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A NOVEL INTERPRETATION OF CONCENTRATION DEPENDENCE OF VISCOSITY OF DILUTE POLYMER SOLUTION*

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Abstract The concentration dependence of the reduced viscosity of dilute polymer solution is interpreted in the light of a new concept of the self-association of polymer chains in dilute solution. The apparent self-association constant is defined as the molar association constant divided by the molar mass of individual polymer chain and is numerically interconvertible with the Huggins coefficient. The molar association constant is directly proportional to the effective hydrodynamic volume of the polymer chain in solution and is irrespective of the chain architecture. The effective hydrodynamic volume accounts for the non-spherical conformation of a short polymer chain in solution and is a product of a shape factor and hydrodynamic volume. The observed enhancement of Huggins coefficient for short chain and branched polymer is satisfactorily interpreted by the concept of self-association. The concept of self-association allows us to predict the existence of a boundary concentration C_s (dynamic contact concentration) which divides the dilute polymer solution into two regions.

Keywords Self-association, Polymer solution, Viscosity, Concentration dependence

INTRODUCTION

The experimentally determined reduced viscosity of a dilute polymer solution usually is a linear function of concentration expressed as:

$$\eta_{sp} / C = a_0 + a_1 C \tag{1}$$

The intercept a_0 is defined as intrinsic viscosity:

$$a_0 = \lim_{C \to 0} (\eta_{sp} / C) \equiv [\eta] \tag{2}$$

Which is related to the size of an isolated polymer chain in solution. It is believed that both the size and intermolecular interactions are attributed to a_1 which can be expressed as[1]:

$$a_1 = k_H [\eta]^2 \tag{3}$$

and hence:

$$\eta_{sp} /C=[\eta]+ k_H [\eta]^2 C \tag{4}$$

The parameter k_H is termed the Huggins coefficient or slope constant. The theory of intrinsic viscosity has been firmly established in the past half century and has become a cornerstone of the modern polymer science[2]. A huge number of experimental data of k_H derived from the slope a_1 has been accumulated[3]. However, the theoretical Huggins coefficient from numerical calculations based on intermolecular hydrodynamic interactions[4~12], and formulations based on phenomenological approaches[13, 14] and thermodynamic interactions[15~17] do not agree with each other. None of them could explain all the experimental results.

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Especially, a unitary quantitative interpretation is still lacking for a number of observed behaviors. For example: 1) an abrupt increase of k_H with decreasing molar mass for short chain polymers; 2) branched polymer possessing a higher k_H than linear polymer with same molar mass; 3) sensitivity to the formation of aggregates for polymer solution mixtures; 4) existence of a boundary concentration separating isolating and interacting chain properties in solution.

Recently, a simple theoretical approach[18, 19] based on the concept of self-association or cluster formation has been proposed for the viscosity of dilute polymer solution. It yields an expression similar to the Huggins equation but involving quite different contents. In the present study, we review the slope constant of viscosity of dilute polymer solution using Huggins coefficient available in the literature and obtained a unified interpretation.

SLOPE CONSTANT

The proposed theory[18, 19] concerning the viscosity of polymer solution in extremely dilute concentration regions involves two basic assumptions: 1) Einstein viscosity law is valid for individual polymer chains in dilute solution, and 2) any deviation is due to self-association or cluster formation. Thereby as all the dissolved chains are in isolated state, the relative viscosity of a monodispersed polymer solution should be:

$$\eta_r = 1 + [\eta]\, C \tag{5}$$

When the self-association occurs, the intrinsic viscosity should be the weight average of the intrinsic viscosities of isolated chains $[\eta]$ and clusters $[\eta]_c$,

$$<[\eta]> = \alpha\,[\eta]_c + (1 - \alpha)\,[\eta] \tag{6}$$

where α is the weight fraction of the clusters. Equation (5) can be rewritten as:

$$\eta_r = 1 + [\eta]\,(1+R\,\alpha)\,C \tag{7}$$

where

$$R = ([\eta]_c - [\eta]) / [\eta] \tag{8}$$

Hence the remaining task is to calculate the product $R\,\alpha$.

