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Viscometric study of polystyrene in mixed solvents and with varying temperature

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Abstract

The viscometric behavior of polystyrene (PS) in a mixed solvent of toluene/cyclohexane and with varying temperature was thoroughly investigated. It has been found that, in the plot of the reduced viscosity (η_{sp}/C) vs. concentration, the intrinsic viscosity of PS increased in the mixed solvent with higher ratio of toluene/cyclohexane or when measured at higher temperature, indicating that the polymer–solvent interaction increased in the mixed solvent with a higher ratio of toluene/cyclohexane or at higher temperature. According to the theoretical consideration discussed in the paper, the correlation between the intrinsic viscosity of PS at finite concentration, $[\eta_{PS}]_C$, and the concentration of PS in solution can be obtained by transforming the plot of the reduced viscosity (η_{sp}/C) vs. concentration of PS in the solvent. It is noted that $[\eta_{PS}]_C$ decreased with an increase in the concentration of PS in solution, indicating that the polymer dimensions decreased in concentrated solution. The concentration-dependent intermolecular excluded volume effect, which can be quantitatively expressed by the parameter b_Y, is believed to be responsible for the results. In good solvent, the polymer coils expand, resulting in an increase of the intermolecular excluded volume effect in solution. As a result, the parameter b_Y in poor solvent is less than that measured in good solvent. In Θ-solvents, the parameter b_Y became zero, indicating that $[\eta_{PS}]_C$ no longer changed with the increase of the concentration of PS in solution and that polymer coils existed in an unperturbed state. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Intrinsic viscosity; Intermolecular excluded volume effect; Polymer dimensions

1. Introduction

As it is well known, in infinite dilute solution ($C < C_s$), the distance between polymer molecules is very large. The intermolecular interaction between the polymer molecules in solution is negligible. In finite solutions ($C > C_s$), however, the intermolecular interaction can no longer be negligible. As a result, the polymer coils shrink in size, resulting in a decrease of the hydrodynamic volume of polymers in solution. With the increase of the concentration, the hydrodynamic volume decreases accordingly. When the concentration is higher than C^*, the polymer coils overlap and interpenetrate each other and the individuality of polymer coils in solution disappears [1–15].Though the existence of the critical concentration C_s has been verified by a number of techniques [3–6], the quantitative correlation between polymer dimensions and the concentration of polymer in solution has never been established by viscosity measurements. Fortunately, the method of polymer solvent to which much attention has been devoted in recent years [12,16–19], has proved to be a useful technique to investigate changes in polymer dimensions in solution. According to this method, the viscometric behavior of polymer A (guest polymer) is determined in solution in which a second polymer B (host polymer) is found at a constant concentration [12,19]. Accordingly, the intrinsic viscosity of polymer A in solution in which the polymer B is at a constant concentration of C_B, $[\eta_A]_B$, should reflect the change in molecular dimensions of polymer A brought about by the presence of polymer B [16–20]. In fact, the changes in $[\eta_A]_B$ can be attributed to both the polymer–polymer interaction (repulsive or attractive intermolecular interaction between polymer A and B) and the concentration-dependent intermolecular excluded volume effect of polymers in solution. This is verified by investigations on the intrinsic viscosity of poly(vinyl chloride) (PVC) in pure solvent of N,N'-dimethylformamide (DMF), and in polymer solvent of poly(ε-carprolactone)(PCL) + DMF, poly(N-vinyl-2-pyrrolidone) (PVP) + DMF and polystyrene (PS) + DMF, respectively [21]. However, if the host and the guest polymer are chosen to be the same polymer, namely polymer A, and the intrinsic viscosity of polymer A is determined in a number of polymer solvents with a different concentration of the same polymer A, the plot of $[\eta_A]_A$

