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Intrinsic Viscosity Variation in Different Solvents for Dendrimers and Their Hybrid Copolymers with Linear Polymers

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ABSTRACT: The intrinsic viscosity of narrow molecular mass distribution polystyrene standards, poly(benzyl) ether dendrimers, and their hybrid block copolymers was measured in a variety of solvents. The relative change in the intrinsic viscosity for all these polymers was almost equivalent, indicating that poly(benzyl ether) dendrimers expand and contract quite readily with a change in solvent. The intrinsic viscosity maximum for all polymers was found to occur at essentially the same solvent solubility parameter demonstrating that the thermodynamic interaction with the selected range of solvents was also equivalent. The intrinsic viscosity for hybrid copolymers in a good solvent for both components was found to fall well below the intrinsic viscosity for neat polystyrene at intermediate molecular masses. Below and above this mass range the intrinsic viscosity was quite similar to polystyrene. Yet, the transition for intermediate to high molecular mass behavior was quite sharp as seen through a rapid intrinsic viscosity rise at 60−70 kDa. A poorer solvent for the dendrimer, one where the dendrimer intrinsic viscosity was found independent of generation number, produced the same intrinsic viscosity for the hybrid copolymer and virgin polystyrene. This unique behavior is due to novel interactions between the linear polystyrene block and the highly branched dendritic block which is a function of the solvent environment.

Introduction

Dendritic polymers are a new class of synthetic macromolecules with a range of unique and potentially interesting features, the most prominent of which is a highly branched, three-dimensional architecture.[1−5] Another special feature of dendritic macromolecules is that they have an essentially monodisperse structure with a precisely controlled number of functional groups, either at the chain ends or at the focal point or core.[6,7] This accurate control over the number and placement of functional groups permits the synthesis of a novel family of block copolymer, hybrid dendritic−linear systems in which a dendrimer is covalently attached to a linear polymer to give a diblock copolymer structure. The structural versatility also permits triblock and multiblock copolymers to be prepared with a variety of different linear/dendrimer arrangements.[8−10] These copolymers are intriguing since they combine the highly branched structure of dendrimers and a linear polymer in a single system with the potential to create unique macromolecules with a radical change in the branching structure along the molecular contour.

The synthesis and properties of hybrid dendritic−linear block copolymers have been studied before;[11−15] however, one of the most fascinating studies has been an examination of stimuli-responsive poly(benzyl ether) dendrimer−linear poly(ethylene oxide), PEO, hybrid diblock copolymers by Gitsov and Fréchet. Significantly, the molecular conformation was shown to be highly dependent on the surrounding solvent and the intrinsic viscosity of the hybrid was lower than that of pure PEO at higher molecular masses.[9] The solvent used was tetrahydrofuran, THF, a marginal solvent for PEO and a good solvent for the dendrimer. Further data on various triblock copolymers, dendrimer−PEO−dendrimer, also supported these observations and in a good solvent for PEO (1:1 water:methanol), which is a very poor solvent for the dendrimer, insoluble compounds were obtained when the PEO block was small and/or the dendrimer block large. However, at a critical size the block copolymer was soluble, and this behavior was explained by the formation of a monomicelle with the PEO shielding the insoluble dendrimer when its relative size was large enough. Note the hydrodynamic radius was smaller than virgin PEO in most cases. In this study, we address whether hybrid copolymers show similar intrinsic viscosity and hydrodynamic radius results when a good solvent for both the linear and dendrimer blocks is used.

In addition, the effect of solvent quality on the intrinsic viscosity of dendrimers and hybrid copolymers is investigated. Several numerical simulations have shown dendrimers can significantly change their size with the nature of the solvent. Murat and Grest[16] found the radius of gyration, R_g, changed dramatically with solvent quality using molecular dynamic simulations. Also, Welch et al.[17] showed a similar effect with R_g changing by a large amount depending on temperature and generation number. Finally, in a related study with dendritic polyelectrolytes, Welch and Muthukumar[18] found R_g could be changed to a large degree by the solvent salt concentration. Thus, it appears from these simulations that the surrounding solvent environment can greatly change the dendrimer size and hence the accessibility of the dendrimer's interior to guests, solvents, etc.

Experimental evidence of the dendrimer size and/or excluded volume change has been gathered through a combination of small-angle neutron scattering (SANS)