Assuming the following equilibrium and an identical molar self-association constant K_a for all the

$$\begin{aligned} &P + P \overset{K_a}{\rightleftharpoons} P_2 \\ &P_2 + P \overset{K_a}{\rightleftharpoons} P_3 \\ &\quad\cdots\cdots \\ &P_{i-1} + P \overset{K_a}{\rightleftharpoons} P_i \\ &\quad\cdots\cdots \end{aligned} \tag{9}$$

equilibria, we have

$$\alpha = [2(K_m C)^2 + (1 + 4\,K_m C)^{1/2} - 2\,K_m C - 1] / [2(K_m C)^2] \tag{10}$$

where

$$K_m = K_a / M \tag{11}$$

by using the mass action law with M being the molar mass of polymer. K_m is denoted as apparent association constant for monodispersed polymer chains in solution.

In a rigid spherical model, it is assumed that a dimer will have twice the hydrodynamic size and molar mass. Therefore the ratio of the intrinsic viscosity of a dimer to that of an isolated chain is

$$[\eta]_2 / [\eta] = ((2L)^3 / 2M) / (L^3 / M) = 4 \tag{12}$$

where L is the hydrodynamic size of an isolated chain. Assuming the intrinsic viscosity of multimer obeys the same Mark-Houwink Equation as that for the dimer, we have

$$[\eta]_i = i^2\,[\eta] \tag{13}$$

The intrinsic viscosity difference between multichain clusters and the unimer is:

$$R = 48\,(K_m C)^3 / \{[2K_m C - 1 + (1 + 4K_m C)^{1/2}]\,[(1 + 4K_m C)^{1/2} - 1]^2\} \tag{14}$$

Multiplying Eq. (10) and Eq.(14), the product $R\alpha$ is just :

$$R\alpha = 6\,K_m\,C \tag{15}$$

Inserting Eq. (15) into Eq.(7), we have an alternative expression for the reduced viscosity of a polymer solution:

$$\eta_{sp}/C = [\eta] + 6\,K_m\,[\eta]\,C \tag{16}$$

with

$$a_1 = 6\,K_m\,[\eta] \tag{17}$$

analogous to the conventional Huggins equation Eq. (4).

Note that both the Huggins coefficient k_H and the apparent self-association constant K_m are evaluated from the slope and intercept of the plot of η_{sp}/C versus C; k_H and K_m are related by

$$K_m = k_H\,[\eta]\,/\,6 \tag{18}$$

Since the numerical magnitude and physical meaning of these two slope constants are quite different, it is desirable to compare how they vary with the chain length.

Figures 1 and 2 show the variations of the slope constants k_H and K_m of polystyrene in toluene and benzene respectively for a wide range of chain length down to oligomers with only a few monomers. The original viscosity data are taken from the literature[3, 20~22] . Inspecting Figs. 1 and 2, one can immediately recognize the differences. k_H increases abruptly with decreasing intrinsic viscosity and the shortest oligomer has a k_H value several times higher than the longer polymer chains. In contrast, K_m is almost directly proportional to intrinsic viscosity for the long polymer chain and bends up only slightly in the oligomeric region. Remember that the definition of K_m is the ratio of molar association constant K_a to the molar mass M of a single polymer chain. Multiplying both the ordinate and abscissa of Fig. 2 by M yields a double logarithmic plot of K_a versus $[\eta]M$ as shown in Fig. 3 similar to Fig. 2. Figure 3 demonstrates that K_a is directly proportional to $[\eta]M$ for the long polymer chain and only a slight positive deviation occurs in the short chain oligomeric region.