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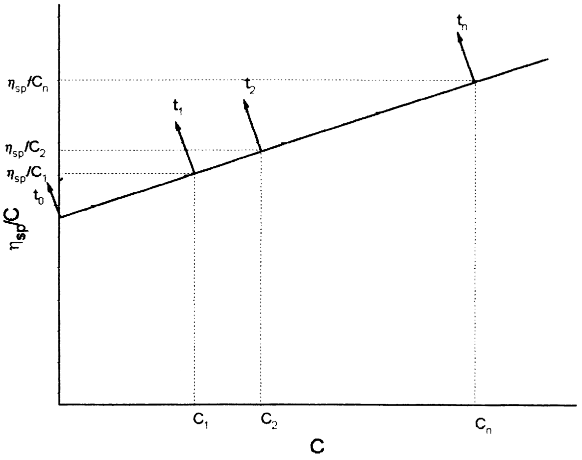

Fig. 1. The plot of the reduced viscosity (η_{sp}/C) vs. concentration (C) is schematically shown.

vs. C_A can be obtained accordingly. This plot should present the quantitative correlation between the dimensions of polymer A and the concentration of polymer A in solution. Since the attractive or repulsive interaction between polymer A and polymer B in solution no longer exists on this occasion, we believe that the plot of $[\eta_A]_A$ vs. C_A should effectively reveal the correlation between polymer dimension and the concentration-dependent intermolecular excluded volume effect of polymers in solution.Theoretical analyses, however, have demonstrated that it was no use obtaining the plot of $[\eta_A]_A$ vs. C_A by determining the intrinsic viscosity of polymer A in a number of polymer solvents with different concentrations of the same polymer A, since this plot can be obtained conveniently by transforming the plot of η_{sp}/C vs. C of polymer A in pure solvent. In this article, the theoretical background concerning the transformation from the plot of η_{sp}/C vs. C to the plot of $[\eta_A]_A$ vs. C_A is presented. As a result, the plots of η_{sp}/C vs. C of PS in mixed solvents and with varying temperature were measured and transformed into the plots of $[\eta_A]_A$ vs. C_A. As can be seen, a linear relationship between $[\eta_A]_A$ and C_A exists. With the increase of C_A, $[\eta_A]_A$ decreased accordingly, due to the concentration-dependent intermolecular excluded volume effect which can be quantitatively expressed by the parameter b_Y.

2. Theoretical

The reduced viscosity (η_{sp}/C) vs. concentration (C) of polymers in solution are schematically displayed in Fig. 1. In general, a linear relationship exists, except for a polyelectrolyte in solvent. As can be seen, for any concentration C, there exists η_{sp}/C. According to the definition, the reduced viscosity η_{sp}/C may be expressed by the equation

$$\eta_{sp}/C = (t/t_0 - 1)/C \tag{1}$$

where t_0 is the flow time of the pure solvent and t is the flow time of solution in which polymer concentration is C. Therefore, on condition that the linear relationship between η_{sp}/C and C be obtained by the viscosity measurement of binary system, the flow time of solution at any concentration C can be calculated by Eq. (1). Accordingly, if the solution with the concentration C_i is used to form polymer solvent, the flow time of this polymer solvent, t_i, can be obtained in this way. According to the Huggins equation, we have

$$\eta_{sp}/C = (t/t_0 - 1)/C = [\eta]_0 + bC \tag{2}$$

$$\eta_{sp}/C_i = (t_i/t_0 - 1)/C_i = [\eta]_0 + bC_i \tag{3}$$

where $[\eta]_0$ is the intrinsic viscosity of the solution, and slope coefficient b is related to the Huggins coefficient K_H by

$$b = K_H[\eta]_0^2 \tag{4}$$

Obviously, Eqs. (2) and (3) can be changed into the form

$$t/t_0 = [\eta]_0 C + bC^2 + 1 \tag{5}$$

$$t_i/t_0 = [\eta]_0 C_i + bC_i^2 + 1 \tag{6}$$

Combining Eqs. (5) and (6) yields

$$\frac{t}{t_i} = \frac{[\eta]_0 C + bC^2 + 1}{[\eta]_0 C_i + bC_i^2 + 1} \tag{7}$$

