ELSEVIER

Polymer 41 (2000) 5847–5854

polymer

Light scattering studies on aggregation behavior of polyvinyl chloride/dioxane solutions

Po-Da Hong*, Che-Min Chou, Jean-Hong Chen

Department of Textile and Polymer Engineering, National Taiwan University of Science and Technology, Taipei, 10607, Taiwan, ROC

Received 7 September 1999; received in revised form 13 October 1999; accepted 19 October 1999

Abstract

In this work, the aggregation behavior of polyvinyl chloride/dioxane (PVC/DOA) solution was discussed through light scattering and viscometric measurements. From the static light scattering results, PVC/DOA solution has a negative value of the second virial coefficient, A_2 value (ca. -3.65×10^{-4} cm^3 mol g^{-2}) at 30°C, implying that a repulsive force appeared between PVC chains and DOA. The dynamic light scattering results indicate that the dynamic behavior of PVC solution could be classified into three regions by increasing the concentration of PVC. In the infinite dilution region, $[\eta]C < 1$, the single relaxation mode is considered related to the translational diffusion of the individual PVC coil. In the hydrodynamic screen region, $1 < [\eta]C < 4$, the relaxation time distribution was divided into two major relaxation modes; i.e. the fast mode resembled that of the individual PVC coil in the dilute solution, and the slow mode is considered related to the cluster formed from the aggregation of several individual coils. At higher concentrations, $[\eta]C > 4$, the polymer coils start to overlap and entangle further, then the third relaxation mode due to the transient gel network originated from the aggregation of the clusters in the concentrated solution was observed. On the other hand, the relative amplitudes of middle and slow modes for semi-dilute solutions decrease with increasing temperature. At a temperature of about 50°C, only a broad relaxation mode was observed indicating that intermolecular aggregation is disintegrated with increasing temperature, but the intramolecular aggregation of an isolated chain still exists due to the poor affinity of DOA to PVC chains in this temperature region. The poor solubility of the solvent used should be more favorable to the intramolecular aggregation of PVC chains, resulting in comparatively complex dynamic behaviors in semi-dilute solutions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Light scattering; Aggregation behavior; Relaxation mode

1. Introduction

It is well known that many factors affect the dynamic behavior of polymer solutions, including temperature, molecular weight and concentration of the polymer, and the types of the solvent used. Recently, our previous works [1–3] reported that the physical properties of PVC gels were as functions of the molecular volume of the solvent and the degree of the polymer–solvent interaction. Regarding the results in the gelation behavior of PVA/DOA solutions, the intramolecular association of PVC chains may occur first because of the poor affinity of DOA to PVC. Then the gelation induced by connecting these aggregates must form a heterogeneous gel. However, we have no other direct evidence to confirm this mechanism of the aggregation behavior in PVC/DOA solutions.

In contrast to many techniques applicable to the characterization of the dynamic behavior of polymer solutions, the dynamic light scattering (DLS) measurement is well known as an efficient tool to aptly describe the aggregation behavior of polymer solutions with a wide range of polymer concentrations [4–16]. Candau et al. [17] reported on the gelation mechanism of PVC in diethyl malonate solutions. According to their results, the dynamic structure factor obtained from the autocorrelation function exhibits an anomalous scattering vector dependence owing to the intramolecular effects. Mutin et al. [18,19] also reported that PVC chain aggregation with two types of physical links are formed in PVC dilute solutions. On the other hand, Brochard and de Gennes [20,21] developed a scaling theory for the θ-condition of a semi-dilute solution. They proposed two limiting regimes: at a small scattering vector, q, the restoring force for the concentration fluctuations, leading to a cooperative diffusion coefficient is linearly proportional to the polymer concentration. Meanwhile, at a large q, they predicted that the correlation function becomes a bimode. The fast mode characterizes the cooperative diffusion and

---

* Corresponding author. Tel.: +866-2-27376539; fax: +886-2-27376544.
E-mail address: phong@hp730.tx.ntust.edu.tw (P.-D. Hong).

PII: S0032-3861(99)00805-8

the other mode, which denotes the independence of the scattering vector, characterizes the structural relaxation of the transient gel network. Chu and Nose [22–24] also discussed the dynamic behavior in polystyrene/*trans*-decalin θ-solutions using DLS. In their investigation, they employed a histogram method and a bimodal function to distinguish the fast and the slow relaxation modes. These assignations were made from the nature of the concentration dependencies of the separated relaxation rates. In a related work, Nicolai and Brown [25] reported on DLS experiments in a θ-solution of polystyrene over a broad range of polymer concentrations from the very dilute to semi-dilute region. In the dilute solutions, the relaxation rate was due to the diffusion of individual chains. Meanwhile, in the semi-dilute solutions, the fast mode was due to the cooperative diffusion of polymer chains between the junction points in the transient gel network and the slow mode corresponded to the self-diffusion of the aggregation coils. Their results also demonstrated that the relaxation time distributions were a function of solvent quality. The relative amplitudes of the slow modes decreased with an increasing solvent quality, thereby increasing the interaction between polymer and solvent.