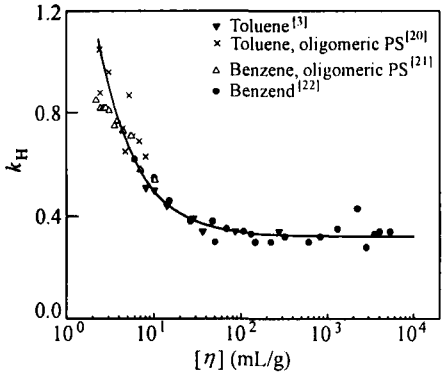

Fig. 1 Variation of k_H with intrinsic viscosity for PS in toluene or benzene
The curve is calculated from eq. (26) with known viscosity constant A and B for polystyrene in toluene listed in Table 1

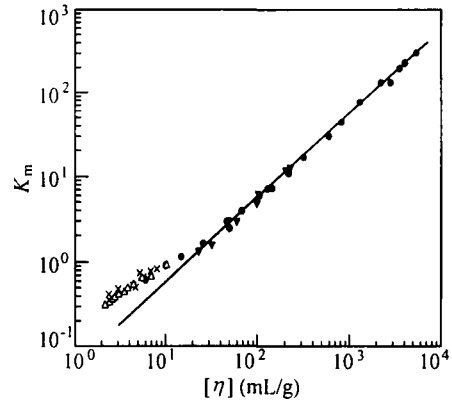

Fig. 2 Variation of K_m with intrinsic viscosity for PS in toluene or benzene
The legends are identical with Fig. 1

According to the theory of intrinsic viscosity[2]:

$$[\eta] = \Phi(R_g^3 / M) \tag{19}$$

where Φ is a universal geometric constant, R_g is the radius of gyration of an equivalent sphere. Hence $[\eta]\,M$ is designated as the hydrodynamic volume of the equivalent sphere

$$V_h = [\eta]\,M = \Phi R_g^3 \tag{20}$$

For short chain oligomers, the chain conformation deviates from a sphere. Mayerhoff[23] included an additional shape function $f(p)$ to account for deviation of the chain conformation from a sphere, where p is the shape factor determined by the asymmetry of the chain conformation. It is reasonable to assume that the effective dynamic volume for cluster formation should also include such a correction,

$$V_{eff} = f(p)\,V_h = f(p)\,[\eta]\,M \tag{21}$$

$f(p)$ should decrease with increasing chain size and approach one for an infinitely long chain. It could be

expressed by a polynomial as:

$$f(p) = 1 + C_2/R_g + \cdots\cdots \quad (22)$$

where R_g is the radius of gyration in a unperturbed state. Since R_g is proportional to $M^{1/2}$ and $[\eta]$ is proportional to $M^{1/2}$ in the θ state, $f(p)$ may be approximated as

$$f(p) = 1 + A / [\eta] \quad (23)$$

where A is a constant depending on the chemical structure and chain rigidity. Inserting Eq. (23) into Eq. (22) we have

$$V_{eff} = (1 + A / [\eta])\,[\eta]\,M \quad (24)$$

The existing data suggest that the molar association constant for a polymer homologous series should be proportional to the effective hydrodynamic volume:

$$K_a = B\,V_{eff} \quad (25)$$

where B is a proportionality constant probably related to polymer-solvent interaction. Combining Eqs. (11), (24) and (25) we have:

$$K_m = K_a/M = AB + B[\eta] \quad (26)$$

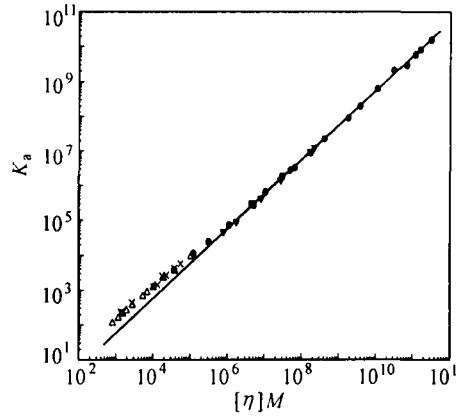

Fig. 3 Variation of molar association constant (K_a) with the hydrodynamic volume ($[\eta]M$) for PS in toluene or benzene
The legends are identical with Fig. 1

It indicates that a linear plot of K_m versus $[\eta]$ for a polymer homologous series permits us to evaluate constants A and B from its intercept and slope. The viscosity constants A and B of polystyrene in various solvents obtained by applying Eqs. (20) and (28) to the literature data of k_H and $[\eta]$ [3, 20~22, 24] are listed in Table 1. The viscosity constants thus obtained for some representative polymers are listed in Table 2.