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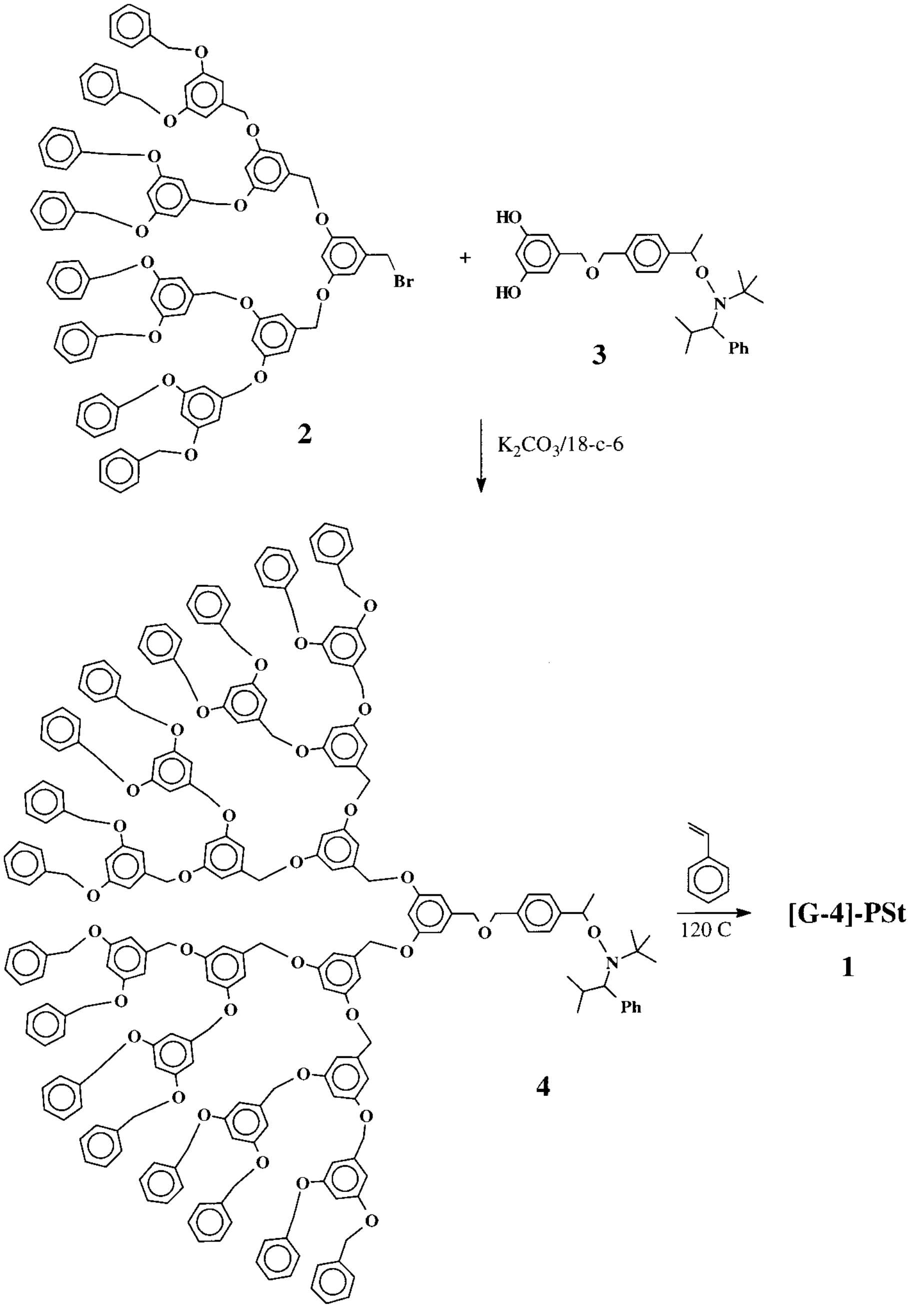
Scheme 1



and rheological measurement[19] and SANS alone.[20,21] Bodnar et al.[19] discuss possible excluded volume and size changes when dendrimer concentration is increased in solution. Topp et al.[20] argued that the dendrimers reduced in size when the dendrimer solution concentration was increased. Presumably and quite remarkably this may be the result of similar effects causing the reduction of linear polymer R_g values when in a good solvent.[22] Crudely, one can describe this phenomenon as the polymer volume is swollen when in a good solvent and in semidilute solution. Since a polymer in bulk form adopts a θ-configuration,[23] the volume or R_g must decrease with polymer concentration. This argument presumes dendrimers must swell in a good solvent; as mentioned above, this is a primary motivation for the present study. Finally, using SANS, Evmenenko et al.[21] showed R_g changed (very) slightly with a change in solvent for 1% solutions of poly(benzyl ether) dendrimers although the results depended on dendrimer generation.

Experimental Section

Materials. Poly(benzyl ether) dendrimers were prepared according to a previous procedure.[24] The third [G-3] generation bromides (**2**, see Scheme 1) were coupled with a hydroxymethyl-functionalized alkoxyamine initiator (**3**).[25] The purified fourth [G-4] dendritic initiators (**4**) were then used to prepare the corresponding hybrid dendrimer−linear block copolymers (**1**) by standard living free radical conditions. Hybrid copolymers with a [G-3] dendrimer were prepared in a similar manner. The degree of polymerization of the linear polystyrene blocks could be simply controlled by the molar ratio of dendritic initiator to monomer.[26] The molecular masses of the hybrid dendritic−linear block were measured by ^{1}H NMR spectroscopy, taking advantage of the exact molecular weight of the dendrimer coupled with the presence of only one dendrimer per chain. Table 1 presents the sample codes and molecular masses for the various dendrimers studied. Narrow molecular mass polystyrene standards (Scientific Polymer Products) were used as received. The supplier-listed number-average molecular masses and polydispersity indices are given in Table 1.