According to above developments, this study investigates the concentration and temperature dependencies on the dynamic behavior of PVC chains in the solution state. The characteristics of the different relaxation modes as well their dependence on the relative amplitudes of modes with temperature are discussed in this work.

2. Experimental

2.1. Sample preparation

The PVC used in this work was a laboratory grade powder with a weight-average molecular weight of $M_w = 50.0 \times 10^4$ g mol^{-1} (Aldrich Chemical Co. Ltd, USA). The solvent, dioxane (DOA) was of analytical grade and purified by distillation and filtered by using a 0.02 μm Teflon filter for removing dust before use. The PVC solutions were prepared in a pre-cleaned wide mouth bottle with stirring at 95°C for 2 h until it dissolved into a homogeneous solution. Then, the solutions with various polymer concentrations were filtered by using 1.0 μm Millipore filters directly into both a light scattering cell and sealed test tubes, respectively. Subsequently, the samples were kept in a thermostat oven at a constant temperature for one day to stabilize the solutions before DLS measurements.

2.2. Measurements

The light scattering measurements were taken using a Malvern series 4700 apparatus. The light source was a 2 W argon ion laser operating at a power of 100 mW and a wavelength of 514.5 nm, which was focused on the sample cell through a temperature-controlled chamber (the temperature controlled within ±0.1°C) filled with distilled water. The values of the second virial coefficient, A_2 value could be directly obtained from the Zimm plot through the following equation [26]:

$$\frac{KC}{R_\theta} = \frac{1}{\bar{M}_W}\left[1 + \frac{16}{3}\pi^2 \frac{(Rg^2)}{\lambda_0^2}\sin^2\theta/2 + \cdots\right] + 2A_2C + \cdots \qquad (1)$$

The optical constant for vertically polarized light is $K = 4\pi^2 n_0^2(\mathrm{d}n/\mathrm{d}c)^2/N_A\lambda^4$, where n_0 is the solvent refractive index, dn/dc the measured refractive index increment for PVC/DOA solutions, λ_0 the wavelength of light in vacuum, N_A the Avogadro's number, R_θ the Rayleigh ratio for the solution, θ denotes the scattering angle and C the polymer concentration. An Optilab DSP interferometic refractometer was operated under the same conditions of light scattering measurements for obtaining the refractive index increment values, dn/dc of PVC solutions. The reduced scattering intensity, KC/R_θ, was derived, where R_θ is the Rayleigh ratio obtained through calibration using toluene, $R_{90} = 18 \times 10^{-6}$ cm^{-1}. This value was used to calculate the Rayleigh ratio of PVC solutions.

The dynamic light scattering measurement was carried out with the 7032 multiple-τ autocorrelator recording on 128-channels. All data, as obtained in the intensity autocorrelation function, were measured at the scattering angle, θ, in the range from 30 to 120°. DLS is a highly effective tool for probing the dynamic behavior of polymer chains, on different length and time scales, in solution states. When the polymer chain obeys Gaussian statistics, the measured normalized intensity correlation function $g^{(2)}(t)$ is related to the normalized electric correlation function $g^{(1)}(t)$ through the Siegert relation [27]:

$$g^{(2)}(t) = 1 + \beta|g^{(1)}(t)^2| \qquad (2)$$

where β takes into account deviations from ideal correlation. Consider a system exhibiting a distribution of collective motions, which can be represented by a superposition of exponential decays, and allowing the monitoring of very widely spaced decays in the same investigation. Laplace inversion routine of the correlation curves $g^{(1)}(t)$ was performed using a CONTIN [28] to obtain the distribution $A(\tau)$ of relaxation times. The Laplace inversion routine was as follows:

$$g^{(1)}(t) = \int_0^\infty A(\tau)\exp(-t/\tau)\,\mathrm{d}\tau \qquad (3)$$

The intrinsic viscosity measurements were made on dilute PVC solutions at 30 ± 0.1°C using an Ubbelohde capillary viscometer. The intrinsic viscosity, $[\eta]$ was obtained using Huggins equation [29]:

$$[(t - t_0)/t_0]/C = \eta_{\mathrm{sp}} = [\eta] + k'[\eta]^2C \qquad (4)$$

where t is the time of flow of the dilute solution, t_0 the time

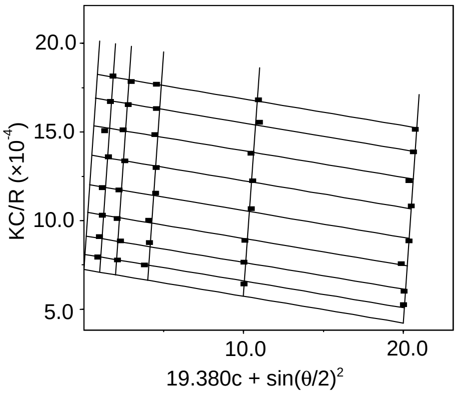

Fig. 1. Zimm plot of PVC/DOA solution at 30°C.

of flow of the pure solvent, C the concentration of polymer, η_{sp} the specific viscosity and k' the Huggins constant.

