

Investigation into the solution properties of hyperbranched polymer

Min Xu, Xiaohu Yan, Rongshi Cheng and Xuehai Yu*

College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210009, People's Republic of China

Abstract: The solution properties of hydroxyl terminated hyperbranched aliphatic polyesters and their acetyl derivatives have been studied by measuring viscosity parameters. The polarity of terminated groups of molecules is the most important factor affecting their properties. The intrinsic viscosity $[\eta]$ cannot reflect the real monomolecular hydrodynamic volume of hydroxyl group-terminated hyperbranched polymer due to the strong intermolecular forces which lead to the formation of stable clusters. The intermolecular association constant K_M depends not only on molecular weight, but also on the polarity of end-groups. However, the dynamic contact concentration C_S can be determined accurately from reduced viscosity *versus* concentration plots. The reason why the intrinsic viscosity does not change linearly with the generation of the hyperbranched aliphatic polyesters is explained using 'free-draining' and 'non-draining' models.

© 2001 Society of Chemical Industry

Keywords: hyperbranched polymer; solution properties; flow model; intermolecular association; viscosity

1. INTRODUCTION

Hyperbranched polymers were first introduced by Flory¹ in 1952, but they have not received much attention until recently.² They may be considered as irregular analogues of dendrimers,³ with well-defined and perfectly branched structures. Though the structures of hyperbranched polymers are a little less regular than those of dendrimers, they can be synthesized much more easily than dendrimers, so in most cases they can take the place of dendrimers. Their unique highly branched structure imparts some unusual properties, e.g. no crystallization, no interchain entanglement and lower melt and solution viscosities than those of linear polymers of the same molar mass.

The large number of terminal functional groups render hyperbranched polymers useful as macroinitiators,⁴ or crosslinking agents; their relatively low melt and solution viscosity properties means they are useful as rheological modifiers.⁵ There are also many possibilities for them in other fields.⁶ However, their chemical and physical properties should be known more fully before they are used in further applications.

Much literature has described the synthesis and physical properties of dendrimers.⁷ Mourey *et al.*⁸ reported the unique solution behaviour of polyether dendrimers, in which the intrinsic viscosity of the dendrimers showed a maximum. Bodna *et al.*^{9,10} studied the solution properties of poly(propylene imine) dendrimers and linear PEO blends. Nunez *et al.*¹¹ studied the solution rheology of hyperbranched polyesters and their blends with linear polymers. Their

investigation was focused on the dilute and semidilute concentration regime, while the knowledge of solution properties in the extremely dilute concentration region of hyperbranched polymers is still poor. Because of their globule-like structure and the high density of end-groups on the molecular surfaces they should show different solution properties than linear polymers. The solution parameters of poly(propylene imine) dendrimers have been studied by our group.¹² Here, the solution properties of hydroxyl terminated hyperbranched aliphatic polyesters and their acetyl derivatives were studied by measuring viscosity parameters. The results showed that the solution properties of hyperbranched polymers are very similar to those of dendrimers. In this paper, we also explain why the intrinsic viscosity of hyperbranched polymer solution does not change linearly with the generation of the hyperbranched aliphatic polyesters. Some interesting phenomena were also found, and some unique rules of hyperbranched polymer solution are given.

2. EXPERIMENTAL

2.1 Materials

Third (3G), fourth (4G) and fifth (5G) generation hydroxyl terminated hyperbranched aliphatic polyesters were purchased from Aldrich (USA), with nominal molecular weights of 3570 g mol^{-1} , 7250 g mol^{-1} and 14600 g mol^{-1} , respectively. Their acetyl derivatives were prepared by acetylation with acetic anhydride in our laboratory and these were

* Correspondence to: Xuehai Yu, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210009, People's Republic of China

E-mail: xyu@nju.edu.cn

(Received 8 January 2001; accepted 27 April 2001)

denoted as G3M, G4M and G5M, respectively. The viscosity properties in dimethyl formamide (DMF) distilled after being dried by 4A molecular sieve were studied by viscometry. Solutions of these samples were prepared by weighing, and filtered through a Millipore filter with pore diameter 0.5 μm to remove dust.

2.2 Instrumentation

IR spectra (KBr disk) were recorded on a Nicolet (USA) 170sx FT-IR spectrometer. A Waters (USA) Model 244 GPC-LC chromatograph which connected with 100 \AA , 500 \AA and 10³ \AA μ -Styragel columns in series was used. The flow rate was kept at 1.0 ml min^{-1} with THF as elution solvent at room temperature. The detector was a Waters model R401 differential refractometer. Detection response was collected and recorded on a personal computer. The column set was calibrated by standard polystyrene samples purchased from Knauer (Germany).