Table 1. Number Average Molecular Mass (*M*) of Compounds Used in This Study[a]

sample code	*M*-dendrimer (Da)/*M*-polystyrene (kDa)/*M* (kDa)	PDI[b]	sample code	*M*-dendrimer (Da)/*M*-polystyrene (kDa)/*M* (kDa)	PDI[b]
G3	1592/0/1.592	~1.0	G4-PS-91K	3288/87.7/91.0	1.15
G4	3288/0/3.288	~1.0	PS12.4K	0/12.4/12.4	1.06
G5	6687/0/6.687	~1.0	PS15.8K	0/15.8/15.8	1.05
G3-PS-11K	1592/9.4/11.0	1.12	PS18.1K	0/18.1/18.1	1.07
G3-PS-31K	1592/29.4/31.0	1.18	PS28.9K	0/28.9/28.9	1.01
G4-PS-14K	3288/10.7/14	1.12	PS41.2K	0/41.2/41.2	1.07
G4-PS-40K	3288/36.7/40	1.15	PS64.9K	0/64.9/64.9	1.17
G4-PS-46K	3288/42.7/40	1.09	PS107.7	0/107.7/107.7	1.04
G4-PS-59K	3288/55.7/59	1.11	PS109.9K	0/109.9/109.9	1.04
G4-PS-70K	3288/66.7/70	1.15			

[a] *M*-dendrimer represents the mass of the dendrimer; *M*-polystyrene, mass of the polystyrene and *M*, total mass. [b] The polydispersity index, PDI, is defined as the weight to number-average molecular mass ratio.

Preparation and Measurements. Solutions were prepared with filtered pure solvent at least 1 day before measurement. Subsequent solution filtration was carried out using a syringe with 1 μm filters; the amount of polymer lost was assumed to be negligible. The polymer solution concentration was measured in mass−polymer/volume−solution (c_2) by taking a known solution volume, evaporating the solvent and determining the residual mass of polymer. Intrinsic viscosities were measured with a Ubbelohde viscometer (size 0C) at 30 °C according to ASTM D446-93. Four concentrations were used for each polymer (measured to 0.66% accuracy) and flow time measurements were conducted in triplicate for each concentration (measured to ~1% accuracy depending on flow time) to determine the intrinsic viscosity. Solution specific volume (V_{sp} in cm^3/g) was measured with a 10 mL capacity pycnometer, calibrated with distilled water, to correct for solution hydrostatic head differences in the intrinsic viscosity measurement (measured to 0.04% accuracy).

The pycnometer−concentration data were also used to determine the polymer partial molar volume, V_2, in solution through[27]

$$V_2 = V_{\mathrm{soln}} - x_1(\partial V_{\mathrm{soln}}/\partial x_1)_{T,P}$$

where x_1 is the solvent mole fraction and V_{soln}, the solution molar volume. The x_1 was calculated via $w_1[M_2/M_1]/\{w_1[M_2/M_1] + w_2\}$, where w_i is the mass fraction of solvent (1) or polymer (2) and M_i is the associated molecular mass. The w_2 was determined from c_2V_{sp}. Numerical derivatives of the data were taken according to the above equation, and the partial molar volume at infinite dilution was determined. In fact, V_2 was found to be essentially constant over the very dilute concentration range used and thus extrapolation was not required since an average sufficed. This volume was converted to more convenient units of volume/mass by dividing with the molecular mass to arrive at the quantity denoted as the thermodynamic volume, V_{th} (cm^3/g).

Five solvents were purchased from Aldrich and used in the intrinsic viscosity and volume measurements. Each solvent had a different solubility parameter (δ in (cal/cm^3)$^{1/2}$ at 25 °C[28]) shown in parentheses: ethylbenzene (8.8), toluene (8.9), tetrahydrofuran or THF (9.1), benzene (9.2) and chloroform (9.3).

Results and Discussion

Dendrimers and Linear Polystyrene. The volume change or swelling of linear polymers with solvent type is well-known.[29] One measure of molecular volume is the intrinsic viscosity; indeed, there are many types of volume to quantify a polymer in dilute solution,[30] yet this is a reasonable and self-consistent one. A technique to determine the polymer solubility parameter is to plot the intrinsic viscosity vs the solvent solubility parameter.[31] The solvent creating the greatest intrinsic viscosity (volume) is assumed to have the same solubility parameter as the polymer. We have used this technique to find a solvent that is good for both polystyrene and poly(benzyl ether) dendrimers and to determine how much the molecular volume will change with solvent quality.

Figure 1a shows the intrinsic viscosity ([η]) for the dendrimers and two polystyrene standards vs solvent solubility parameter (δ). The intrinsic viscosity is made dimensionless with that at the maximum to compare each polymer's relative volume change. The intrinsic viscosity values are given in Table 2 together with their hydrodynamic radii determined from the intrinsic viscosity.[5] One can clearly see that dendrimers and linear polystyrene all change by almost the same relative amount. Furthermore, [η] displays a maximum at similar values of the solubility parameter, 9.1 (cal/cm^3)$^{1/2}$ (THF) or 9.2 (cal/cm^3)$^{1/2}$ (benzene), for both linear polystyrene and the dendrimers. This indicates the polymers' solubility parameter is essentially 9.1−9.2 (cal/cm^3)$^{1/2}$ and equivalent to that frequently quoted for polystyrene.[28] Thus, polystyrene and poly(benzyl ether) dendrimers are most swollen in THF and benzene, and toluene is an almost equally good solvent. Note that the θ-temperature for the dendrimers in THF is probably much below 30 °C since [η] decreases with temperature as shown in Table 2 (see the discussion by Flory[29] on page 623).

