

Effects of dissolution temperature on the rheological properties of polyvinyl alcohol solutions in dimethyl sulfoxide

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(Received February 20, 2008; final revision received April 24, 2008)

Abstract

The rheological properties of polar solutions are very sensitive to preparative methods as well as measuring conditions. The effects of dissolution temperature on the rheological properties of the solutions of polyvinyl alcohol (PVA) in dimethyl sulfoxide were investigated over the range of dissolution temperatures 70-130 °C. Viscosity was increased as dissolution temperature was increased. PVA solutions prepared at 120 and 130°C showed Bingham behavior, which became less noticeable with decreasing dissolution temperature. The modified Cole-Cole plot of the solutions gave slope less than 2, suggesting the solutions were a heterogeneous system irrespective of optical transparency. Further, the slope was decreased with increasing dissolution temperature, indicating that the solid character got more prominent as dissolution temperature was increased. However, the relaxation time of the solutions was little dependent on dissolution temperature.

Keywords : PVA solution, rheology, dissolution temperature, relaxation time

1. Introduction

The physicochemical properties of polymers are dependent on the type of physical bonds across the polymer chains as well as the type of chemical bonds along the polymer chains. In the case of polymers with strong polar intermolecular interactions such as cellulose and polyvinyl alcohol (PVA), the molecular aggregation has a significant effect on the physical properties, which is greatly affected by conformation of polymer molecules (Masuda, 1991). PVA is a zig-zag chain polymer, in which hydroxyl groups produce hydrogen bonds, which are primarily dependent on the content of syndiotactic diad (S-content) (Kim *et al.*, 2000; Lyoo *et al.*, 1998). Recently, very unusual rheological responses were reported for the solutions of PVA with S-content higher than 58% in dimethyl sulfoxide (DMSO) (Choi *et al.* 2001; Lyoo *et al.*, 2001) More recently, we reported that PVA with S-content 52% also exhibited very unusual rheological behavior, a double sol-gel phase transition with shear rate (Lee *et al.*, 2004).

In the case of athermal polymer solution systems, the dissolution temperature has little effect on the rheological properties of the systems. However, the dissolution temperature surely affects the rheological properties of the solution when a polar polymer is dissolved in a polar solvent. This is because the resultant conformation of polymer molecules in the solution would be dependent on the chain

mobility during dissolution. In these thermal polymer solution systems, the chain mobility is increased with increasing temperature owing to reduced physical interactions as well as increased thermal energy. Consequently, the dissolution temperature would have a significant effect on the rheological responses of polar polymer solutions in polar solvents. However, there has been little study on this point in spite of practical importance. We systematically traced the effect of dissolution temperature on the rheological properties of the solutions of polar PVA in polar DMSO.

2. Experimental

Aldrich PVA resins were used; degree of saponification 99%+, weight average molecular weight (M_w) from 124,000 to 186,000, and the S-content 52% (determined by 300-MHz ^1H NMR, Varian Gemini). EP grade DMSO (Aldrich Chemical Co. Inc.) was used without further purification. To keep the thermal and shear histories constant during dissolution, all the solutions were prepared in the same procedure; PVA was dissolved in DMSO at desired temperature (70-130°C) with stirring for 5 hours to produce optically transparent solutions. Rheological measurement was also carried out in the same procedure by Advanced Rheometric Expansion System (ARES, Rheometric scientific. Co.) at 30°C; the PVA solution was loaded between parallel plates whose diameter and gap were 50 and 1 mm, respectively, then fully relaxed for 20 minutes prior to measurement.