Differential scanning calorimetry (DSC) thermograms were recorded at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ with second scanning in N_2 atmosphere; the temperature ranged from -40°C to 150°C and a Netzsch-DSC 204 (Germany) analyser was used.

2.3 Viscosity

An Ubbelohde viscometer with capillary diameter 0.410 mm was used in all experiments. The experiments were carried out at $30 \pm 0.05^{\circ}\text{C}$. The flow time of a known mass of pure solvent DMF in the clean viscometer was first measured as t_0 . Afterwards, a DMF stock solution with known mass concentration was added successively into the viscometer by weighing, to increase the solution concentration in the viscometer, and the flow times were recorded as t_i values. The stock solutions of these samples were prepared by weighing, and filtered through a Millipore filter with a pore diameter of 0.5 μm to remove the dust before the viscosity measurements. The mass concentration was converted into a mass-volume concentration (mg ml^{-1}) by applying density corrections. The relative viscosity was calculated as the ratio of flow time of solution to that of solvent directly.

3. RESULTS AND DISCUSSION

FTIR spectroscopy was employed to determine qualitatively the extent of acetylation. It clearly indicated that the characteristic peak of hydroxyl at 3500 cm^{-1} almost disappeared in the G3M sample, suggesting that most of the hydroxyl groups had been converted to acetyl groups. The spectra for the higher generations were very similar.

Samples of G3, G4 and G5 were semitransparent brittle solids which were insoluble in less polar solvents such as acetone and THF, whereas G3M, G4M and G5M were transparent syrups, which could easily be dissolved in these solvents. This phenomenon resulted from the change of the strong polar hydroxyl groups to weak polar acetyl groups, which decreased intermolecular interactions. As the consequence, the glass transition temperature of the modified samples decreased to below room temperature. For example, the DSC results showed that the T_g of G5 was 32.6°C whereas that of G5M was -12.7°C . The T_g decreased by about 45°C upon modification.

The solution properties were re-examined by our group both from the theoretical and experimental viewpoints.¹³ Considering the adsorption of the solute onto the capillary surface, the following equation is introduced:

$$\frac{\eta_{\text{sp,exp}}}{C} = \frac{k}{C_a + C} + ([\eta] + 6K_M[\eta]C) \left(1 + \frac{kC}{C_a + C} \right) \quad (1)$$

Here the C_a is a critical concentration at which half of the active points on the capillary surface were covered by adsorbed solutes, K_M is an equilibrium constant which represents the intermolecular association tendency, k measures the thickness of the adsorption layer and $[\eta]$ is the intrinsic viscosity. This equation can satisfactorily describe all the viscosity behaviours from normal concentrations to extremely low range.

The viscosity properties of these hyperbranched samples were explored within a wide concentration range from extremely dilute to several percent. All the experimental data were treated by the above equation using the method suggested by Cheng *et al.*¹⁴ The four parameters of intrinsic viscosity $[\eta]$, C_a , K_M and k can be determined at same time and the results obtained are listed in Table 1. The parameters k and C_a concern the adsorption of solute in polymer solution and will be discussed in another paper. It can be seen that the calculated line with the four determined parameters fitted the experimental points satisfactorily as shown in Fig 1 for the samples G3 and G3M. Several interesting features should be noted when comparing these parameters. Firstly, the intrinsic viscosity $[\eta]$ values of the original hyperbranched samples were even larger than values for acetyl modified samples. Secondly, as shown in Fig 2, the intrinsic viscosity of both original and modified samples did not change linearly with generation number. Thirdly, values of the associating equilibrium constant K_M for modified samples were much lower than those of the original samples; in

Parameter	G3	G3M	G4	G4M	G5	G5M
$[\eta]$	6.07	4.32	6.94	4.81	7.48	4.84
K_M	0.426	0.000	0.507	0.149	0.452	0.0651
C_s	0.0126	0.0405	0.00986	0.0361	0.0181	0.0394