Subtracting 1 from both sides of Eq. (7) yields

$$\begin{aligned} \frac{t}{t_i} - 1 &= \frac{[\eta]_0 C + bC^2 + 1}{[\eta]_0 C_i + bC_i^2 + 1} - 1 \\ &= \frac{[\eta]_0 (C - C_i) + b(C + C_i)(C - C_i)}{[\eta]_0 C_i + bC_i^2 + 1} \end{aligned} \tag{8}$$

On division by $(C - C_i)$, Eq. (8) can be changed into the form

$$\begin{aligned} \frac{(t/t_i) - 1}{C - C_i} &= \frac{[\eta]_0 + b(C - C_i)}{[\eta]_0 C_i + bC_i^2 + 1} \\ &= \frac{[\eta]_0 + 2bC_i}{[\eta]_0 C_i + bC_i^2 + 1} + \frac{b(C - C_i)}{[\eta]_0 C_i + bC_i^2 + 1} \end{aligned} \tag{9}$$

Expressing $[\eta]_{C_i}$ and b_{C_i} by the equation

$$[\eta]_{C_i} = \frac{[\eta]_0 + 2bC_i}{[\eta]_0 C_i + bC_i^2 + 1} \tag{10}$$

$$b_{C_i} = \frac{b}{[\eta]_0 C_i + bC_i^2 + 1} \tag{11}$$

Eq. (9) may be rewritten as

$$\frac{(t/t_i) - 1}{C - C_i} = [\eta]_{C_i} + b_{C_i}(C - C_i) \tag{12}$$

Obviously Eq. (12) can be referred to as the Huggins equation of the guest polymer with the concentration $(C - C_i)$ in the polymer solvent in which the host polymer, the same as the guest polymer in this instance, is at the concentration of

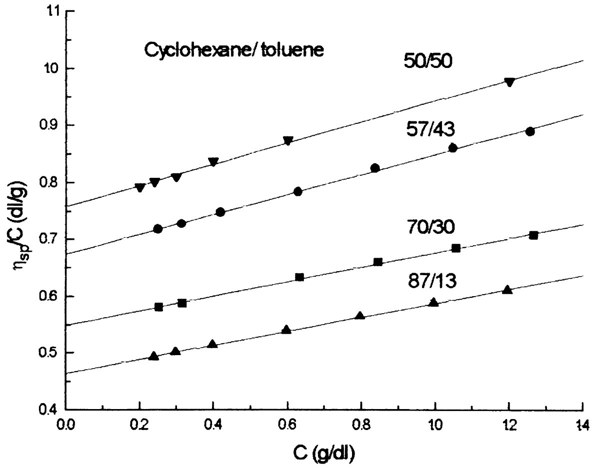

Fig. 2. The plot of the reduced viscosity (η_{sp}/C) vs. concentration of PS in mixed solvents of cyclohexane/toluene with different volume ratios at 25°C.

C_i. Accordingly, $[\eta]_{C_i}$ represents the intrinsic viscosity of the guest polymer in the polymer solvent with the concentration of C_i. Since the guest polymer and the host polymer are chosen to be the same polymer as discussed above, we believe $[\eta]_{C_i}$ directly reflects polymer dimensions in solution with the concentration of C_i. Therefore, once $[\eta]_0$ and b are obtained from the plot of η_{sp}/C vs. C, then, letting C_i equals 0.1,0.2,…, $[\eta]_{C_i}$ at the concentration of 0.1,0.2,…, can be calculated by Eq. (10). In this way, the plot of $[\eta]_{C_i}$ vs. C_i was obtained. In fact, in the early 1950s, Cragg and Bigelow presented the concept of the intrinsic viscosity at finite concentration [22]. It was pointed out that, when polymer molecules come closer in concentrated solution, the polymer dimension decreased due to the repulsive intermolecular interactions. As a result, Huggins equation should be expressed as