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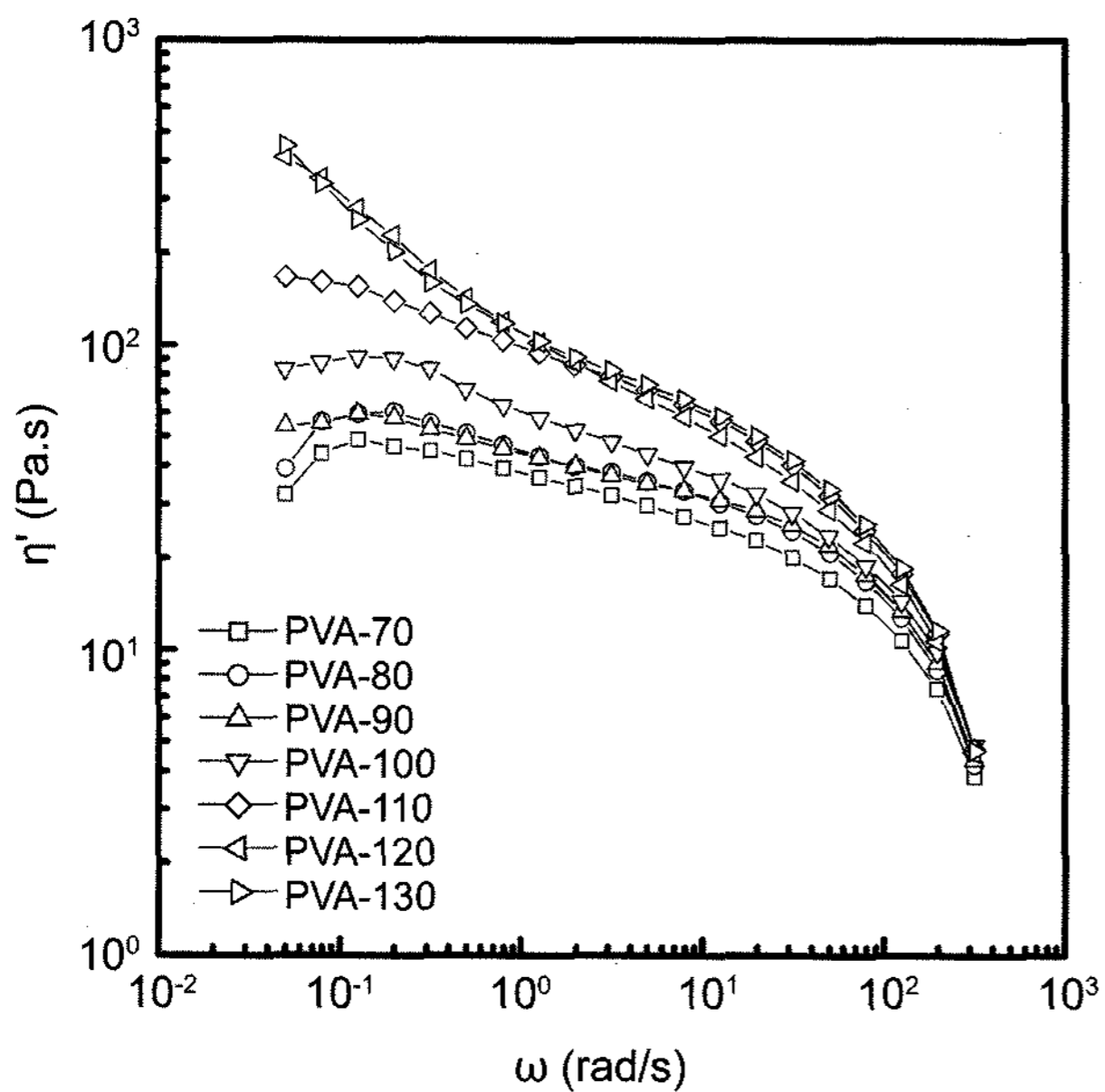


Fig. 1. Dynamic viscosity curve of PVA solutions in DMSO at 30°C.