The viscosity of PVC semi-dilute solution was measured using a CJV1000 vibroviscometer [30] (Tohoku Densi Co. Ltd, Japan). PVC solutions were heated at 95°C until they dissolved into a homogeneous solution, then the solutions were quickly cooled to 30°C.

3. Results and discussion

The second virial coefficient, A_2, which is obtained from the SLS measurement, denotes the degree of the polymer–solvent interaction in the dilute solution. Fig. 1 shows the Zimm plot of PVC/DOA dilute solution at 30°C. The A_2 is about -3.65×10^{-4} cm^3 mol g^{-2} at 30°C. The negative A_2 values are still found at the whole range of the measuring temperature in this work. As concluded in our previous work [3], the PVC/DOA solution exhibited a larger degree of the liquid–liquid phase separation or the spinodal decomposition than that of the PVC solution from a good solvent (bromobenzene). This result might be considered owing to fact that the poor affinity of the solvent used might be more favorable to the intramolecular aggregation of PVC chains, resulting in a comparatively heterogeneous solution. Generally, the chain aggregation in polymer solutions should take place above the chain overlapping concentration (C^*). The intrinsic viscosity, $[\eta]$, is a characteristic function for the single polymer chain in solution, depending much on the molar mass, the structure and conformation of the polymer, the polymer–solvent interaction and the temperature. Furthermore, the dimension of $[\eta]$ is volume per unit mass so that the intrinsic viscosity has been aptly reflected by the effective hydrodynamic volume of the polymer chain in solution [31]. Then the overlapping concentration is generally defined by the reciprocal of the intrinsic viscosity, $C^* = 1[\eta]$. Fig. 2 shows the η_{sp}/C versus C for the PVC/DOA solution at 30°C. From the linear relationship in Fig. 2, the intrinsic viscosity could be obtained from the intercept of η_{sp}/C at $C = 0$. The C^* value is about 12.4 g l^{-1} for the PVC/DOA solution at 30°C in this work.

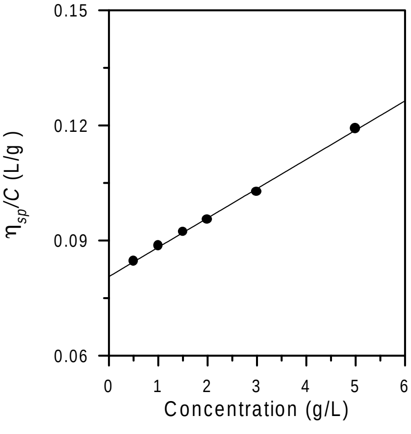

Fig. 2. Plot of the η_{sp}/C versus C for PVC/DOA dilute solutions at 30°C.

The concentration dependence on the dynamic behavior of polymer solutions has been extensively studied through DLS measurements. Owing to the various mechanisms of chain aggregation in polymer solutions, the origins of the relaxation modes in DLS results become very complex [32–39]. Herein, we also try to investigate the aggregation behavior of PVC/DOA solutions from the dilute ($C < C^*$) to the semi-dilute ($C > C^*$) solution regions through DLS analyses. Fig. 3(a) and (b) shows the intensity time correlation functions, $g^{(2)}(t) - 1$, as functions of C and q for PVC/DOA solutions at 30°C, respectively. According to these results, the decaying of the correlation function shifts to a longer time along the relaxation time axis with increasing C; meanwhile, it shifts to the shorter time region with increasing q. The inversion Laplace transformation method was applied to obtain a distribution of the relaxation time, $\tau A(\tau)$ from the autocorrelation function. Fig. 4(a)–(d) shows the distribution of the $\tau A(\tau)$ as a function of q for various concentrations of PVC/DOA solutions at 30°C, respectively. The distribution of the $\tau A(\tau)$ was obtained using a parallel program that had been permitted to analyze the autocorrelation function with very wide time distribution. The $\tau A(\tau)$ results indicate that the PVC/DOA dilute solutions, in which the concentration is below the C^*, only exhibit a single relaxation mode related to the translational diffusion of individual PVC coil. At the region above the C^*, two or three relaxation modes denoted as the fast, middle and slow modes from the $\tau A(\tau)$ distribution at the short τ to the long τ in order were observed. This result indicates that the chain aggregation behavior is much dependent on the polymer concentration for PVC/DOA semi-dilute solutions. Fig. 5(a) and (b) shows the plots of the relaxation rate, $\Gamma(\Gamma = 1/\tau)$, versus the square of the scattering vector, q^2. The Γ value is obtained from the τ value at the maximum in the $\tau A(\tau)$ distribution. According to these, Γ value increases linearly with q^2, indicating that the PVC chains are formally diffusive in the PVC/DOA solutions since $\Gamma = Dq^2$.