$$\eta_{sp}/C = [\eta]_C + k[\eta]_C^2 C \tag{13}$$

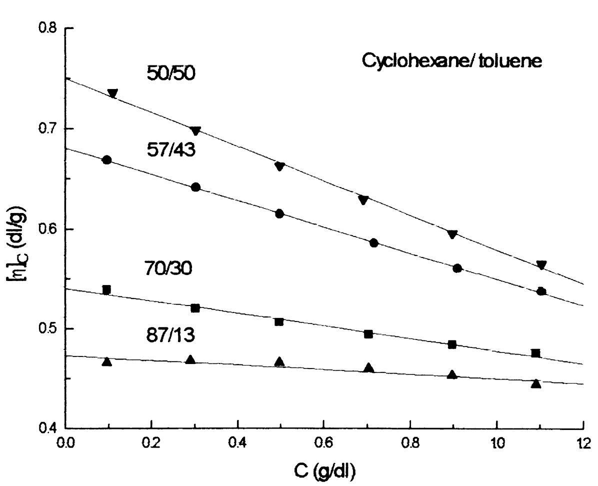

Fig. 3. The intrinsic viscosity of PS at finite concentration vs. concentration of PS in mixed solvents with different volume ratios of cyclohexane/toluene at 25°C.

where $[\eta]_C$ is the intrinsic viscosity of polymers in solution with the concentration C. However, they failed to find a way to determine $[\eta]_C$. Now, using the method of polymer solvent, it can be determined conveniently. The concept of the intrinsic viscosity at concentrated solution had been employed by Staszewska et al. [20] to deduce the equation by which the Huggins mutual interaction parameter K_{AB} was determined. However, Eq. (10) presented an quantitative relationship between $[\eta]_{C_i}$ and C_i. When C_i is low and the higher terms of C_i are neglected, Eq. (10) can be expressed as follows:

$$[\eta]_{C_i} = [\eta]_0 + (2b - [\eta]_0^2)C_i \tag{14}$$

Combining Eqs. (14) and (4) yields

$$[\eta]_{C_i} = [\eta]_0 - (1 - 2K_H)[\eta]_0^2 C_i \tag{15}$$

Considering that in good solvents the Huggins parameter K_H of flexible polymers is always less than 0.5 as has been pointed out by Bohdanecky and Kovar [23], we believe that $(1 - 2K_H)[\eta]_0^2$ is larger than zero, indicating that polymer dimensions should decrease with the increase of the concentration of polymers in good solvents.

3. Experimental

Polystyrene (PS) was supplied by Hefei Chemical Plant (China), with a viscosity-average molecular weight of 250 000. Cyclohexane and toluene were A.R. grade and were used as received. Viscosity measurement was carried out using a dilution Ubbelohde viscometer which was immersed in a constant temperature bath. The temperature was measured by a thermometer with an accuracy of 0.02°C.

4. Results and discussion

Fig. 2 shows the plots of the reduced viscosity (η_{sp}/C) vs. concentration (C) for PS in mixed solvents of cyclohexane/toluene with different volume ratios at 25°C. It can be seen that there is a linear relationship between η_{sp}/C and C in the whole range of concentration. On extrapolating to zero concentration, the intrinsic viscosity of PS in mixed solvents can be obtained. It is noted that the intrinsic viscosity of PS increased in mixed solvents with a lower ratio of cyclohexane/toluene, indicating that the polymer–solvent interaction increased in mixed solvent with a lower ratio of cyclohexane/toluene. According to Eq. (10) Fig. 2 can be transformed into the plot of $[\eta]_C$ vs. C which is shown in Fig. 3. As can be seen, a linear relationship exists between $[\eta]_C$ and C. With the increase of concentration, $[\eta]_C$ decreases accordingly due to the concentration-dependent intermolecular excluded volume effect. Furthermore, in the mixed solvent with a lower ratio of cyclohexane/toluene, $[\eta]_C$ decreases more rapidly than in mixed solvent with higher ratios of cyclohexane/toluene. A reasonable interpretation