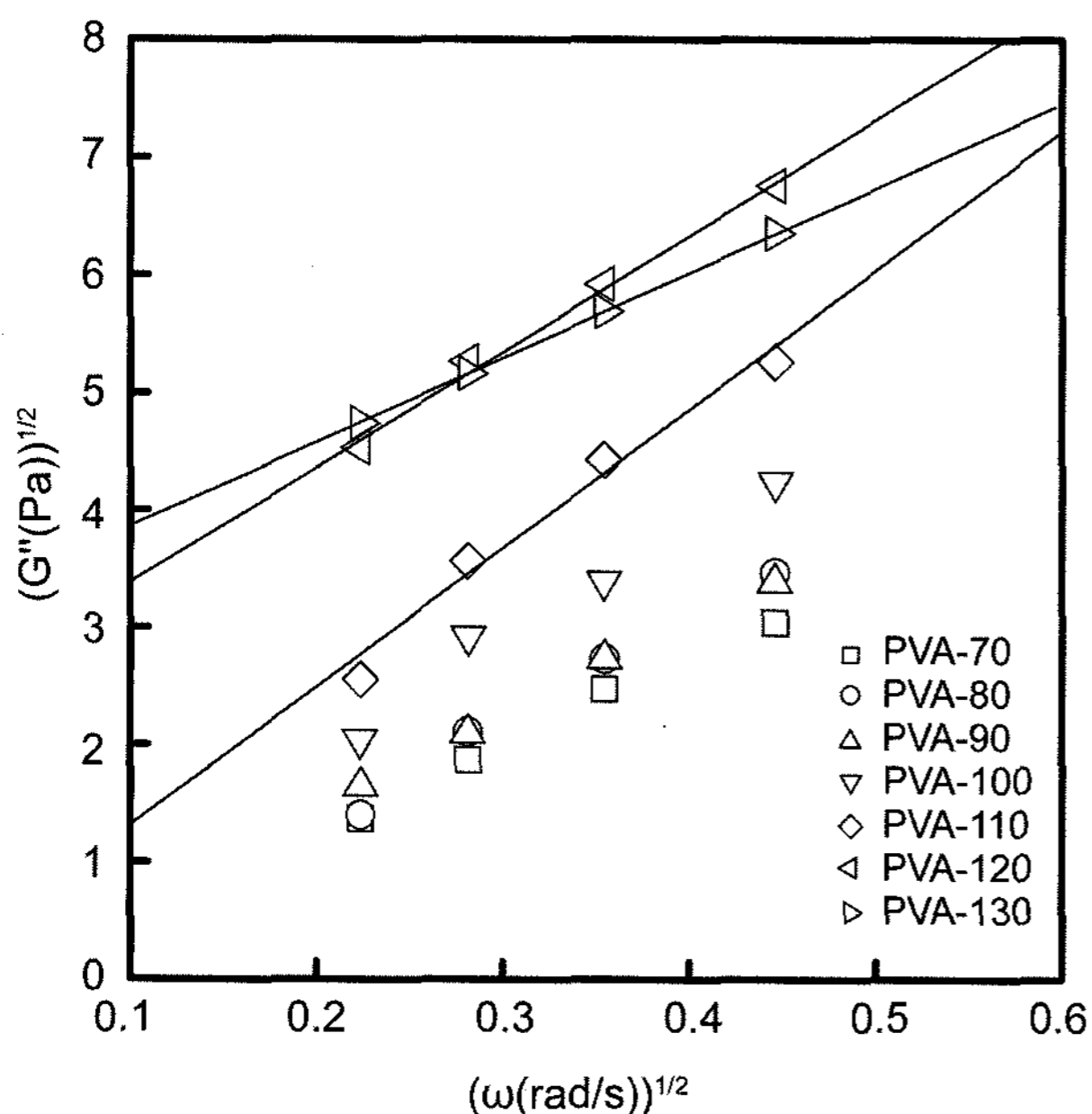


Fig. 2. Plot of square root of loss modulus vs. square root of frequency for PVA solutions in DMSO at 30°C.

3. Results and Discussion

Fig. 1 shows the dynamic viscosity curve of PVA solutions in DMSO at 30°C. PVA solutions show non-Newtonian flow behavior. It is worth mentioning that dissolution temperature of PVA has a notable effect on the viscosity of the solutions. With increasing dissolution temperature, dynamic viscosity is increased and the onset shear rate to bring about shear thinning is lowered and the extent of shear thinning is decreased. This is ascribable to

Table 1. Yield stress of PVA solutions in DMSO prepared at different temperatures

Dissolution temperatures (°C)	110	120	130
Yield stress (Pa ^{1/2})	0.04	2.41	3.15

the dissolution temperature-dependent dissolution mechanism of PVA in DMSO. At higher dissolution temperature (120 and 130°C) the diffusivity of PVA molecules gets enhanced due to the reduced intermolecular interactions and increased chain mobility by stirring. So higher dissolution temperature would produce polymer solutions in which polymer molecules are more homogeneously distributed. This in turn makes the hydrogen bonding more efficient during cooling without stirring. As a consequence, the resultant solutions would contain some physical networks at room temperature and give rise to Bingham body-like flow behavior during rheological measurement at 30°C.

Disappearance of lower Newtonian flow region is indicative of the existence of positive yield stress. The yield stress of heterogeneous polymer systems can be determined by Eq. (1) for the modified Cason plot in dynamic shear measurement (Mill, 1959; Hong *et al.*, 1993):

$$G''^{1/2} = G_0''^{1/2} + K' \omega^{1/2} \quad (1)$$

in which, G'' is loss modulus, G_0'' is yield stress, K' is constant, and ω is frequency. Plot for the PVA solutions are shown in Fig. 2. The yield stress is determined from the intercept of G'' -axis at $\omega=0$. The result is given in Table 1. Yield stress measured at very low shear rates is increased with increasing dissolution temperature. This coincides with viscosity result. However, these physical networks are too weak to be retained under high shear. So viscosity is decreased drastically with increasing shear rate due to the breakdown of the physical structures. Further the oriented PVA molecules would be readily stabilized by effective intermolecular interactions by polar hydroxyl groups, suppressing relaxation of the molecules. In consequence, the increase of viscosity by increasing the dissolution temperature is most prominent in the range of low shear rates (<0.1 rad/s) but viscosities of the solutions converge at high shear rates. Thus it may be said that unusually high viscosity at low shear rates comes from the three-dimensional physical networks formed by hydrogen bonding.