Table 1. Viscosity parameters of hyperbranched polymers

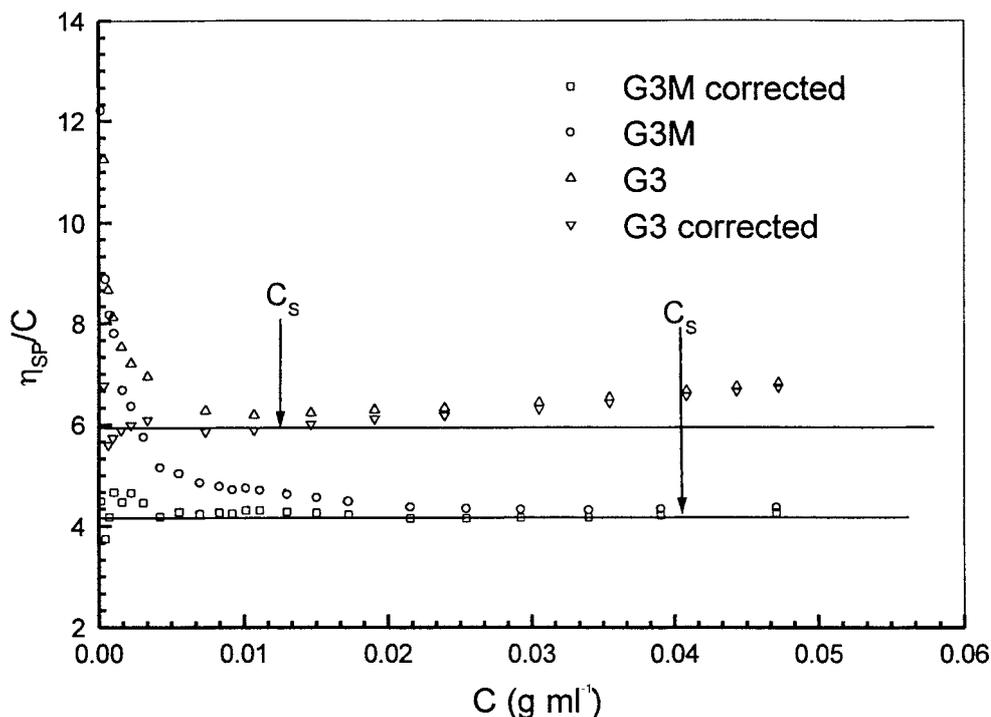


Figure 1. Intrinsic viscosities of all samples.

particular, K_M of G3M approaches zero within the experimental concentration. The generation dependence of K_M is shown in Fig 3. Fourthly, there was a broad level line in the plot of reduced viscosity *versus* concentration when the adsorption effect was corrected, as also shown in Fig 1. These unusual behaviours showed that the hyperbranched polymers are very different from the linear polymer samples.

The intrinsic viscosity is a semi-quantitative measurement of the hydrodynamic volume of polymer in solution according to polymer solution theory. The

larger the intrinsic viscosity, the larger the hydrodynamic volume of polymer under the same experimental conditions. It seems plausible from the data in Table 1, that the acetyl groups on the surface layer should be thicker than the original hydroxyl group layer by simple calculation, but the experimental results showed that the intrinsic viscosity of the modified sample was much lower than that of unmodified sample. This suggested that the stable associations (or clusters) in the original sample solution were formed by hydrogen bonding. As a result,