Frisch and Simha [40] reported that the dynamic behavior of polymer solution can be classified into several regions

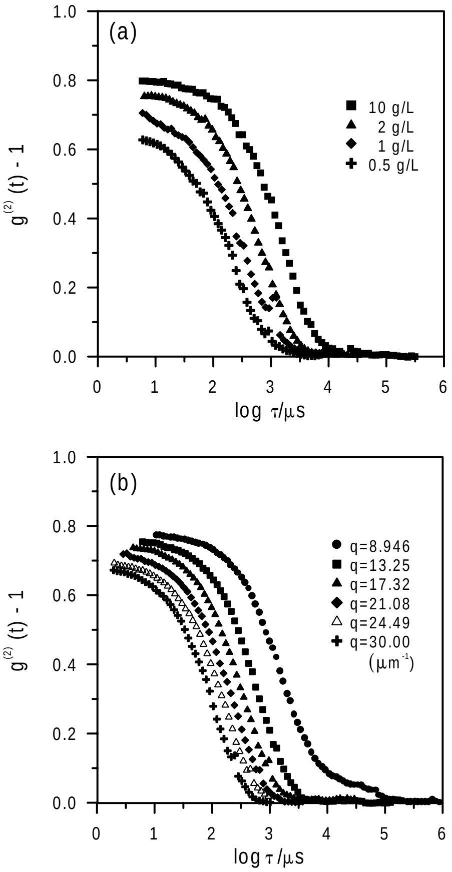

Fig. 3. Autocorrelation functions versus logarithmic relaxation time for PVC solutions at 30°C: (a) dependence of concentration for PVC/DOA solution ($q = 24.49\ \mu\mathrm{m}^{-1}$); (b) dependence of scattering vector q for PVC/DOA solution ($C = 20\ \mathrm{g\,l}^{-1}$).

using the semi-empirical rules according to the interaction degree of the polymer with its environment. According to their classification the effects of change in concentration is usually separated into four different concentration regions, i.e. the infinite dilution limit, hydrodynamic screening limit, polymer–polymer contact region and polymer chain entanglement region. In the infinite dilution limit, defined as a concentration below $[\eta]C \sim 1$, the polymer chain acts as an isolated coil. If the concentration of polymer in solution is raised, the hydrodynamic screening limit will be reached when the relative proximity of neighboring chains allows polymer–polymer intermolecular interactions to influence the motion of the polymer chains. Perturbation of the polymer motion by this mechanism is expected to occur above a concentration defined by $[\eta]C > 1$. The effects may be expected to be cumulative up to concentrations corresponding to the chain overlapping concentration, which is the close-packing of polymer coils in solution, $[\eta]C \sim 4$. Once the overlapping concentration has been reached, the polymer motion will be dominated by the presence of direct polymer–polymer interactions. If the increasing concentration raises above limit $[\eta]C \sim 10$, the interpenetration of the polymer coils or the pseudo-matrix-gel will be formed. In order to obtain more detailed information on the characteristics of the PVC/DOA solution over a wide concentration region, including both dilute and semi-dilute solutions, the values of $[\eta]C$ can be employed as a simple, approximate, overlap criterion for the dynamic behavior of polymer solution.

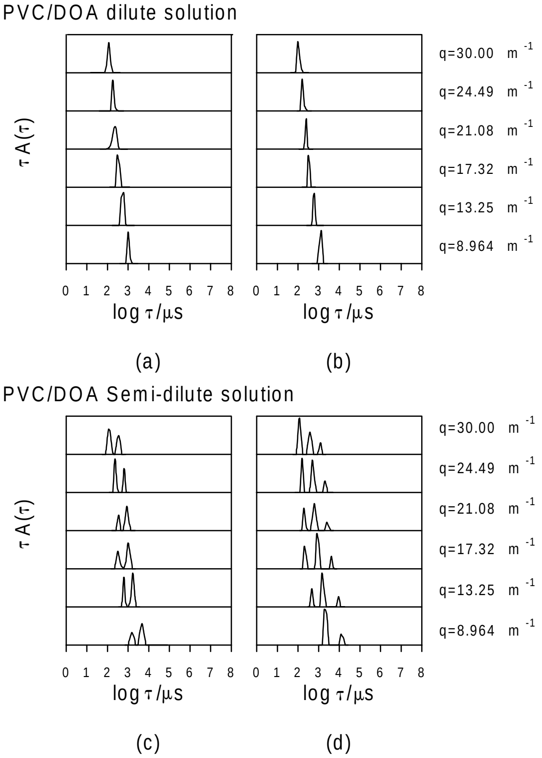

Fig. 4. Laplace inversions of the correlation functions obtained from various PVC solutions at the indicated scattering vector and the concentrations are: (a) $2\ \mathrm{g\,l}^{-1}$ and (b) $5\ \mathrm{g\,l}^{-1}$ for PVC/DOA dilute solution; and (c) $20\ \mathrm{g\,l}^{-1}$ and (d) $100\ \mathrm{g\,l}^{-1}$ for PVC/DOA semi-dilute solutions.