On the other hand, the PVA solutions prepared at low temperature (70 and 80°C) exhibit very unique viscosity behavior; shear-thickening below a critical shear rate 0.1 rad/s followed by shear-thinning above the critical shear rate. Shear-thickening below the critical shear rate is accounted for as follows. The extraordinary low viscosity of the solutions below 0.1 rad/s results from reduced coil dimension. At low dissolution temperature the solvating power of DMSO to PVA is not so good as at high dissolution temperature. So, coil dimension would be smaller,

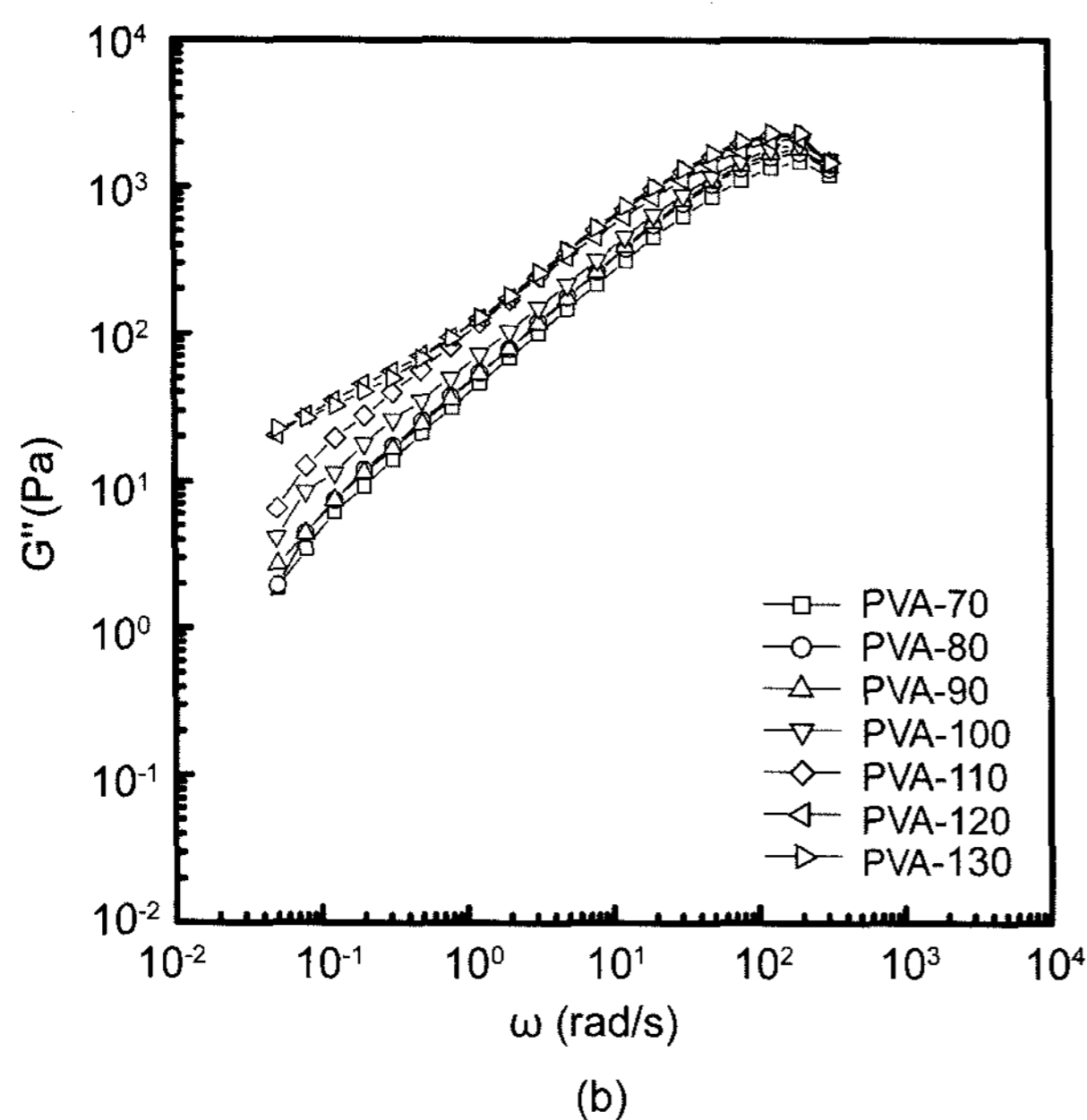
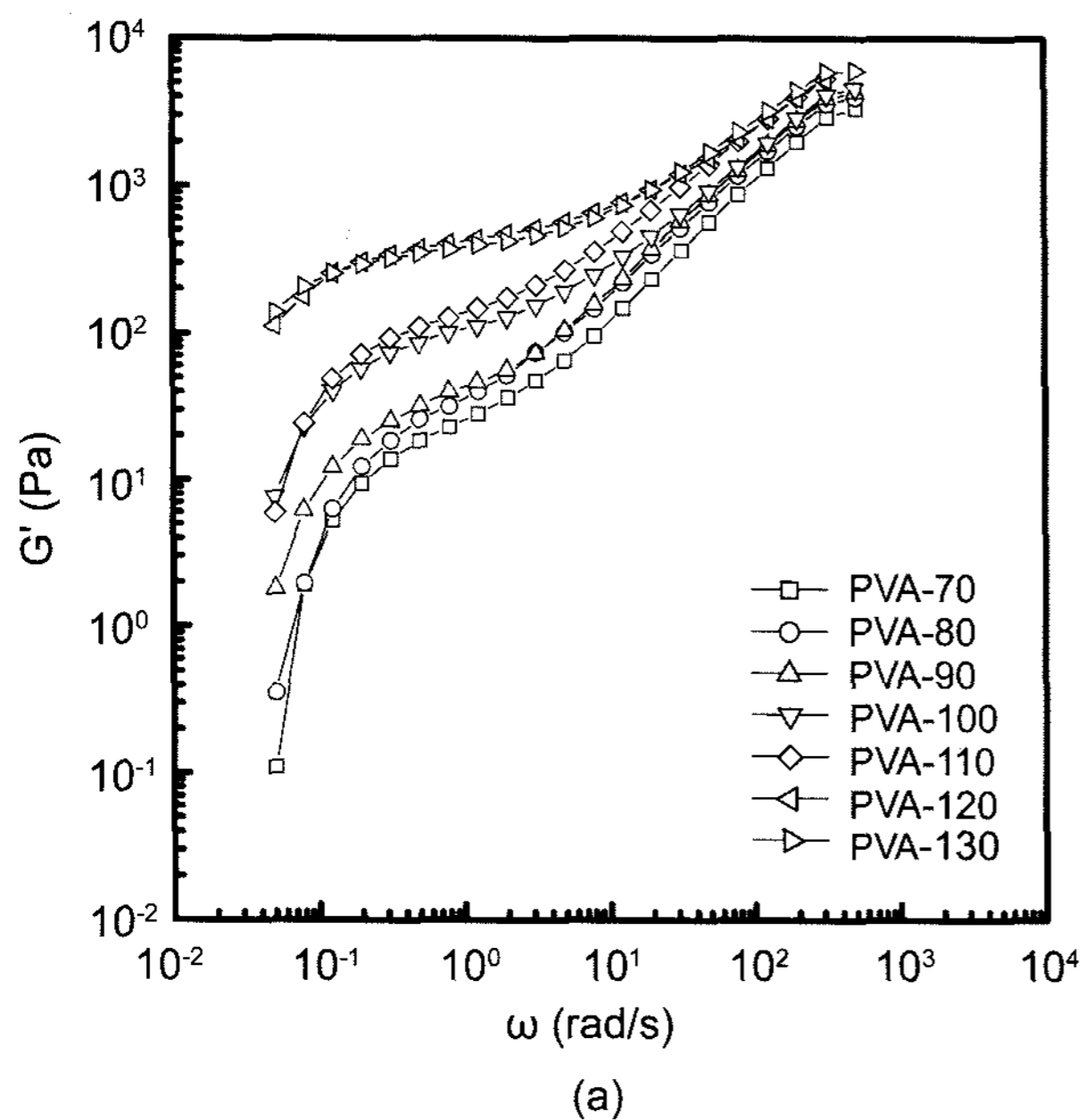