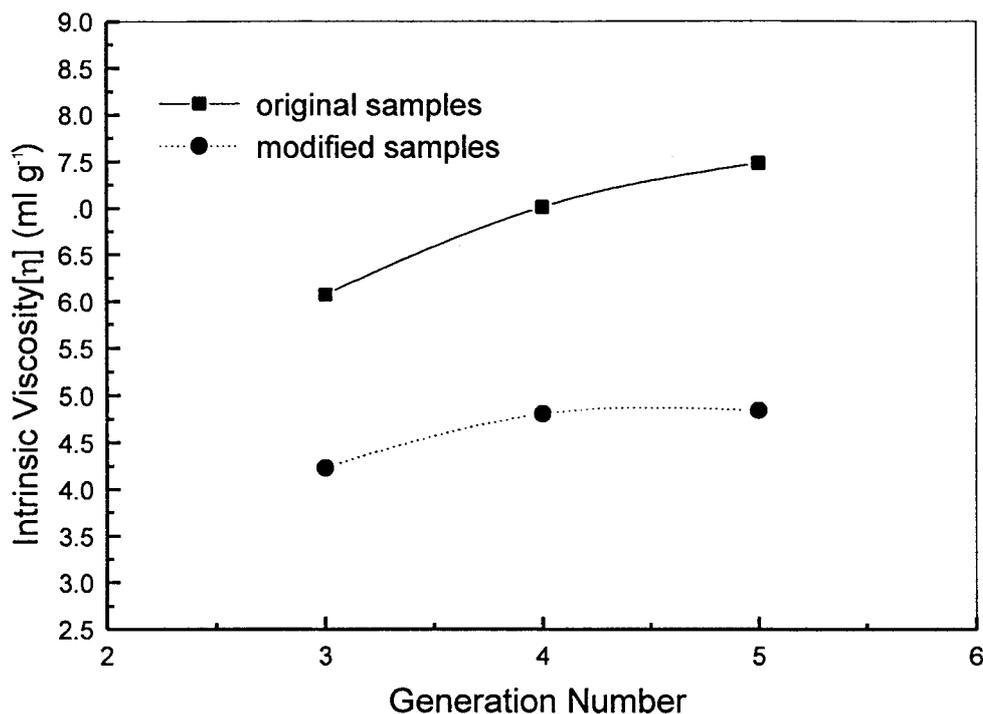


Figure 2. Intermolecular association constants K_M of all samples.

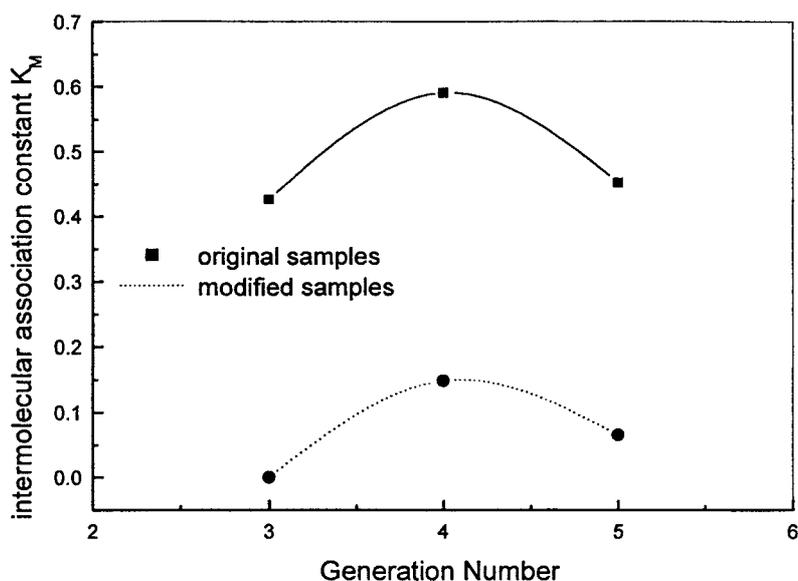


Figure 3. Reduced viscosity plotted versus concentration for G3 and G3M.

the measured intrinsic viscosity was only the apparent value including the monomolecule and the clusters. On the contrary, the real intrinsic viscosity could be obtained when the hydroxyl groups were converted to less polar acetyl groups, which exhibited much weaker van der Waals interaction. Here the important conclusion can be drawn that unrealistic results may be obtained when strong intermolecular interactions are neglected as when the end-groups of dendrimer or hyperbranched polymers are highly polar (such as hydroxyl, amine, etc.). Therefore attention should be paid to explaining such experimental data. For example, the weight average molecular weight in light scattering experiments may be overestimated. The molecular weight distribution may be broader than its real distribution measured by size-exclusion chromatography. Therefore, it is better to convert the end-groups to less polar groups before characterization of the hyperbranched polymer in solution.

The intrinsic viscosity did not change linearly with generation number. This unique behaviour has been found by other workers.^{8,15} The position of the peak changed with different dendrimers or hyperbranched polymers.^{8,15} The curves of Fig 2 have no maximum in intrinsic viscosity observable up to the fifth generation; these results are comparable with those reported for dendrimers.¹⁵ This phenomenon results from the unique chemical structure of hyperbranched polymers. There are still no developed theories to explain such unique behaviour. Lescanec and Muthukumar¹⁶ and Mansfield and Klushin¹⁷ have tried to simulate the viscosity parameters of hyperbranched polymer solution, but their model gave only the upper and lower bounds, the reasons for the observed behaviour are still unknown.

In this paper, we try to explain the phenomenon from the view of a flow model. In low generations, the hyperbranched polymer molecules are still extended and the solvents can drain through them freely; in this

case, the solution behaviour obeys the 'free-draining' model.¹⁸ In subsequent generations, the density of the polymer molecules increases and they can be treated as hard globules; the solvent molecules cannot drain through the hyperbranched polymer molecules freely. In this case, the solution behaviour obeys a 'non-draining' model.¹⁸ Because of the change from the 'free-draining' to the 'non-draining' model, the intrinsic viscosity $[\eta]$ does not increase linearly with generation number; sometimes it even decreases.⁸ SEC has been employed here and the data also agree with this result. According to SEC, the apparent numerical molecular weights of G3M, G4M and G5M are 6041 g mol⁻¹, 9165 g mol⁻¹ and 9038 respectively. It was found that the apparent molecular weight of G5M is even smaller than that of G4M, because SEC determines molecular weight only from the hydrodynamic volume of polymer.