According to the semi-empirical rules proposed by Frisch

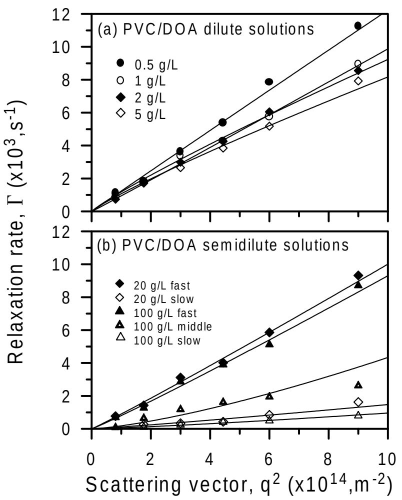

Fig. 5. q^2 dependence of the relaxation rate, Γ of PVC/DOA solutions at the concentrations were indicated.

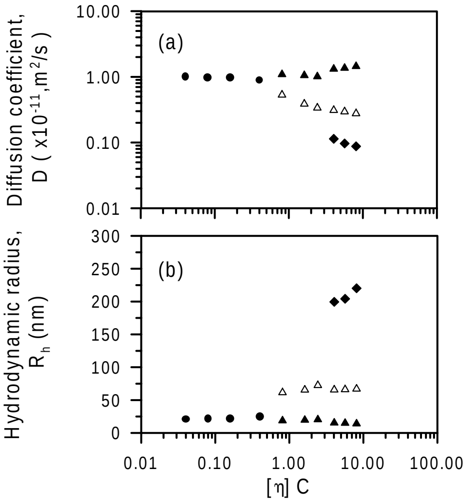

Fig. 6. (a) Double logarithmic plot of the diffusion coefficient, D versus $[\eta]C$. (b) The hydrodynamic radius, R_h versus $[\eta]C$ for PVC/DOA solutions at 30°C, respectively.

and Simha, Fig. 6(a) and (b) shows the value of the diffusion coefficient, D, and the hydrodynamic radius, R_h, which is evaluated from the diffusion coefficient using the Stokes–Einstein relationship: $D_c = K_B T/6\pi\eta_0 R_h$ for each relaxation mode as a function of the $[\eta]C$ value, respectively. At concentrations below $[\eta]C \sim 1$, which is in the infinite dilution region, the D value and the hydrodynamic radius have no remarkable change with increasing concentration, indicating that the translational diffusion of the individual chain and the hydrodynamic radius in the dilute solution are difficult to change because of the poor affinity of DOA to PVC chains. As stated earlier, there are two or three relaxation modes at the semi-dilute region. It is important to make clear the origins of these relaxation modes for understanding the aggregation behavior of PVA/DOA solutions. The two major relaxation modes (fast and slow) are observed in the concentration region, $1 < [\eta]C < 4$. According to the classification proposed by Frisch and Simha, this concentration range is located within the hydrodynamic screening region. In this region, the polymer–polymer intermolecular interactions will begin to influence the dynamic behavior of polymer chains in solution. The value of the diffusion coefficient for the fast mode in this concentration region shows no remarkable change with the concentration. Moreover, these values are still closed to those in the dilute solution, indicating that the relaxation mode resembling the individual PVC coil in the dilute region is still clearly observed. Similarly, the value of the R_h of the fast mode in this concentration region shows the same result. On the other hand, the slow mode observed in the hydrodynamic screening region slightly decreases by increasing the concentration of polymer. This fact is considered related to the cluster formed from the aggregation of several individual coils; besides, the cluster formation must make the hydrodynamic radius larger. On the other hand, three relaxation modes denoted as the fast, middle and slow modes appeared at the concentration above $[\eta]C \sim 4$. This concentration region corresponds to a condition where the polymer coils start to overlap, the aggregation behaviors of polymer solutions become more complex. At this region, both the middle, which is the same as the slow mode observed in the hydrodynamic screening region, and the fast mode is still observed. The D values of the middle and slow mode decrease rapidly as the concentration is further increased. The decrease rate in the D values with the concentration for the slow mode is larger than that for the middle mode. The significant decrease in the D values of the middle mode indicates the formation of the clusters further proceeds with increasing concentration. At the $[\eta]C > 4$ region, the appearance of the slow mode is considered owing to the transient gel network originated from the aggregation of the clusters in the concentrated PVC/DOA solutions. The remarkable decrease in the D values with concentration suggested that the gelation becomes more pronounced with increasing concentration. At the same time, the change in the D value for the middle mode become much less, implying that the larger clusters may be connected with each other to form a microgel domain. It is interesting that the fast mode related to individual PVC coil still appears and the D value shows only a slight increase compared with the D values at the $1 < [\eta]C < 4$ region. If the gelation takes place when the physical crosslinks are mainly formed from the intermolecular association, the D value of the fast mode should obviously increase with increasing the concentration at this concentrated region. This is because the relaxation rate of polymer chains between junction points should be faster than that of the individual chain in the dilute solution. However, the D values of the fast mode shows no remarkable change even at the high concentration region for the formation of the microgel structure. It may be considered that the intermolecular association is not the main mechanism to dominate the gelation of PVC/DOA solutions.