Using the intrinsic viscosity−molecular mass relation discussed by Fox and Flory[32] for low molecular mass polystyrene in benzene at 25 °C ([η](cm^3/g) = 0.0417 M(Da)$^{0.60}$) one finds the intrinsic viscosity of polystyrenes with equivalent molecular mass to G3 and G4 are 3.5 and 5.4 cm^3/g, respectively. The slight temperature difference is not expected to produce a significant effect on the intrinsic viscosity, so the dendrimers appear to have a similar intrinsic viscosity to linear polystyrene in an equivalent solvent (see Table 2).

The G5 dendrimer shows a slightly different swelling behavior in benzene. The solvent THF is the best swelling solvent for all dendrimers while benzene is a much worse swelling solvent for G5 than for either G3 or G4. This may highlight the difference in thermodynamic interactions between a given solvent and chemically similar dendrimers when the generation is varied. Interestingly, difference in behavior between various generation dendrimers has been noted for a number of other physical properties in Fréchet-type dendrimers as well as other dendritic systems. For example, Hawker et al.[33] found a discontinuity in the core nanoenvironment on going from one generation to the next by solvatochromic studies and the observed change in

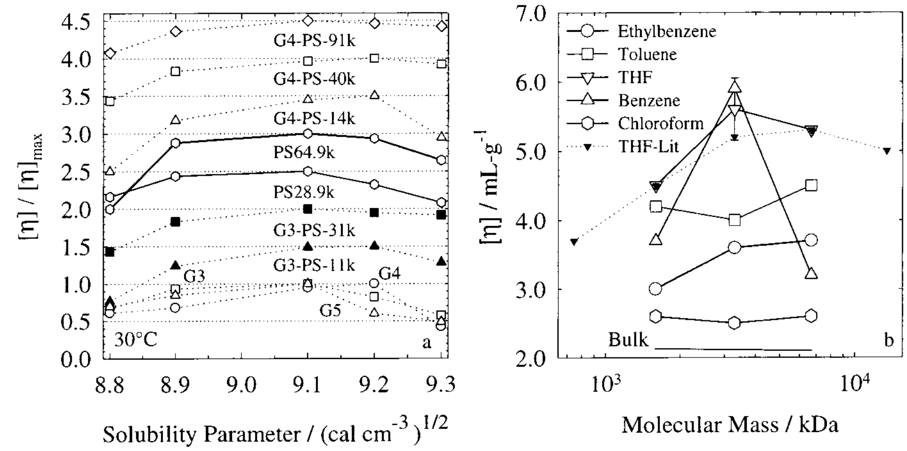


Figure 1. (a) Intrinsic viscosity normalized to the maximum intrinsic viscosity vs solvent solubility parameter for the dendrimers, linear polystyrene and hybrid copolymers. The open squares are data for G3, the open circles, G4, and the open triangles, G5. For clarity, a multiple of 0.5 was added to the polystyrene and hybrid copolymers' data. All results at 30 °C. From left to right the solvents correspond to: ethylbenzene, toluene, THF, benzene and chloroform. (b) Intrinsic viscosity for the dendrimers in various solvents at 30 °C as a function of molecular mass. The curve labeled THF−Lit represents data for G2−G6 dendrimers in THF from Mourey et al.,[5] these data agree well with that presented here. An example (maximum) error bar is shown for our G4 dendrimer data in THF. The line labeled "Bulk" represents the intrinsic viscosity determined from the bulk polymer density as described in the text.

Table 2. Intrinsic Viscosity (cm^3/g) for the Polymers Used in This Study as a Function of Solvent Type at 30 °C[a]