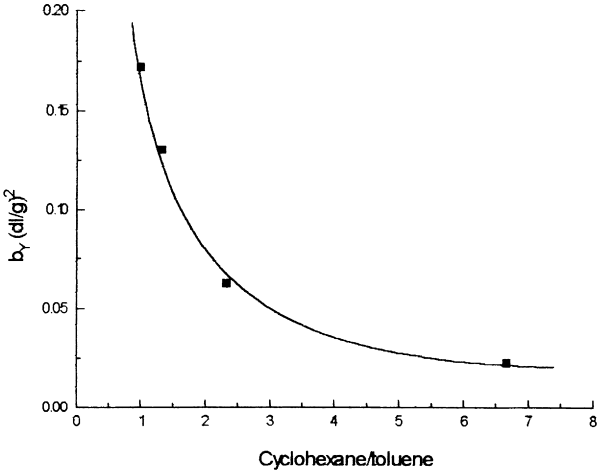

Fig. 4. The plot of the parameter b_Y as a function of the volume ratios of cyclohexane/toluene at 25°C.

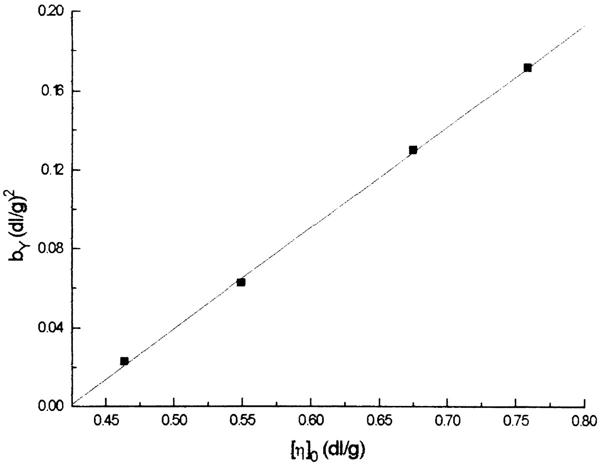

Fig. 5. The plot of the parameter b_Y as a function of the intrinsic viscosity of PS in mixed solvents of cyclohexane/toluene with different volume ratios at 25°C.

may be that, in the mixed solvent with the lower ratio of cyclohexane/toluene, PS coils expanded due to the strong polymer–solvent interaction. As a result, the intermolecular excluded volume effect in solution increased. Therefore, $[\eta]_C$ decreased more rapidly with the increase of the concentration. The equation that indicates the relationship between $[\eta]_C$ and C can be employed here as follows

$$[\eta]_C = [\eta]_0 - b_Y C \tag{16}$$

The parameter b_Y is a quantitative representation the intermolecular excluded volume effect of macromolecules in solution. From Fig. 4 and Table 1 it can be seen that b_Y decreases in mixed solvent with a higher volume ratio of cyclohexane/toluene, indicating that b_Y is large in good solvent and decreases in poor solvent. If $[\eta]_0$ is used to indicate the solvent power, then, b_Y should increase in mixed solvent with a large value of $[\eta]_0$ as can be seen from Fig. 5.