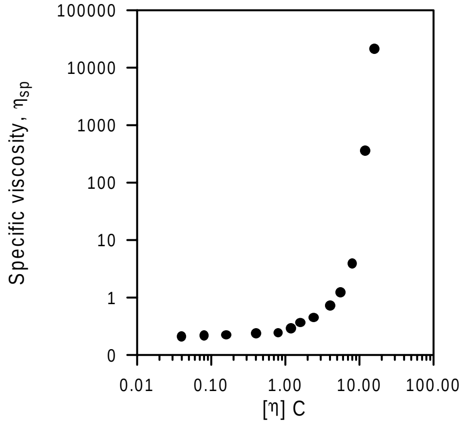

Fig. 7. The log–log plot of η_{sp} versus $[\eta]C$ for PVC/DOA solutions at 30°C.

The relation between the dynamic behavior and properties of polymer solutions is commonly investigated in terms

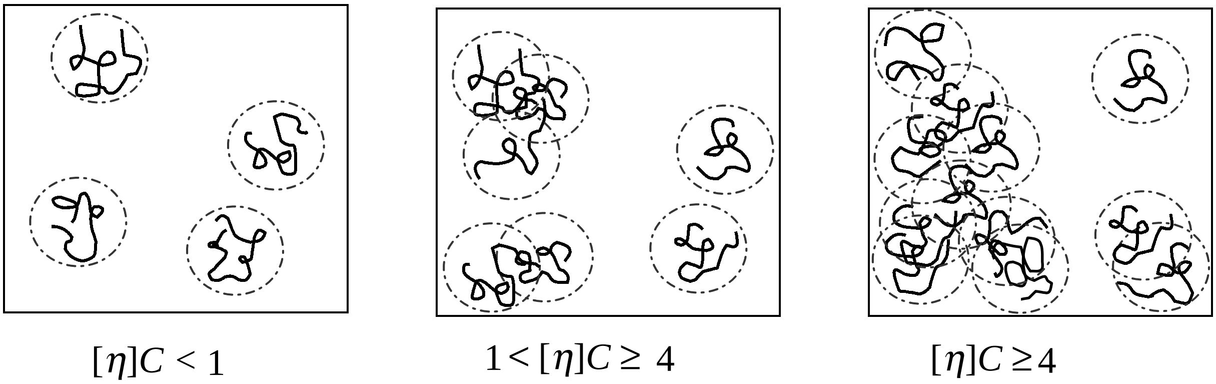

Fig. 8. Schematic picture of the aggregation mechanism for PVC/DOA solution.

of the viscometric study. As the concentration of polymer is increased, the viscosity is mainly governed by the degree of the intermolecular interaction, which is connected, with the overlapping of polymer chains [41]. Fig. 7 shows the log–log plot of η_{sp} versus $[\eta]C$ of PVC/DOA solutions, in which η_{sp} is defined by $\eta_{sp} = \eta/\eta_0 - 1$ using η and η_0 corresponding to the viscosity of polymer solution and pure solvent, respectively. The viscometric result shows that the viscosity of the solution has no significant change with the concentration below the $[\eta]C < 1$. In this region, the polymer is sufficiently isolated and the other chains could not perturb the flowing behavior on polymer chains. Then the viscosity increases slightly at the concentrations between about $[\eta]C \sim 1$ and $[\eta]C \sim 4$. As mentioned above, the polymer–polymer intermolecular interactions will be allowed to influence the polymer motion in this region. These interactions can be considered to be of two types, i.e. the relatively close proximity of neighboring chains described by the hydrodynamic screening interaction and the collision of the chain coils for the cluster formation. The poor affinity of DOA to PVC chains must increase the hydrodynamic friction, resulting in the increase in the viscosity of polymer solution. When the concentration is further increased more than the overlapping concentration, $[\eta]C \sim 4$, the viscosity increases markedly. Furthermore, at much high concentrations, $[\eta]C \sim 10$, the viscosity rises very rapidly, indicating that the polymer chains entangle with each other and, ultimately, infinite junction points are formed over the whole solution, resulting in a three-dimensional network structure.

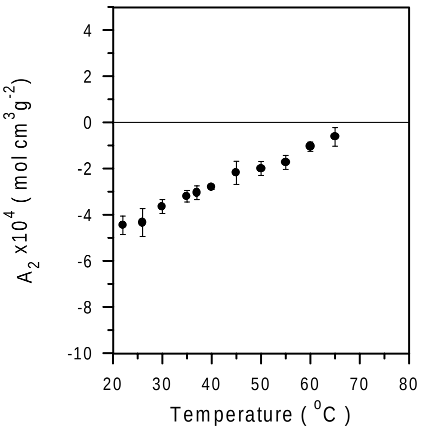

Fig. 9. Plot of the second virial coefficient, A_2, as a function of temperature for PVC/DOA dilute solutions.