Table 1. The viscosity constants A and B of polystyrene in various solvents

Solvent	T (℃)	δ (cal/cm^3)$^{1/2}$	A	B	Literature*
Cyclohexane	34.5	8.2	2.859	0.0827	[21-22]
Benzene	25	9.2	4.361	0.0541	[21-22]
Toluene	25	8.9	5.543	0.0533	[3, 20]
Ethylbenzene	40	8.8	10.22	0.0483	[24]
CCl_4	30	8.6	15.68	0.0474	[24]

* The original viscosity data of k_H and $[\eta]$ are taken from the listed literature references

The molar mass dependence of the slope a_1 could be described by these two constants. For example, the Huggins coefficient could be expressed as

$$k_H = 6B\,(1 + A/[\eta]) \quad (27)$$

which could quantitatively explain the behavior shown in Fig. 1. Constants A and B both depend on the nature of the solvent. A minimum and maximum appear at the solubility parameter of polystyrene (around 8.5) in the plots of A and B versus the solvent solubility parameter as shown in Fig. 4.

Table 2. The viscosity constants A and B of some representative polymers

Polymer	Solvent	T(℃)	A	B	Literature*
Polyethylene	*p*-Xylene	100	5.849	0.0835	[31]
Polyvinyl acetate	Acetone	30	7.37	0.0559	[3]
Polyisobutene	Cyclohexane	25	12.56	0.0421	[3]
Polymethylmethacrylate	Benzene	25	23.05	0.0314	[3]

* The original viscosity data of k_H and $[\eta]$ are taken from the listed literature references

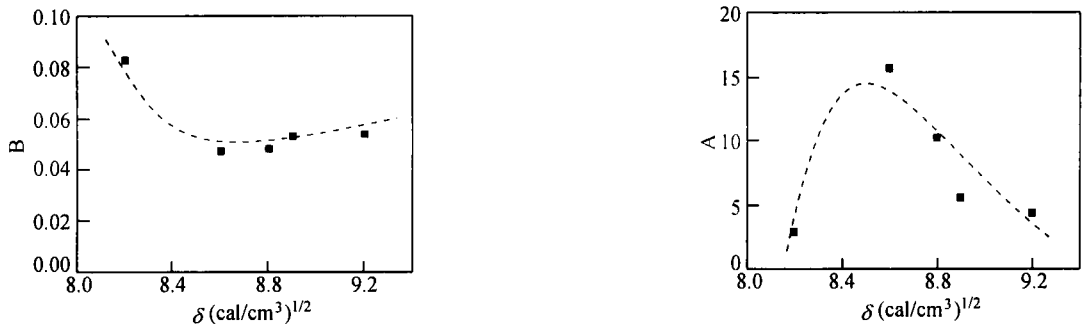

Fig. 4 Variation of viscosity constants A and B with solubility parameter of solvent for polystyrene solution
The dotted line is drawn for guiding the eye

It is worth emphasizing here that the direct proportionality between the K_a deduced from the intercept and slope of the plot of reduced viscosity versus concentration for a polymer homologous series and V_{eff} has great significance. As an example, the double logarithmic plot of K_a versus V_{eff} for polystyrene in benzene and toluene demonstrates this proportionality as shown in Fig. 5. It provides a clue for investigating the behavior of macromolecule in solution via a different route.