It is well known that, in infinite dilute solution, the intermolecular interaction between polymers in solution is negligible. As a result, the polymer dimension is determined by the effect of mutual volume exclusion of the segments (intramolecular interaction), which tends to enlarge the molecule. The effect of a positive energy of mixing, which encourages first-neighbor contacts between polymer segments, a more compact conformation for the molecule results [24]. In finite dilute solution, the intermolecular interaction (the effect of mutual volume exclusion of the segments of the different polymer coils) was introduced. However, under θ-conditions, all these interactions are compensated and the polymer coils in solution exist in an unperturbed state, indicating that $[\eta]_C$ should remain constant with the increase of the concentration. As a result, the parameter b_Y should equal zero under θ-condition. It has been reported [25] that, for the mixed solvent of cyclohexane/toluene with the volume ration of 86.9/13.1, the θ-temperature for PS is 17°C. Since the viscosity of PS in this mixed solvent (87/13) was measured at 25°C, the parameter b_Y was a little higher than zero as can be seen from Table 1. We believe that this is because the poor solvent became a good one at higher temperature. When determined at 25°C, the θ-condition for PS should appear in the mixed solvent of cyclohexane/toluene with the volume ratio a little higher than 86.9/13.1.

Table 1
Viscosity parameters for polystyrene in mixed solvents of cyclohexane/toluene with different volume ratios at 25°C

Cyclohexane/toluene	$[\eta]_0$ (dl/g)	b (dl/g)^2	K_H	b_Y (dl/g)^2
50/50	0.758	0.184	0.320	0.171
57/43	0.675	0.175	0.384	0.130
70/30	0.549	0.127	0.421	0.063
87/13	0.464	0.124	0.576	0.023

Fig. 6 shows the plots of the reduced viscosity (η_{sp}/C) vs.

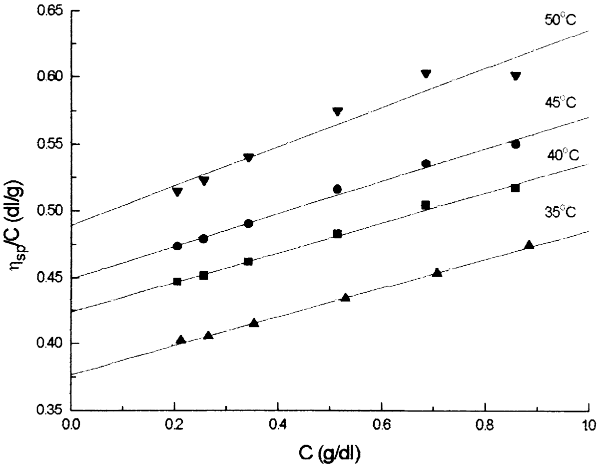

Fig. 6. The plot of the reduced viscosity (η_{sp}/C) vs. concentration (C) of PS in cyclohexane at different temperatures.

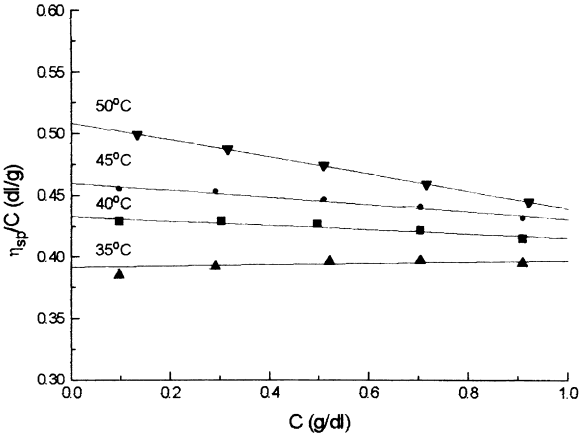

Fig. 7. The intrinsic viscosity of PS at finite concentration vs. concentration of PS in cyclohexane at different temperatures.

concentration for PS in cyclohexane at different temperatures. It can be seen that, when measured at higher temperatures, the intrinsic viscosity of PS is larger than those measured at lower temperatures, indicating that at higher temperatures, the polymer–solvent interaction increases and the PS coils expand. Based on Eq. (10), Fig. 6 was transformed into the plot of $[\eta]_C$ vs. C as shown in Fig. 7. It can be seen that, at higher temperatures, $[\eta]_C$ decreases more rapidly with concentration. Obviously the increased intermolecular excluded volume effect of PS at higher temperature should be responsible for the results. Fig. 8 shows directly that b_Y increases at higher temperatures. Using $[\eta]_0$ to indicate the solvent power of cyclohexane at different temperatures, it should also increase with increase in $[\eta]_0$ as can be seen from Fig. 9.