solvent	δ(cal/cm^3)$^{1/2}$	G3	G3-PS-11K	G3-PS-31K	PS-28.9K	PS-64.9K
ethylbenzene	8.8	3.0 (0.91)	2.5 (1.63)	7.7 (3.36)	14.5 (4.05)	
toluene	8.9	4.2 (1.02)	6.9 (2.29)	14.8 (4.18)	20.5 (4.56)	32.5 (6.95)
THF	9.1	4.5 (1.04)	9.2 (2.52)	17.8 (4.44)	21.9 (4.65)	36.9 (7.25)
benzene	9.2	3.7 (0.98)	9.3 (2.53)	16.9 (4.36)	18.0 (4.36)	34.5 (7.09)
chloroform	9.3	2.6 (0.87)	7.3 (2.34)	16.3 (4.31)	12.7 (3.88)	23.8 (6.26)
solvent	δ(cal/cm^3)$^{1/2}$	G4	G4-PS-14K	G4-PS-40K	G4-PS-46K	G4-PS-59K
ethylbenzene	8.8	3.6 (1.23)	4.9 (2.22)	10.4 (4.04)		
toluene	8.9	4.0 (1.28)	9.3 (2.74)	15.6 (4.63)		
THF	9.1	5.6 (1.43)	10.8 (2.88)	18.1 (4.86)		
benzene	9.2	5.9 (1.45)	11.2 (2.92)	17.4 (4.80)	20.2 (5.29)	23.4 (6.03)
chloroform	9.3	2.5 (1.09)	10.3 (2.84)	16.7 (4.74)		
solvent	δ(cal/cm^3)$^{1/2}$	G5	G4-PS-70K	G4-PS-91K		PS12.4K
ethylbenzene	8.8	3.7 (1.57)				
toluene	8.9	4.5 (1.68)		48.8 (8.90)		
THF	9.1	5.3 (1.78)		49.6 (8.95)		
benzene	9.2	3.2 (1.50)	37.2 (7.45)	44.7 (8.65)		9.20 (2.63)
chloroform	9.3	2.6 (1.40)		28.0 (7.40)		6.82 (2.38)
solvent	δ (cal/cm^3)$^{1/2}$	PS15.8K	PS18.1K	PS41.2K	PS107.7K	PS109.9K
benzene	9.2	11.4 (3.06)	12.2 (3.27)	23.5 (5.36)		50.3 (9.57)
chloroform	9.3				28.3 (7.85)	
solvent	T (°C)	G2	G3	G4	G5	G6
THF[b]	30	3.7 (0.76)	4.5 (1.04)	5.2 (1.40)	5.3 (1.78)	5.0 (2.20)
THF[b]	40	2.8 (0.69)	3.5 (0.96)	3.9 (1.27)	-	-

[a] Also included is the hydrodynamic radius (nm) in the parentheses calculated as described in the text. The solubility parameter at 25 °C (δ) is shown for each solvent. [b] Data from Mourey et al.[5] and Gitsov and Fréchet[9] is given for poly(benzyl ether) dendrimers in THF at two temperatures.

swelling behavior/molecular conformation may be intimately linked.

The results in Figure 1a are quite remarkable and demonstrate the dendrimers used here can change volume as predicted through simulation. Yet, the volume change may not be as much as predicted. For example, Murat and Grest[16] showed a volume change with solvent quality based on R_g on the order of 5−25 times, depending on generation, while the results in Figure 1a show a more moderate change of a factor of 2.

The results for the solvent THF gathered here are similar to those of Mourey et al.[5] validating our experimental technique and revealing the unique intrinsic viscosity−molecular mass relation as shown in Figure 1b. The argument for the maximum relies on the ratio of molecular hydrodynamic volume (v_h) to molecular mass (M) to determine the intrinsic viscosity ($[\eta] = {}^5/_2 v_h/N_A M$, for hard spheres, where N_A is Avogadro's number).[5] The molecular mass scales as $N_b{}^g$, with N_b being the branch multiplicity (two here) and g the generation number. The assumption in this model is that each generation contributes linearly to the radius so v_h scales as g^3, it is simple to show $[\eta]$ scales as $g^3/N_b{}^g$. This result has a maximum at a generation of $3/\ln(N_b)$, or between the fourth and fifth generations for the dendrimers used here, and agrees very well with the experimental results with THF as the solvent. Linear addition to the radius with each generation is questionable and assuming a Gaussian distribution of the branching units[34,35] one can find $[\eta]$ scales approximately as $[g - 1]^{3/2}\ N_b{}^{[g+1]/2}$ for generation three and above. This relation does not represent the data in THF well and in fact has an ever increasing $[\eta]$, so it appears as if in a good solvent linear addition of each generation to the hydrodynamic radius is a good approximation.

The intrinsic viscosity−molecular mass relation depends on the solvent. A poorer solvent such as chloroform has a lower intrinsic viscosity independent of molecular mass. Chloroform is classified as a poorer solvent since the intrinsic viscosity is effectively half that in THF (Figure 1b). We can write the intrinsic viscosity ($[\eta]$) as

$$[\eta] = {}^5/_2 V_\eta \qquad (1)$$

where V_η is a hydrodynamic specific volume (cm^3/g).[29] Since $[\eta]$ is independent of mass in chloroform one can discern V_η is constant and the hydrodynamic radius scales with $M^{1/3}$. Thus, since the molecular density is constant with generation, collapsed behavior is found in this solvent. We have measured the bulk specific volume (V) for these dendrimers to be: 0.8518 cm^3/g (G3), 0.8416 cm^3/g (G4) and 0.8321 cm^3/g (G5),[36] and inserting these values into eq 1 one finds the line labeled “Bulk” in Figure 1b. The intrinsic viscosity calculated this way is slightly lower than the experimental values and thus the molecular density in this solvent is lower than the bulk. (N.b.: These are the bulk specific volumes at 30 °C; since the glass transition temperature is above this temperature,[37] these specific volumes can change depending on thermodynamic history. However, the bulk specific volume would have to be ~1 cm^3/g for the calculated intrinsic viscosity to follow eq 1 and this is outside of the range measured in experiment.) Since chloroform has a specific volume lower than the bulk dendrimers (~0.67 cm^3/g) one cannot fully explain the difference in terms of solvent penetration into the molecule. Below we discuss likely causes for the difference and present other possibilities in Appendix 1.