According to the Rouse-Zimm model,¹⁸ the intrinsic viscosity of a polymer can be determined by

$$[\eta] = (N_A b^2 \rho / 6M\eta) \sum_{k=1}^N 1/\lambda_k (1 + i\omega\tau_k) \quad (2)$$

where N_A is Avogadro's number, b is a constant, ρ is a friction constant, M is the molecular weight, η the viscosity of the solvent. τ_k (the relaxation time) is given by $\tau_k = 1/2\sigma\lambda_k$, and ω is the frequency of the applied sinusoidal shear k :

$$k = k_0 e^{i\omega t} \quad (3)$$

For steady flow, $\omega = 0$. Then

$$[\eta] = (N_A b^2 \rho / 6M\eta) \sum_{k=1}^N 1/\lambda_k \quad (4)$$

For the free-draining model,

$$\sum 1/\lambda_k = N^2/6 \quad (5)$$

Then,

$$[\eta] = \frac{N_A b^2 \rho}{36 \eta} \left(\frac{N^2}{M} \right) \quad (6)$$

where N_A , b , ρ and η are constants, so

$$[\eta] \propto \left(\frac{N^2}{M} \right) \quad (7)$$

For an ideal hyperbranched polymer, the molecular weight approximately doubles when the generation number increases by one. Let the bead number double when the molecular weight doubles. If $[\eta]_1$ is constant, then

$$\begin{aligned} [\eta]_2 &= 2[\eta]_1 \\ [\eta]_3 &= 2^2[\eta]_1 \\ [\eta]_4 &= 2^3[\eta]_1 \\ &\vdots \\ &\vdots \\ [\eta]_i &= 2^{i-1}[\eta]_1 \end{aligned}$$

where $[\eta]_i$ means the intrinsic viscosity of hyperbranched polymer of generation i .

For the non-draining model,

$$[\eta] = (N_A b^2 \rho / 6 M \eta) \sum_{k=1}^N 1 / \lambda'_k (1 + i \omega \tau_k) \quad (8)$$

where

$$\lambda'_k = \left(\frac{4h}{N^2} \right) \lambda_k \quad (9)$$

and

$$h = \frac{N^{1/2} \rho}{(12 \pi^3)^{1/2} b \eta} \quad (10)$$

Then

$$[\eta] = (N_A b^2 \rho / 6 M \eta) \frac{N^2 (12 \pi^3)^{1/2} b \eta}{4 N^{1/2} \rho} \sum_{i=1}^N 1 / \lambda'_k \quad (11)$$

where

$$\sum_{i=1}^N 1 / \lambda'_k = 0.586 \quad (12)$$

In the same conditions N_A , b , ρ and η are constants; then

$$[\eta] \propto \left(\frac{N^{3/2}}{M} \right) \quad (13)$$

If $[\eta]_1$ is constant, then

$$\begin{aligned} [\eta]_2 &= 2^{1/2} [\eta]_1 \\ [\eta]_3 &= 4^{1/2} [\eta]_1 \\ [\eta]_4 &= 8^{1/2} [\eta]_1 \\ &\vdots \\ &\vdots \\ [\eta]_i &= (2^{i-1})^{1/2} [\eta]_1 \end{aligned}$$

Hence, if $[\eta]_1$ is the same, according to the 'free-draining' model or the 'non-draining' model, we obtain two different curves, as shown in Fig 4. If the generation number increases, the flow model of hyperbranched polymer dilute solution changes from the 'free-draining' to the 'non-draining' model, and