Fig. 3. Plot of (a) storage moduli (G') and (b) loss (G'') moduli against frequency (ω) for PVA solutions in DMSO at 30°C.

leading to lower viscosity. Further, not all of the physical bonds may be fully decoupled during dissolution. The pre-existing physical associates would be broken down and homogenized during rheological measurement by applied shear. Consequently, viscosity is increased over the very low frequency range. The solutions prepared at 90, 100, and 110°C show viscosity behavior intermediate of the two cases. Song and Kim (2004) observed similar phenomenon for PVA/DMSO/water ternary systems.

Fig. 3 shows the storage modulus (G') and loss modulus (G'') curves of PVA solution in DMSO measured at 30°C.

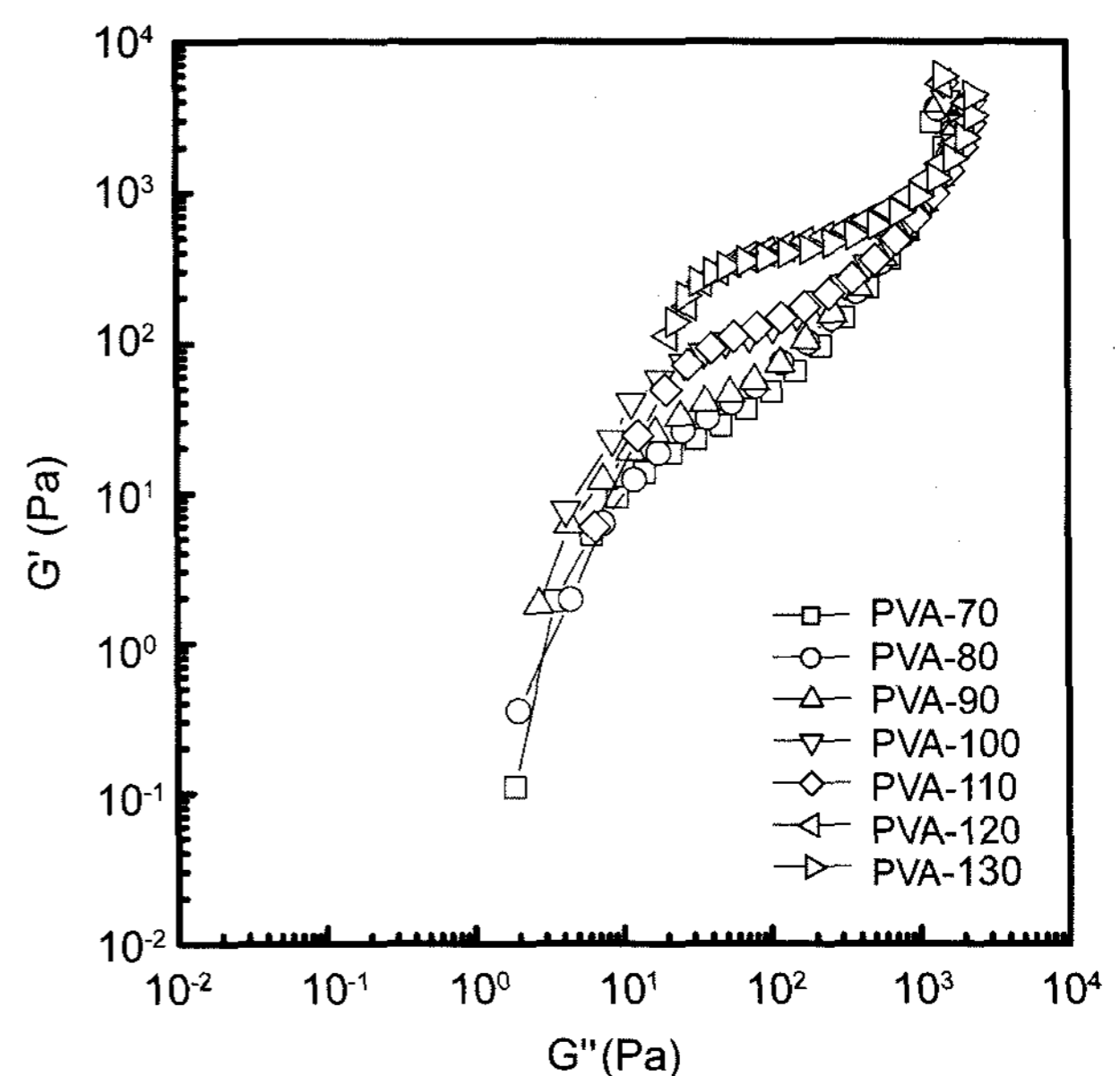


Fig. 4. Cole-Cole plot of PVA solutions in DMSO at 30°C.

According to the molecular theories, the perfectly homogeneous and isotropic melt and solution of a polymer give curves whose slope is 2 and 1 in the terminal zone on the logarithmic plot of G' and G'' against frequency, respectively (Ottenbrite *et al.*, 1987). However, the PVA solutions do not give the predicted slopes but dissolution temperature dependent slopes at the given measured temperature. Further, these curves are classified to three groups according to dissolution temperature. On the whole, the G' is increased but the slope is decreased as dissolution temperature is increased. This means that the stronger intermolecular interactions are present in the solution, which indicates that the solution gets more heterogeneous when the polymer is dissolved at higher temperature. Replotting G' against G'' is shown in Fig. 4. The so-called modified Cole-Cole plot also gives a master curve whose slope is 2 for homogeneous polymer melts and solutions (Ottenbrite *et al.*, 1987; Aoki *et al.*, 1979). All the PVA solutions give slopes less than 2, indicating that these solutions are rheologically heterogeneous in spite of optical transparency. Further, the slope is decreased with increasing dissolution temperature. The slope goes down to as low as 0.2 at 120 and 130°C. This also reflects that the chain conformation is changing with dissolution temperature.

The value of loss tangent ($\tan\delta$) is a quantitative measure of solid-like elastic body or liquid-like viscous fluid of a system. In principle, fluid character is dominant when G'' is greater than G' and solid character is dominant when G' is greater than G'' . At the balance point of G' and G'' is defined as the gel point (Winter and Chambon, 1986). Fig. 5 presents plot of $\tan\delta$ of PVA solutions in DMSO against frequency at 30°C (Hyun *et al.*, 2001). The $\tan\delta$ changes with dissolution temperature as well as shear rate. It is