Three possible effects that could explain the difference are biased experimental error, the molecular density in solution is different to the bulk and/or the molecule is not spherical. The first effect is dismissed since a biased measurement time error on the order of 10−20 s would be needed, and our results in the solvent THF agree well with those from another group. The second effect is possible if the solution molecular specific volume is ~1.0 cm^3/g, which is higher than the bulk. One way this can be true is if the dendrimers interpenetrate in the bulk to make the bulk density higher than the collapsed molecular density in solution; this is discussed in Hay et al.[36] and is certainly a possibility.

The third possibility is that the dendrimers are not spherical in solution and using relations derived by Brenner[38] reveals an equation such as

$$[\eta] = CV$$

applies, where C is a nonnegative function of axis dimension ratio (r_p). For example, the values of C can be represented by the following two approximate empirical relations:

prolate spheroids ($1 \le r_p \le 5$):

$$C = 2.5\ \exp(0.185[r_p\text{-}1])$$

oblate spheroids ($0.2 \le r_p \le 1$):

$$C = 2.5 + 0.528[1/r_p - 1]$$

Thus, for either geometry the intrinsic viscosity will be significantly increased above the value for a sphere. An oblate spheroid is disklike in nature and letting the molecular density equal the bulk one finds a particle aspect ratio of 0.53 is required for this geometry to represent the dendrimer in solution. Should the dendrimers form a prolate spheroid (rodlike) in solution then an aspect ratio of 1.9 is required. We cannot postulate whether a nonspherical collapsed molecule is present and leave it as a possibility. Other experimental techniques could reveal which of the final two possibilities occur.

In summary, we have shown the intrinsic viscosity maximum for G3 and G4 dendrimers occurs essentially at the same solubility parameter as that for linear polystyrene. Thus, the two polymers' solubility parameters are the same for the range and types of solvents used. Also, linear polystyrene has the same intrinsic viscosity as G3 and G4 dendrimers at equivalent molecular mass in benzene. The fifth generation dendrimer, G5, shows some unusual properties by changing volume much more in benzene than the other, lower generations. Results below are gathered in benzene as the solvent; however, data for hybrid copolymers made from G5 are not presented. Figure 1 shows benzene is similar in swelling behavior for either polystyrene or G4 and so we believe this demonstrates similar solvent−polymer interactions. Remarkably, the intrinsic viscosity−molecular mass relation for dendrimers can change significantly with solvent type. In fact, it appears as if a collapsed molecule, spherical or otherwise, is present when the solvent is chloroform and the intrinsic viscosity is independent of molecular mass.

Hybrid Copolymers. The relative intrinsic viscosity change for the hybrid copolymers is shown in Figure 1a. The smaller molecular mass hybrids seem to show a larger change in intrinsic viscosity at lower solubility parameter, however, PS64.9K shows similar behavior and this change may not be significant. The larger molecular mass hybrids show a very slight volume change at the largest solubility parameter, 9.3 (cal/cm^3)$^{1/2}$ (chloroform). Clearly, the hybrid copolymers interact differently with the solvent chloroform and this could be a factor in explaining the results below.

The most striking observation is the intrinsic viscosity−molecular mass data plotted in Figure 2a for the solvent benzene at 30 °C, a relatively good solvent for both hybrid components. Here it is seen that the intrinsic viscosity of intermediate molecular mass hybrid copolymers deviate significantly from linear polystyrene. Also included in this figure is our data for polystyrene standards which agree well with relations from Brandrup and Immergut[28] and Fox and Flory.[32] (N.b.: We obtain $[\eta](\text{cm}^3/\text{g}) = 1.32M\ (\text{kDa})^{0.775}$.)

Higher molecular mass hybrids have a similar intrinsic viscosity to linear polystyrene while lower molecular mass hybrids also seem to approach the linear polysty-