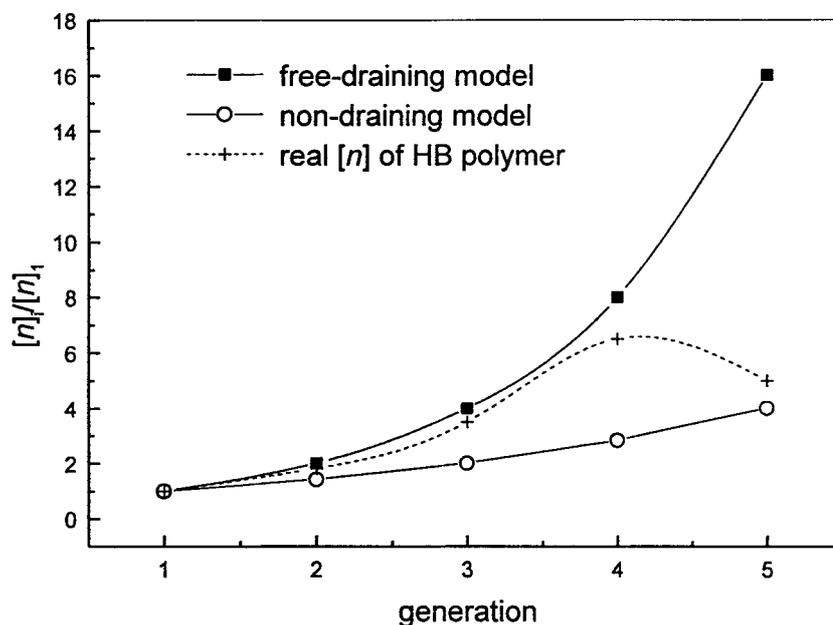


Figure 4. Scheme of intrinsic viscosity versus generation number according to different flow models.

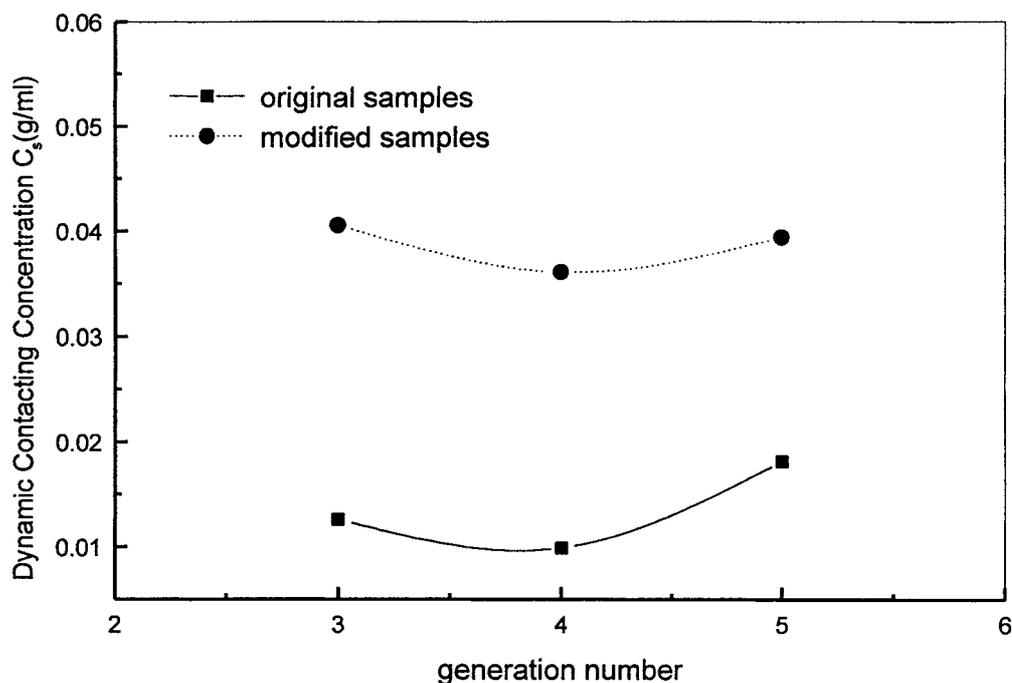


Figure 5. Dynamic contacting concentration C_s of hyperbranched polymers.

the intrinsic viscosity may have a maximum as shown by the dashed line in Fig 4. The obtained theoretical indexes of the 'free-draining' and 'non-draining' models were reached from ideal conditions with some presumptions, so the index values must be different from reality. However, it is certain that the two models must have different indexes: α for the 'free-draining' and β for the 'non-draining' model.

From the above discussion, a conclusion can be drawn: with increasing generation numbers, the density of the molecular surface increases, and the flow model of hyperbranched polymer dilute solution may change from 'free-draining' to 'non-draining', which is why the intrinsic viscosity of hyperbranched polymer solutions does not change linearly with generation number; sometimes even increases first and then decreases. The maximum will be determined by when the flow model changes.