Combining the DLS result with that in the viscometric measurement, Fig. 8 shows the aggregation mechanism of PVC/DOA solution. These facts let us consider that the individual PVC coils in the dilute solution first associates with each other to form several clusters with an increasing concentration above $[\eta]C \sim 1$ in hydrodynamic screening region. These clusters are assumed to become larger, absorbing the surrounding free PVC chains with an increasing concentration. Finally, these clusters should form a transient gel network when the concentration is above the chain overlapping concentration, $[\eta]C \sim 4$. The poor affinity of the solvent used should be more favorable to intramolecular aggregation of PVC chains, resulting in comparatively complex dynamic behaviors in semi-dilute solutions. In our previous work [3], the logarithm of the light scattering intensity at $\theta = 90°$ was found as a function of scattered time for PVC/DOA solutions at 30°C. The increment of scattering intensity with scattered time for semi-dilute PVC/DOA solutions was found at initial liquid–liquid phase separation. On the other hand, the scattering profiles ($I(q)$ versus q) revealed that a distinct scattering maximum appeared in the more concentrated PVC/DOA solutions and the intensity of scattering maximum increased with increasing time. The appearance of a scattering maximum is attributed to the significant degree of the phase separation or of the chain aggregation in PVC/DOA solutions.

Fig. 9 shows the A_2 value as a function of temperature. The result indicates that the A_2 value slightly increases with an increasing temperature in the measuring range. This further implies that the degree of PVC/DOA interaction only slightly increases with an increasing temperature. The repulsive interaction force balances the attractive

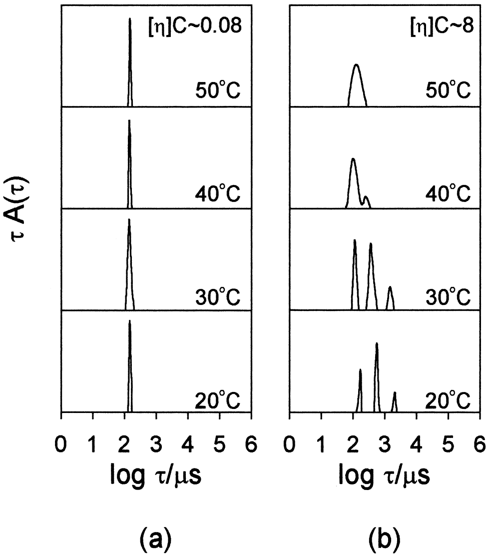

Fig. 10. Relaxation time distributions as a function of temperature at $q = 24.49\ \mu\mathrm{m}^{-1}$ for various PVC/DOA solutions: (a) $1\ \mathrm{g\,l^{-1}}$ and (b) $100\ \mathrm{g\,l^{-1}}$.

force between PVC chains and the solvent, i.e. the A_2 value becomes zero at the θ-temperature. The θ-temperature of PVC/DOA solution determined from the slope extrapolated to $A_2 = 0$ in Fig. 9 is about 68°C. Polymer chains in a poor solvent must easily collapse and then aggregate. Meanwhile, those in a good solvent must be favorable to exhibit extended coil conformation. As discussed earlier, the intramolecular aggregation is first considered to occur in the dilute PVC/DOA solutions. Owing to the affinity of DOA to PVC still poor with increasing temperature below 68°C, the dimension of individual coil should be not changed with temperature. However, the aggregation behavior between chain coils in the semi-dilute solution may show various relaxation modes by changing the temperature. Fig. 10(a) and (b) shows the relaxation time distributions as a function of temperature for PVC/DOA solutions at the concentrations of $1\ \mathrm{g\,l^{-1}}$ ($[\eta]C \sim 0.08$) and $100\ \mathrm{g\,l^{-1}}$ ($[\eta]C \sim 8$), respectively. The result shows clearly that the temperature dependence in these two concentration regions is quite different. The relaxation time distribution is independent of temperature in the dilute solution, whereas it becomes dependent in a semi-dilute solution ($[\eta]C > 4$) with increasing temperature. The relative amplitudes of the middle and slow modes decrease with increasing temperature, which might be due to the fact that the clusters or the transient gel networks have been dissolved with an increasing temperature in the semi-dilute solutions. Only a single relaxation mode with a broader distribution could be observed at 50°C as compared with that in dilute solution, indicating that various sizes of entanglement coils exist in semi-dilute solutions at higher temperatures. These facts mean that the intermolecular aggregation or the phase separation domains of PVC chains is disintegrated with an increasing temperature, but the intra-chain aggregation (the collapsed coil) still exists due to the negative A_2 values in this temperature region.