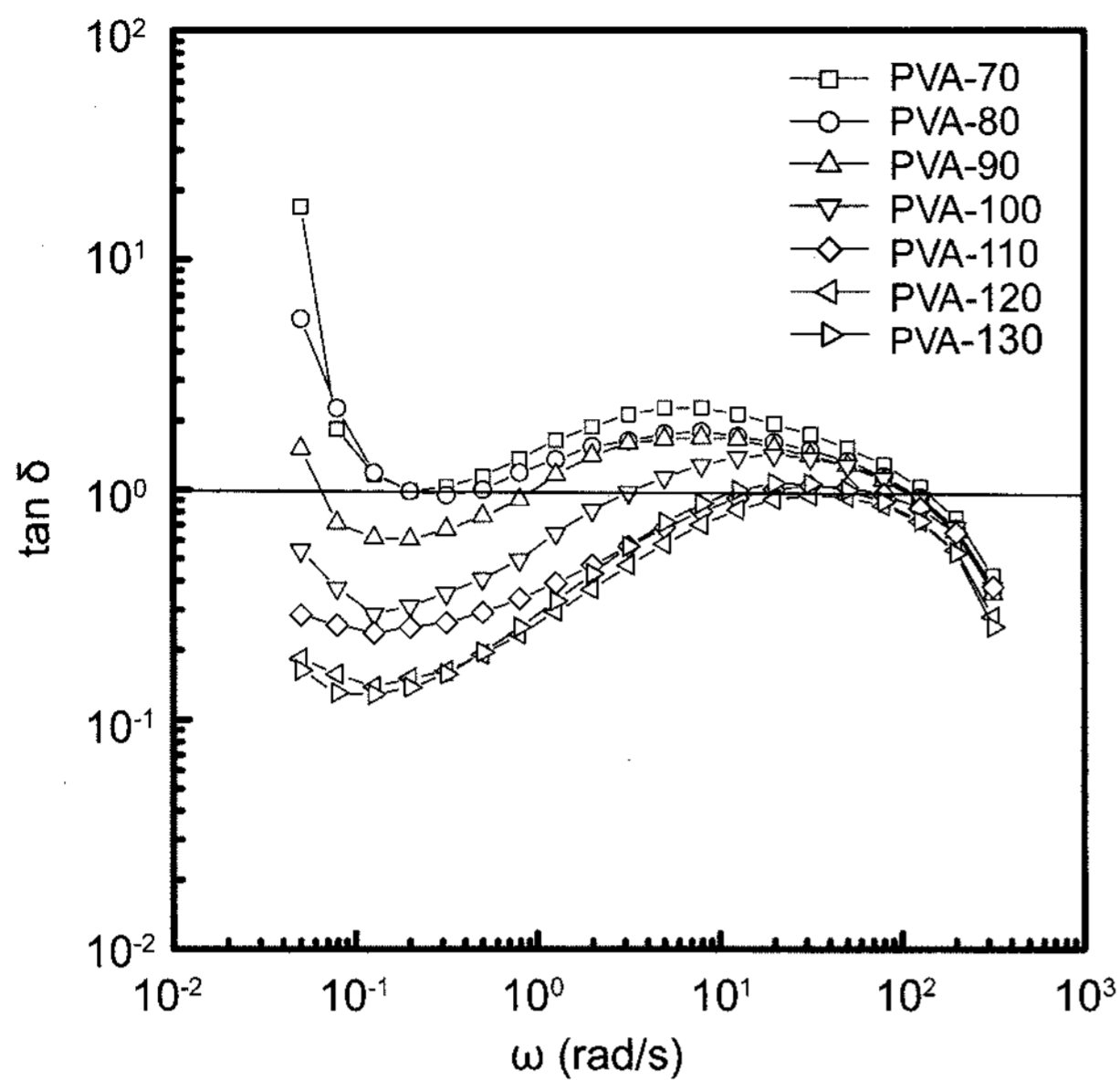


Fig. 5. Variation of loss tangent with frequency for PVA solutions in DMSO at 30°C.

worth mentioning that the PVA solutions dissolved at 70, 80, and 90°C exhibit a double sol-gel phase transition with shear rate. The $\tan\delta$ is first decreased up to 0.2 rad/s, then increased up to 4 rad/s. Among them the phenomenon is most noticeable with the solution prepared at 90°C. The PVA solution prepared at 100°C exhibit a gel-sol-gel transition. On the other hand, the PVA solutions prepared at 110, 120, and 130°C remain gels over the entire frequency range observed. However, the elastic solid character is diminished with increasing shear rate up to 10 rad/s due to break down of hydrogen bonds by shearing action. However, $\tan\delta$ goes down above 70 rad/s due to formation of strong shear-induced oriented gels.

The presence of pseudo-structure by physical aggregation affects the relaxation behavior. For the polymeric systems in which some pseudo-structures are involved, relaxation time (λ) under dynamic shear can be calculated by Eq. (2) (Wissbrun and Griffin, 1982):

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

in which, J' and η^* are compliance and complex viscosity, respectively. If there are notable interactions between polymer molecules, much longer relaxation time is expected (Wissbrun and Griffin, 1982). The longer λ of the PVA solutions at low frequency in Fig. 6 further ascertains the presence of some physical structure. In addition, the $\dot{\epsilon}$ is decreased as the shear rate is increased but not so notably dependent on dissolution temperature. As mentioned the heterogeneity of PVA solutions comes from physical interactions between polymer molecules including hydrogen bonding, whose strength would not notably change with the conformation of polymer molecules. Consequently, the dissolution temperature does not have a significant influ-