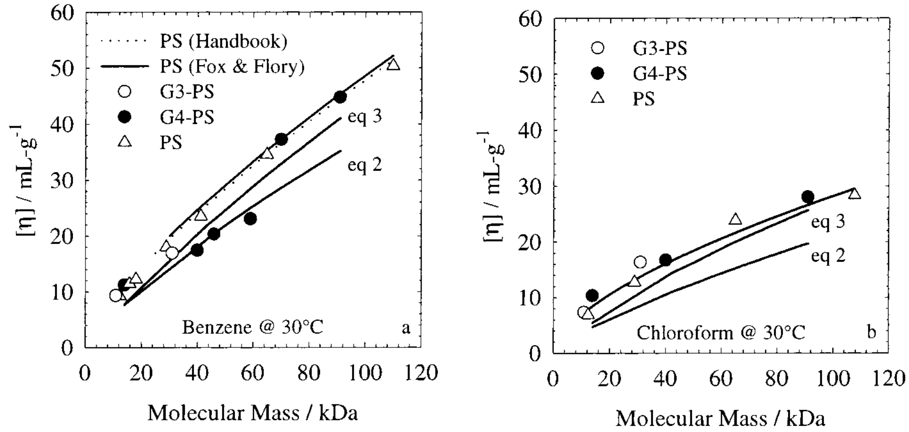


Figure 2. (a) Intrinsic viscosity vs molecular mass for polystyrene and hybrid copolymers in benzene at 30 °C. The intrinsic viscosity for the hybrid copolymers deviates from the polystyrene at intermediate molecular masses Note the intrinsic viscosity values for polystyrene standards measured in this work agree well with relations from refs 28 (Handbook) and 32 (Fox and Flory), a regression of our data yields: $[\eta](\mathrm{cm}^3/\mathrm{g}) = 1.32M\ (\mathrm{kDa})^{0.775}$. The lines labeled "eq 2" and "eq 3" are calculated from eqs 2 and 3 and discussed in the text. (b) Intrinsic viscosity vs molecular mass for polystyrene and hybrid copolymers in chloroform at 30 °C. The intrinsic viscosity is approximately the same for all polymers and a regression of the polystyrene data gives: $[\eta](\mathrm{cm}^3/\mathrm{g}) = 1.26M\ (\mathrm{kDa})^{0.681}$. The intrinsic viscosity error is approximately equal to the symbol size for both sets of data.

rene curve. We have shown that the intrinsic viscosity for G3 and G4 dendrimers are equivalent to linear polystyrene and this may account for the similarity at low molecular mass. Also, the hydrodynamic radius ($R_h = [3M[\eta]/10\pi N_A]^{1/3}$; see refs 5, 29, 30) is small for each molecular component, see Table 2, and one may expect that even though the conformation of either component may be affected within the copolymer the overall effect is minimal. The molecules at high molecular mass are made of at most 5% dendrimer and thus one may not expect the intrinsic viscosity to deviate from pure polystyrene.

The intermediate molecular mass data for the hybrids' intrinsic viscosity deviate significantly from the linear polystyrene, the intrinsic viscosity for the hybrid copolymer is approximately 30% lower compared to virgin polystyrene at a molecular mass of 40−60 kDa. We noted the data of Gitsov and Fréchet above which showed the G4-PEO hybrid copolymer had a reduced intrinsic viscosity compared to virgin PEO. This was explained as due to differences in the relative solubility of either component. Here we have a solvent/polymer system that can be classified as good for each component, and one cannot accept an argument based on these types of differences.

The results in Figure 2b show the intrinsic viscosity for the hybrids and virgin polystyrene in the solvent chloroform are equivalent over the entire molecular mass range. The intrinsic viscosity for polystyrene is found to be: $[\eta](\mathrm{cm}^3/\mathrm{g}) = 1.26M\ (\mathrm{kDa})^{0.68}$, in this solvent. As discussed above, chloroform significantly reduces the dendrimers' intrinsic viscosity to be molecular mass independent.

Two simple models that could represent this unique intrinsic viscosity behavior are derived in Appendix 2. The first is the volume fraction model

$$1/[\eta] = \phi_1/[\eta]_1 + \phi_2/[\eta]_2 \qquad (2)$$

and the second is the mass fraction model

$$1/[\eta] = w_1[\eta]_1 + w_1[\eta]_2 \qquad (3)$$

where the subscripts denote the linear polymer tail (1) and dendrimer (2), ϕ_i is the volume fraction and w_i is the mass fraction. The individual, independently measured, intrinsic viscosities $[\eta]_i$ were used in calculations.

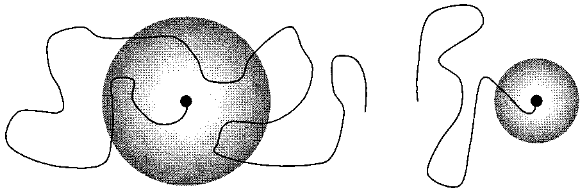


Figure 3. Cartoon showing the effect of dendrimer size on the conformation of polystyrene. A good solvent for the dendrimer expands the dendrimer and the linear polymer can wander within the dendrimer thereby exposing less of the polystyrene to the free solvent (left diagram). A poorer dendrimer solvent creates a smaller, higher density dendrimer and hence less probability that the linear polymer will wander within the dendrimer (right diagram).

Results from eqs 2 and 3 are given in Figure 2, and it is seen that the volume fraction model, represented by eq 2, compares well with the intrinsic viscosity data when deviation from the pure polystyrene data is present (Figure 2a). The mass fraction model, eq 3, is close to the hybrid copolymer's data when the dendrimer is collapsed (Figure 2b) or in the low and high molecular mass regions when the dendrimer is expanded (Figure 2a). This model implies additive hydrodynamic volumes which provides some physical insight, however, neither model is entirely satisfactory and another explanation is needed.