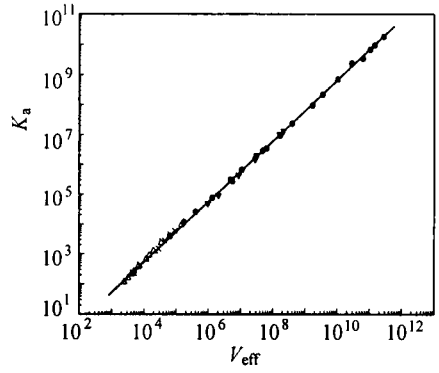

Fig. 5 Variation of molar association constant (K_a) with the effective dynamic volume (V_{eff}) for PS in toluene or benzene
The legends are identical with Fig. 1

BRANCHED POLYMER

It is generally known that branched macromolecules have higher k_H, e.g. amylopectin[25], co-polymers of styrene and divinylbenzene[26~28], copolymers of methylmethacrylate and ethylene bismethacrylate[29], star-branched

polystyrene[30], random branched polyethylene[31], polyvinyl-acetate[32] and styrene-butadiene rubber[33].

Converting the available data of k_H and $[\eta]$ into K_m by Eq. (18), then multiplying it by M to get the K_a, we found that K_a is proportional to the hydrodynamic volume $[\eta]M$ irrespective of whether the macromolecule is branched or linear for a given polymer-solvent system. The data of the linear and branched polymers lie on the same line as shown in Fig. 6. This leads to several important insights into the concept of cluster formation:

1) The self-association behavior of branched polymer is identical with that of linear ones. It means that the molar self-association constant, i.e. the collision probability of a branched macromolecule is the same as that of the linear chain possessing the same hydrodynamic volume; 2) the higher Huggins coefficient of a branched chain originates from the lowering of intrinsic viscosity as compared to the linear chain with the same molar mass; 3) the effect of branching on the slope of the plot of η_{sp} / C versus C resembles the effect of branching on the retention volume in size exclusion chromatography.

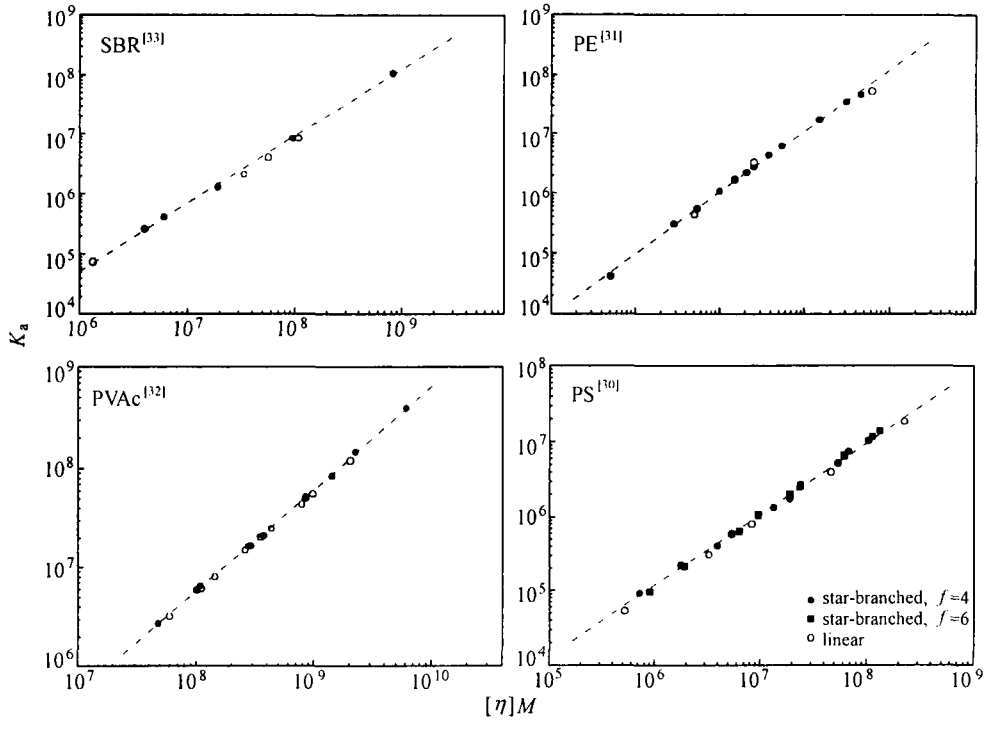

Fig. 6 Variation of K_a with hydrodynamic volume ($[\eta]M$) for some linear and branched polymers
The solid circle represents branched polymers, the open circle represents linear polymers