It has been reported [26,27] that the θ-temperature for PS in cyclohexane is 34°C. To avoid potential sedimentation of PS in solution we measured the viscosity of polymer solution at 35°C, slight higher than the θ-temperature. As a result, the parameter b_Y should approach zero, which was verified by the experimental results as shown in Table 2.

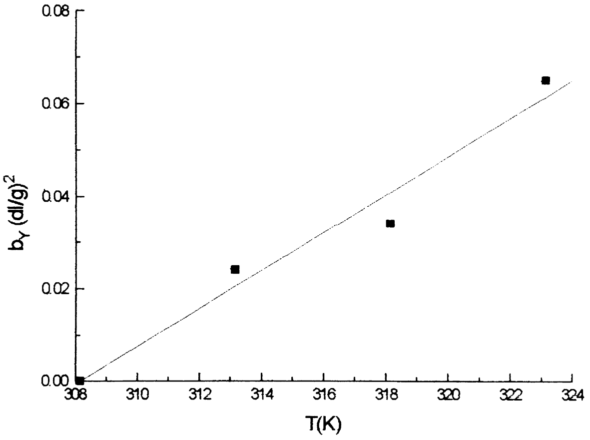

Fig. 8. The plot of the parameter b_Y as a function of the temperature at which the viscosity behavior of PS in cyclohexane was measured.

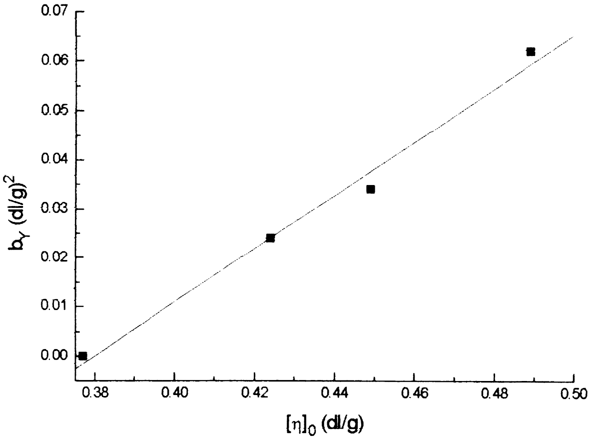

Fig. 9. The plot of the parameter b_Y as a function of the intrinsic viscosity of PS in cyclohexane at different temperatures.

Table 2
Viscosity parameters for polystyrene in cyclohexane at different temperatures

Temperature (°C)	$[\eta]_0$ (dl/g)	b (dl/g)^2	K_H	b_Y (dl/g)^2
35	0.377	0.109	0.767	− 0.002
40	0.424	0.112	0.623	0.024
45	0.449	0.121	0.600	0.034
50	0.489	0.141	0.589	0.065

5. Conclusion

In conclusion, the plot of the reduced viscosity (η_{sp}/C) vs. concentration (C) can be transformed into the plot of $[\eta]_C$ vs. C, which indicates the quantitative correlation between the polymer dimension and the concentration of polymer in solution more directly and effectively. With an increase of concentration, $[\eta]_C$ decreases accordingly due to the concentration-dependent intermolecular excluded volume effect which can be quantitatively expressed by the parameter b_Y. In good solvents b_Y is larger and $[\eta]_C$ decreases more rapidly with the increase of the concentration. On the contrary, in poor solvent, b_Y decreases in magnitude. Under θ-conditions, the parameter b_Y becomes zero and $[\eta]_C$ no longer changes with the increase of the concentration of polymers in solution.

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