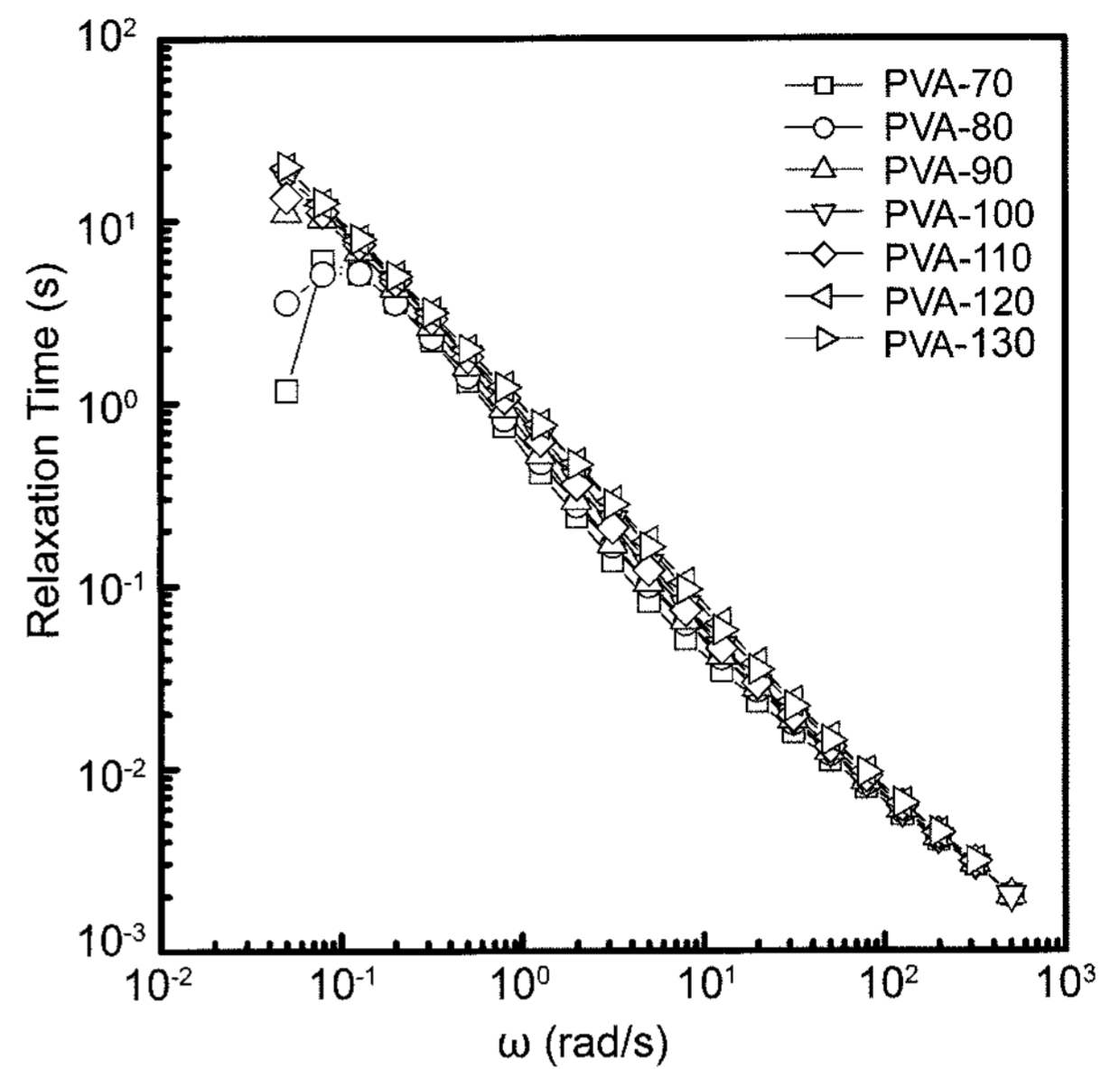


Fig. 6. Variation of loss tangent with frequency for PVA solutions in DMSO at 30°C.

ence on λ .

4. Conclusion

Thermodynamics suggests that a homogeneous solution is produced if polymer-solvent interactions prevail over polymer-polymer interactions. In the presence of strong interactions between polymer molecules, however, the dissolved polymer molecules under shear may be associated at rest in long term even in the exothermic systems. In the case of PVA solutions in DMSO hydrogen bonding is significantly affected by spatial arrangement of PVA molecules. With increasing temperature the enhanced chain mobility and diffusivity of PVA molecules led to more uniform distribution of molecules and more effective intermolecular hydrogen bonding, causing faster gelation on cooling. Thus, dissolution temperature had a significant influence on the physical properties of the solutions. Since rheological properties are the very fundamentals for spinning and film casting this result may be of help to the process design of PVA fabrication.

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