With these findings in mind, it is easy to deduce that Eq. (25) is applicable both to linear and branched polymer. A branched polymer chain, owing to its higher segmental density in solution, will possess smaller hydrodynamic volume and hence smaller intrinsic viscosity as compared to that of linear polymer with the same molar mass. Conventionally, a branching parameter g' is defined as:

$$g' = [\eta]_{br} / [\eta]_{li} \tag{28}$$

where $[\eta]_{br}$ and $[\eta]_{li}$ are the intrinsic viscosities of the branched polymer and linear polymer with the same molar mass, respectively. For a linear polymer with a definite molar mass M_{li} and intrinsic viscosity $[\eta]_{li}$, $(k_H)_{li} = 6B(1+ A/[\eta]_{li})$. Assuming the intrinsic viscosity of a branched polymer with the same molar mass M_{li} is $[\eta]_{br}$ $(k_H)_{br} = 6B(1 + A/[\eta]^*_{li})$, where $[\eta]^*_{li}$ is the intrinsic viscosity of a linear polymer with the same hydrodynamic volume as the branched polymer with M^*_{li}, i.e.

$$[\eta]_{br} M_{li} = [\eta]^*_{li} M^*_{li} \tag{29}$$

Introducing the branching parameter g' and neglecting the difference between M^*_{li} and M_{li}, we have:

$$(k_H)_{br} = 6B\,(1 + A / g'\,[\eta]_{li}) \tag{30}$$

and

$$(k_H)_{br} / (k_H)_{li} = (1 + A/g'\,[\eta]_{li}) / (1 + A / [\eta]_{li}) \tag{31}$$

Equation (31) and Eq. (30) indicate that two factors could affect the value of the Huggins coefficient of the branched polymer: the branching parameter g' and $[\eta]_{li}$. These two equations can satisfactorily explain the experimental data of the Huggins coefficient of branched polymer. Figure 7 shows the dependence of the ratio of the Huggins coefficient of star-branched polystyrene in cyclohexane to that of linear polystyrene with the same molar mass on the parameter of branching[30], where the two dashed lines represent the calculated lines according to Eq. (31) with known viscosity constant A and B listed in Table 1 and two fixed $[\eta]_{li}$ values corresponding to the least and highest intrinsic viscosity of the linear sample in cyclohexane. Figure 8 shows the variation of the Huggins coefficients of the randomly branched polyethylene fractions with the branching parameter[31], where the dashed lines are drawn according to Eq. (30) with the viscosity constant A an B listed in Table 2 for two fixed $[\eta]_{li}$ values of the sample fractions.

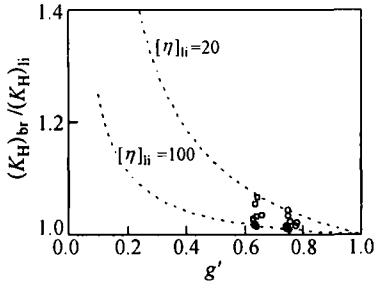

Fig. 7 Branching parameter dependence of the ratio of the Huggins coefficient of star-branched polystyrene in cyclohexane to that of linear polystyrene with the same molar mass
square point: f = 6; circle point: f = 4. Ref. [30]; dash line: calculated according to eq. (31) with known viscosity constant; A and B for polystyrene in cyclohexane listed in Table 1

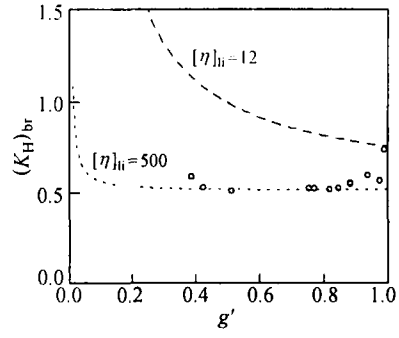

Fig. 8 Variation of k_H of randomly branched polyethylene fractions with branching parameter
The experimental data points are taken from literature [31]; the dash lines are drawn according to Eq. (30) with the viscosity constants A and B listed in Table 2.

