8) proposed a new reducing parameter called characteristic concentration (C_{ch}), which can scale the viscosity data over a wide range of concentration, molecular weight and temperature. To get C_{ch}, η_{sp}/C^2 was plotted versus concentration and the concentration corresponding to minimum value of η_{sp}/C^2 was taken as C_{ch}. The same procedure has been adopted for Nylon-12 (Fig 8). Data gives well defined minimum and hence easy to determine C_{ch}. The values of C_{ch} increase with temperature (see inset of fig.8) as observed in case of polystyrene in 1-chlorodecane (8). Using these values of C_{ch} the reduced concentration, $\tilde{C}(=C/C_{ch})$ is calculated. Log η_r is plotted versus reduced concentration, for all the temperatures (Fig.9). Though apparently these curves are not very important, as the data are only for one sample, however the initial slopes of such curves can be used for scaling the data obtained at different temperatures. Therefore the initial slopes of these curves are determined and called as shift factor, B. The shift factor is plotted versus temperature and intrinsic viscosity (Fig.10). The B factor increases with the rise in temperature with intrinsic viscosity as in case of polystyrene (8). Log η_r is plotted versus $B\tilde{C}$ in figure 11. The data show complete overlapping, except for the lowest temperature and having more than 0.06 g cm^{-3} concentration . This is due to the fact that it has less degree of coiling and hence behave as stiff chains. By means of this technique all such data collected at various polymer concentrations over a wide range of temperature can be represented by a single curve.

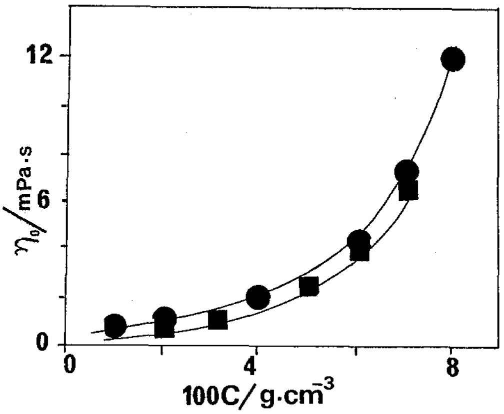

Figure 7.
Zero shear viscosity of Nylon-12 in (●) mixed solvents and in (■) metacresol as a function of concentration and measured at 308.2K.

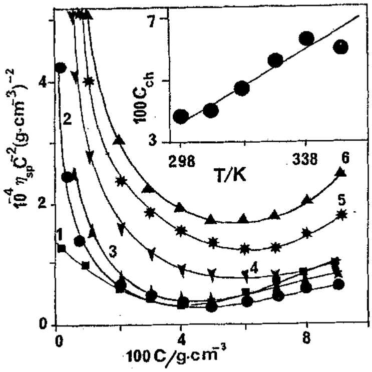

Figure 8. η_{sp}/C^2 of Nylon-12 in mixed solvents as a function of concentration and obtained at (1) 298.2 (2) 308.2 (3) 318.2 (4) 328.2 (5) 338.2 and at (6) 348.2K. The inset shows variation of characteristic concentration with temperature.

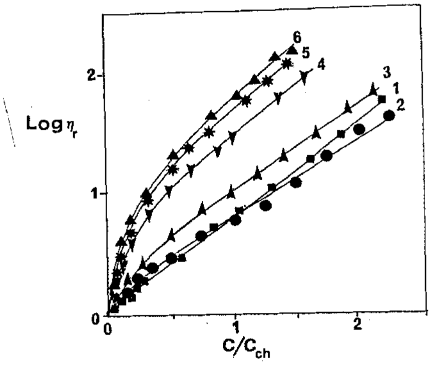

Figure 9. Relative viscosity as a function of reduced concentration $\tilde{C}(=C/C_{ch})$ as obtained at different temperatures. The numbers on the plots have the same meanings as in fig. 8.

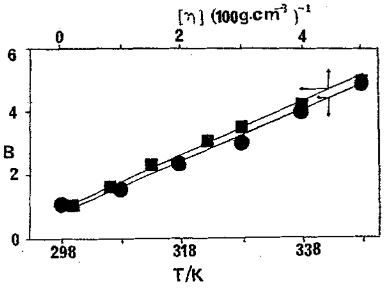

Figure 10. Variation in the initial slopes, B of the curves, shown in Fig.9 as a function of (●) temperature and (■) intrinsic viscosity.

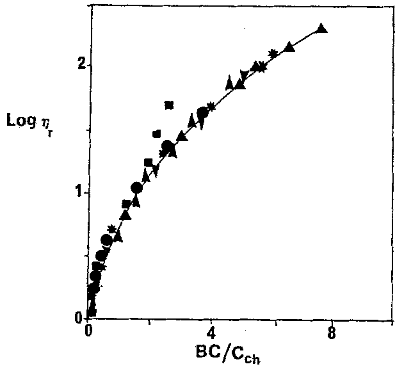

Figure 11. Relative viscosity Nylon-12 in mixed solvents as a function of $B\tilde{C}$ as obtained at different temperatures. The symbols have the same meanings as in Fig.8.

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