As mentioned above, the reduced viscosity does not depend on the concentration over a relatively wide concentration range. This phenomenon was not easily observed in the usual linear polymer solutions. The unique behaviour of the hyperbranched polyester meets the prediction in the famous Einstein viscosity theory¹⁹. There, the solute molecules should take on a hard globule shape and lack interaction. These two conditions can be fulfilled by hyperbranched polymers, especially by the acetyl-modified samples in the low concentration range. However, the curve would be upward when the concentration increased further. The reason is the polymer molecules are close enough, and get an adequate chance to collide with each other. As a result, an association effect can be detected when the possibility of cluster formation is larger than that of the disassociation of the clusters. Furthermore, the physical picture coincides with the dynamic contacting concentration C_s proposed by Qian *et al*²⁰ from

fluorescence spectra, and then indicated by SEC²¹ and dynamic light scattering experiments.²² This critical concentration characterizes a point at which a polymer molecule would begin to affect the existence of the other polymer molecules when the concentration is higher than C_s . From this point, C_s is lower than the critical overlap concentration C^* as proved by experimental data.²¹ Figure 5 shows the dependence of C_s upon molecular weight. Figure 6 is a comparison of linear polystyrene in a good solvent with the samples studied in this paper. The estimated overlap concentration C^* is also shown in the figure. There were large differences between these two types of polymer both for the absolute value of C_s and for the scaling index as listed in Table 2. The C_s of linear polymer changed with molecular weight linearly, while the C_s of hyperbranched polymer decreased with generation number at first and then increased when the generation number increased. This phenomenon does not meet the scaling index theory. The gap can only come from the unique chemical architectures of the hyperbranched polymer. The intermolecular interactions are mostly limited to the surface layer and do not contribute to intermolecular entanglement. More theoretical work needs to be done in this new area. From Fig 1, another feature should be noted; it is unnecessary to make any extrapolation to zero concentration for the determination of its intrinsic viscosity, because the reduced viscosity is exactly equal to the intrinsic viscosity at any point at low concentrations.

Intermolecular interactions have not been considered because the experimental system has previously been limited to linear polystyrene. The intermolecular interactions in the polystyrene system are the much weaker van der Waals forces. Intermolecular interactions should play an important role in molecular

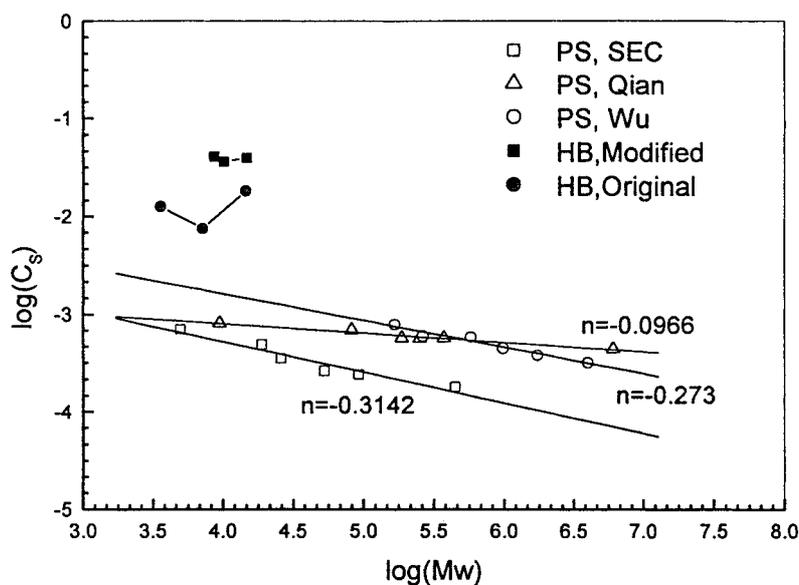


Figure 6. C_s and scaling index for linear and hyperbranched polymers. ■, hydroxyl terminated hyperbranched aliphatic polyester; ●, acetyl derivatives of hyperbranched aliphatic polyester; □, linear polymer decided from SEC by Yan and Cheng;²¹ △, linear polymer decided from EFS by Qian *et al.*²⁰ ○, linear polymer decided from LALLS by Wu.²²

association (or the parameter K_M), and further affect the dynamic contacting concentration C_s as listed in Table 1. If there were no molecular associations, K_M would be zero, as it is in the acetyl-modified G3 system within the explored concentrations. However, the parameter K_M would have a certain value as soon as the cluster formed, as is shown in the other systems. Therefore, the parameter K_M is closely connected to the dynamic contacting concentration C_s . That is to say, the stronger the intermolecular interaction is, the lower C_s is. This is shown by our experimental data. The deviations from the level line in Fig 1 for the hydroxyl end-group samples took place at a lower concentration than that of the corresponding acetyl end-group samples. The generation dependence of the intermolecular interaction parameter (K_M) is very similar to that of the intrinsic viscosity as shown in Fig 3, and this controlled the generation number dependence of the dynamic contacting concentration C_s .