From the above discussions, we firmly believe that the problem regarding why and how chain branching affects the slope constants has been clarified. In the sense of self-association or cluster formation of macromolecules in solution, there is no difference between branched and linear polymers. The observed enhancement of the Huggins coefficient for branched polymer originates from the lowering of intrinsic viscosity as compared to that of linear polymer with the same molar mass.

DYNAMIC CONTACT CONCENTRATION

The presence of a boundary concentration to separate a dilute polymer solution into two regimes was first noticed in the early 1950s by many investigators[34~39] as judged from the abnormal behavior of the reduced viscosity versus concentration plot in the very low concentration region. The results of a well-designed experiment carried out later by Ohrn[40, 41] showed that the observed abnormality is caused by the reduction in capillary radius of viscometer due to adsorption of macromolecules. The boundary concentration between a dilute and a semi-dilute solution has been widely accepted as the overlap concentration, C^*, which signifies the starting point of physical contact among the polymer coils in solution as presented by de Genne *et al.*[42, 43]. Qian[44, 45] suggested that there exists a dynamic contact concentration C_s at which the chain segments of the polymer coil start to feel the repulsive interaction between segments of neighboring coils, and the coils start to shrink in dimension when the solution concentration $C > C_s$. The existence of C_s has been confirmed later by precise size exclusion

chromatographic[46] and dynamic light scattering[47] studies. The observed abnormality of reduced viscosity occurs in an extremely dilute concentration region very close to the experimentally found dynamic contact concentration C_s. The conventional theory about the concentration dependency of the viscosity of polymer solution fails to predict the existence of a boundary concentration in this region though recent experimental studies of Dondos[48, 49] still claimed its occurrence. The problem of whether the observed viscosity abnormality is caused by polymer adsorption or originates from the existence of a boundary concentration remains unsolved until a quantitative theoretical treatment on the effect of solute adsorption on relative viscosity measurements appears. According to this theory[19, 50, 51], the experimental measured relative viscosity of a polymer solution relates to the true value as:

$$\eta_{r,exp} = \eta_{r,true}\left(1 + \frac{kC}{C_a + C}\right) \tag{32}$$

where parameter k accounts for the maximum fractional change of the flow time of solvent due to radius reduction and surface property variation of the viscometer capillary caused by polymer adsorption and the particular concentration C_a is the concentration at which the active sites of the contacting wall surface are half occupied by polymer chain segments. If the wall effect on the experimental relative viscosity of a dilute polymer solution is corrected by Eq. (32), the behavior of the resulting corrected reduced viscosity will be normal, i.e. showing a linear dependence of η_{sp}/C on C. However if the abscissa C is expressed on a logarithmic scale, we can see that the value of the reduced viscosity is a constant in the extremely dilute concentration region and only begins to grow at a certain definite concentration. Figure 9 shows such an example. It represents the variation of the reduced viscosity with concentration for poly(ethylene glycol) aqueous solutions measured in a glass capillary viscometer coated with paraffin[51]. A boundary concentration C_s really exists as demonstrated in Fig. 9. The existence of a boundary concentration is readily predictable based on the concept of polymer self-association as described in the preceding sections[18, 19]. Defining the boundary concentration C_s at which the cluster formed by self-association just become noticeable, say as the value of α starts to deviate from zero to 0.001, we have