4. Conclusions

This work investigated the concentration and temperature dependencies on the dynamic behavior of PVC/DOA solutions from the dilute solution to semi-dilute solution regions through light scattering and viscometric measurements. Static light scattering results indicated that the PVC solution exhibited a repulsive force between PVC chain and DOA within the measuring temperature in this work. Combination of the DLS and viscometric results indicate that the dynamic behavior of polymer solutions could be classified into three regions. In the infinite dilution region, $[\eta]C < 1$, a single relaxation mode, independent of the temperature, is observed which is derived from the translational diffusion of individual coil in the dilute solution. In the hydrodynamic screening region, $1 < [\eta]C < 4$, the two major modes are observed. Firstly, the fast mode resembled that of the individual PVC coil in the dilute region, and secondly, the slow mode is considered related to the cluster formed from the aggregation of several individual PVC coils. At even higher concentrations, $[\eta]C > 4$, the polymer coils start to overlap and entangle; then, the third relaxation mode is observed. This mode is considered owing to the transient gel network originated from the aggregation of the clusters in the concentrated solution. On the other hand, the relative amplitudes of the middle and slow modes decrease with an increasing temperature. Moreover, only a broad relaxation mode was found at 50°C. These results indicate that intermolecular aggregation between chain coils is disintegrated with an increasing temperature. As a result of the affinity of DOA to PVC being poor below the θ temperature, the dynamic behavior of an isolated PVC chain has no remarkable change in the dilute region. The temperature effect on the dynamic behavior only exhibits at the much-concentrated region where the aggregation of chain coils or the gel network is formed.

Acknowledgements

The authors would like to thank the National Science Council of the Republic of China for financially supporting this research under Contract No. NSC-87-2216-E011-005.

References

[1] Hong PD, Chen JH. Polymer 1998;39:711.
[2] Hong PD, Chen JH. Polymer 1998;39:5809.
[3] Hong PD, Chen JH. Polymer 1999;40:4077.
[4] de Gennes PG. Scaling concepts in polymer physics, New York: Cornell University Press, 1979.
[5] de Gennes PG. Macromolecules 1976;9:587.
[6] de Gennes PG. Macromolecules 1976;9:594.

[7] Daoud M, Cotton JP, Farnoux B, Jannink G, Sarma G, Benoit H, Duplessix R, Picot C, de Gennes PG. Macromolecules 1975;8:804.

[8] Adam M, Delsanti M. Macromolecules 1985;18:1760.

[9] Amis EJ, Han CC, Matsushita Y. Polymer 1984;25:650.

[10] Takahai M, Nose T. Polymer 1986;27:1071.

[11] Nicolai T, Brown W, Johnsen RM, Stepanek P. Macromolecules 1990;23:1165.

[12] Nicolai T, Brown W, Hvidt S, Heller K. Macromolecules 1990;23:5088.

[13] Wang CH. Macromolecules 1992;25:1524.

[14] Sun Z, Wang CH. Macromolecules 1996;29:2011.

[15] Brown W. Dynamic light scattering, New York: Oxford University Press, 1993.

[16] Brown W. Light scattering principles and development, New York: Oxford University Press, 1996.

[17] Candau SJ, Dormoy Y, Mutin PH, Debeauvais F, Guenet JM. Polymer 1987;28:1334.

[18] Mutin PH, Guenet JM, Hirsch E, Candau SJ. Polymer 1988;29:30.

[19] Mutin PH, Guenet JM. Macromolecules 1989;22:843.

[20] de Gennes PG. Macromolecules 1976;9:594.

[21] Brochard F, de Gennes PG. Macromolecules 1977;10:1157.

[22] Nose T, Chu B. Macromolecules 1979;12:590.

[23] Chu B, Nose T. Macromolecules 1979;12:599.

[24] Chu B, Nose T. Macromolecules 1980;13:122.

[25] Nicolai T, Brown W, Johnsen RM. Macromolecules 1990;23:1165.

[26] Zimm BH. J Chem Phys 1948;16:1093.

[27] Chu B. Laser light scattering, 2. San Diego: Academic Press, 1991.

[28] Provencher SW. Comput Phys Commun 1982;27:229.

[29] Spering LH. Introduction to physical polymer science, New York: Wiley, 1986.

[30] Ishiwata S, Hayashi M, Ohshima H, Suzuki O. J Soc Rheol Jpn 1991;19:83.

[31] Bohdanecky M, Kovar J. Viscosity of polymer solutions, New York: Elsevier, 1982.

[32] Nakamura Y, Inoue N, Norisuye T, Teramoto A. Macromolecules 1997;30:631.

[33] Kjoniksen AL, Nystrom B. Macromolecules 1996;29:7116.

[34] Burchard W, Schmidtn M, Stockmayer WH. Macromolecules 1980;13:580.

[35] Schmidt M, Burchard W. Macromolecules 1981;14:210.

[36] Herning T, Djabourov M, Leblond J, Takerkart G. Polymer 1991;32:3211.

[37] Bhatt M, Jamieson AM. Macromolecules 1988;21:3015.

[38] Fang L, Brown W. Macromolecules 1990;23:3284.

[39] Brown W, Fang L, Stepanek P. Macromolecules 1991;24:3201.

[40] Frisch HL, Simha R. In: Eirich FR, editor. Reology theory and applications, New York: Academic Press, 1956.

[41] Forsman WC. Polymer in solution, New York: Plenum Press, 1986.