CONCLUSIONS

From the preceding discussions, the following conclusions were reached:

- (1) The physical state of hyperbranched polymer depends mainly on the polarity of terminal groups. The glass transition temperature will decrease with the decrease in polarity of the surface end-groups.
- (2) Much attention should be paid to the study of the solution properties of hyperbranched polymers if the end-group is highly polar such as hydroxyl, etc. The experimental data may lead to the wrong conclusions, such as whether the clusters exist in solution. Here, intrinsic viscosity $[\eta]$ of the acetyl modified aliphatic hyperbranched polymer is much lower than that of the corresponding hydroxyl end-group samples.

- (3) From the view of the flow model, the unique viscosity behaviour is explained. The non-linear trend (or maximum) of intrinsic viscosity comes from the flow model changing from 'free-draining' to 'non-draining'.
- (4) The results suggest that it is unnecessary to extrapolate to zero concentration to calculate the intrinsic viscosity, because the reduced viscosity is exactly equal to the intrinsic viscosity in the dilute regime.
- (5) The hyperbranched polymer with the fewer polar end-groups gives a suitable model system for examining the viscosity theory. The dynamic contacting concentration can be easily defined in the plot of the reduced viscosity *versus* concentration. The big difference in the dependence of C_s on its molecular weight for hyperbranched polymer can be attributed to its chemical architecture.
- (6) Intermolecular interactions should be taken into consideration when the solution properties are explored. The dynamic contacting concentration C_s and the association equilibrium constant K_M depend on not only the generation number (or molecular weight) but also the intermolecular interaction force.

REFERENCES

- 1 Flory PJ, *J Am Chem Soc* 74:2718–2723 (1952).
- 2 Malmstrom E and Hult A, *J Macromol Sci C* 37:555–579 (1997).
- 3 Newkome GR, *Advances in Dendritic Molecules*, Vol 1, JAI Press, Greenwich, CT (1994).
- 4 Kim YH and Webster OW, *J Am Chem Soc* 112:4592–4593 (1990).
- 5 Johansson M, Malmstrom E and Hult A, *J Polym Sci Part A Polym Chem* 31:619–624 (1993).
- 6 Kim YH, *J Polym Sci Part A Polym Chem* 36:1685–1698 (1998).
- 7 Tomalia DA, Naylor AM and Gaddard III WA, *Angew Chem Int Ed Engl* 29:137–175 (1990).

- 8 Mourey TH, Turner SR, Rubinstein M, Fréchet JMJ, Hauker CJ and Wooley KL, *Macromolecules* **25**:2401–2406 (1992).
- 9 Bodnar I, Silva AS, Deicher RW, Weisman NE, Kim YH and Wanger NJ, *J Polym Sci Part B Polym Phys.* **38**:857–873 (2000).
- 10 Bodnar I, Silva AS, Deicher RW, Weisman NE, Kim YH and Wanger NJ, *J Polym Sci Part B Polym Phys.* **38**:874–882 (2000).
- 11 Nunez CM, Chiou BS, Andray AL, Khan SA, *Macromolecules* **33**:1720–1726 (2000).
- 12 Xu M, Yan XH and Yu XH, *Chem J Chin Univ* **22**:703–705 (2001).
- 13 Yang Y, Cheng RS and Yan XH, *J Macromol Sci Phys B* **38**:237–249 (1999).
- 14 Cheng RS, Yang Y and Yan XH, *Polymer B* **12**:3773–3779 (1999).
- 15 Scherrenberg R, Coussens B, Vliet P, Edouard G, Brackman J, Brabander E and Maneusen K, *Macromolecules* **31**:456–461 (1998).
- 16 Lescanec RL and Muthukumar M, *Macromolecules* **31**:2280–2288 (1990).
- 17 Mansfield ML and Klushin LI, *J Phys Chem* **96**:3994–3998 (1992).
- 18 Zimm BH, *J Chem Phys* **24**:269–278 (1956).
- 19 Yamakawa H, *Modern theory of polymer solution*, 252–273, Harper & Row, NY (1971).
- 20 Qian R, Cao T, Chen S and Bai F, *Chin Sci B* **12**:1080–1087 (1983).
- 21 Cheng R and Yan X, *J Appl Polym Sci Appl Polym Symp* **48**:123–132 (1991).
- 22 Wu C, *J Polym Sci Part B Polym Phys* **32**:1503–1509 (1994).