$$C_s = 0.001 / 2K_m = 0.003 / k_H [\eta] \tag{33}$$

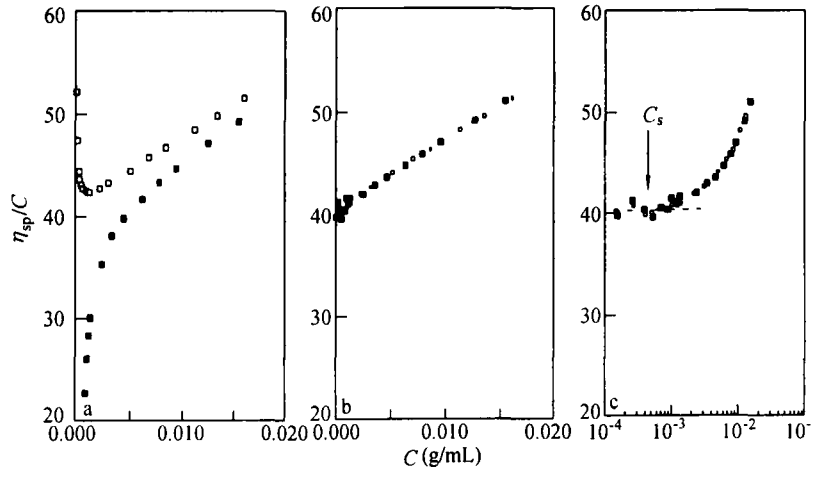

Fig. 9 Reduced viscosity versus concentration plots for PEG aqueous solution measured in a glass capillary viscometer coated with paraffin
open square: original viscometer; solid square: paraffin coated; a) original experimental, b) after correction for wall effects, c) semi-logarithimic plot for the corrected values

This boundary concentration subdivides a dilute polymer solution into an extremely dilute regime in which macromolecules appear as isolated chains and another dilute regime where interchain interactions become operative. The value of C_s lies in the concentration region of 10^{-3} to 10^{-5} g/mL, much lower than the theoretically estimated static overlap concentration C^*. While the particular concentration for polymer adsorption C_a is nearly one order of magnitude lower than C_s[52].

It should be noted here that the linear relationships describing the concentration dependence of the reduced viscosity of a dilute polymer solution, such as Eqs. (4) and Eq. (16), are only ap-plicable to polymer solutions with $C > C_s$. In the extremely dilute concentration region with $C < C_s$, we have:

$$\left| \eta_{sp}/C \right|_{C<C_s} = [\eta] \tag{34}$$

Since the weight fraction of cluster formed in this concentration regime is zero. This prediction is in accordance with the experimental findings reported by Haney[53] using a bridge type differential capillary viscometer. With these facts in mind we may declare that the necessary condition for preparing single polymer chain particulate[54] from a polymer solution is that its concentration must be less than the dynamic contact concentration.

In the preceding sections we have shown that using the apparent association constant K_m instead of the conventional Huggins coefficient k_H to describe the slope of reduced viscosity versus concentration plot of a dilute polymer solution could successfully explain the enhancement of the Huggins coefficient of short chain and branched polymer and could also predict the existence of a boundary concentration to subdivide a dilute polymer solution into two regimes. This success originates from the concept of macromolecule self-association in solution. It is well- known that the viscosity of polymer solution is very sensitive to polymer association. The previous theoretical approaches dealing with this problem[55~60] failed to give a proper explanation for the variation of the Huggins coefficient as noted above. The major reason is that all of them add the contribution of association onto the preexisting Huggins coefficient of the quadratic term and lead to an overestimation of the effect of association. In the present approach we regards the cluster formation as the embodiment of all kinds of interchain interactions.

CONCLUSIONS

The following conclusions are reached: 1) The concentration dependence of reduced viscosity of dilute polymer solution is interpreted in the light of a new concept of self-association of polymer chains. The molar self-association constant is directly proportional to the effective hydrodynamic volume of the polymer chain in solution for a homologous polymer series. 2) The observed enhancement of the Huggins coefficient for short chain and branched polymers is satisfactorily interpreted by a novel simple theoretical approach based on the concept of self-association of macromolecules in solution. The mathematical relationship between the Huggins coefficient and the self-association constant is given. 3) The concept of self-association allows us to predict the existence of a boundary concentration C_s (dynamic contact concentration) which separates a dilute polymer solution into two regimes. In the extremely dilute concentration regime where polymer chains are isolated and do not suffer interchain interaction, the reduced viscosity is the intrinsic viscosity and independent of polymer concentration. In the dilute concentration regime with $C > C_s$, the interchain interaction leads to the cluster formation.

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