We noted above that the dendrimer is a collapsed molecule of constant molecular density in chloroform while it is an expanded molecule in benzene. Thus, it is expected the polystyrene will have more difficulty wandering from the core and back within the dendrimer when it is collapsed. Figure 3 shows a cartoon to demonstrate this effect. When the dendrimer is expanded (left figure) it is possible for the polystyrene to roam throughout the open structure while it cannot wander as effectively within the collapsed dendrimer (right figure). For this effect to occur the free volume available to the linear polymer must be significant when the dendrimer is expanded. Two techniques are presented in Appendix 3 where estimates are made. In the first technique, the free volume is estimated through the difference in the hydrodynamic and van der Waals

Table 3. Dendrimer Free Volume (nm^3) in Various Solvents Calculated According to Eq A1 with v_{molq} and v^* Given by v_h and v_W, Respectively

		solvent				
dendr	*M*/Da	ethylbenzene	toluene	THF	benzene	chloroform
G3	1592	0.34	1.14	1.41	0.75	0.18
G4	3288	1.42	2.03	5.41	6.19	0.30
G5	6687	3.21	6.00	9.54	1.88	0.76

Table 4. Dendrimer Free Volume (nm^3) in Various Solvents Calculated According to Eq A1 with v_{molq} and v^* Given by v_h and v_h(chloroform), Respectively

		solvent				
dendr	M/Da	ethylbenzene	toluene	THF	benzene	chloroform
G3	1592	0.00	0.11	0.18	0.04	-
G4	3288	0.09	0.21	1.28	1.58	-
G5	6687	0.18	0.74	1.77	0.03	-

(hard core) volumes to yield free volumes (v_f) of 6.19 and 0.30 nm^3 for G4 in benzene and chloroform, respectively (see Table 3). The second technique has the assumption there is no free volume when G4 is collapsed in chloroform yielding v_f equal to 1.58 nm^3 in benzene (see Table 4). The van der Waals volume for the repeat unit in polystyrene is 0.103 nm^3, showing it is possible for 15−60 units to wander within G4 in benzene.

Recent work by Skvortsov et al.[39] and Mansfield[40] shows a polymer chain tethered in a region of high energy achieves a random coil configuration similar to the configuration in a low-energy region. However, when the chain is tethered in a high-energy half-space (the dendrimer) connected to a low-energy half-space (the surrounding solvent) the chain can sample the low-energy region. If the molecular mass is high enough a first-order transition occurs where a coil−flower (coil−stretch) transition occurs with the chain placing as many of its segments in the low-energy region as possible. This transition is quite sharp and is present at a certain molecular mass (actually the parameter is z/R_g, where z is the distance from the low-energy region and R_g is the chain radius of gyration in the work of Skvortsov et al.). We hypothesize a similar phenomenon occurs with the dendrimer−linear hybrid copolymer and the rapid intrinsic viscosity increase at 60−70 kDa is in fact a transition. When this occurs the intrinsic viscosity is expected to be similar to virgin polystyrene due to the small dendrimer size. Thus, the mass fraction model will be more applicable (eq 3, additive hydrodynamic volumes). We imply, of course, the linear polymer conformation is affected enough to reduce the intrinsic viscosity at intermediate molecular masses in the solvent benzene.

A second possibility is that the dendrimer is centrally located within the polystyrene coil and above a certain molecular mass the dendrimer is hydrodynamically shielded from the external flow. More precisely, the linear polymer still wanders within the dendrimer, however, the polymer outside the dendrimer has become so massive as to shield the centrally located dendrimer. Assuming the “transition” occurs at a molecular mass of 65 kDa, where the hydrodynamic radius of polystyrene and G4 dendrimer are approximately 7 nm and 1.5 nm (see Table 2), suggests the hydrodynamic penetration depth is 5.5 nm for polystyrene in benzene. This hypothesis is not as appealing since the very sharp rise in the intrinsic viscosity will probably not occur.

In summary, we find that the dendrimer−linear hybrid copolymers’ intrinsic viscosity is considerably reduced at intermediate molecular mass when the dendrimer is in expanded form while no effect is seen when the dendrimer is collapsed. The intrinsic viscosity is equivalent at low mass due to the similarity of intrinsic viscosity between the dendrimers and linear polystyrene plus the fact that the intrinsic viscosity is small in magnitude. A sharp increase in the intrinsic viscosity is seen when a molecular mass of 60−70 kDa is achieved. Thus, it is suspected that a “transition” of some sort occurs and we have used the model of Skvortsov et al. to rationalize this effect.

Intermolecular Interactions. Additional information can be gained by determining the Huggins coefficients (k) for the various polymers given through

$$\eta_{sp}/c_2 = [\eta] + k[\eta]^2 c_2$$

where η_{sp} is the specific viscosity. The Huggins coefficient is a function of the hydrodynamic as well as thermodynamic interactions between the molecules and solvent. Note that theoretical calculation of k is laborious;[41] however, a reasonable value has been found for hard sphere, Brownian suspensions by Batchelor[42]

$$\eta_{sp} = {}^5/_2\phi + 6.2\phi^2$$

where ϕ is the hard sphere volume fraction. Combining the above two equations finds k equal to 1.0 for a hard sphere suspension.

Values are plotted in Figure 4 for the two systems, benzene and chloroform. Clearly, the Huggins coefficients for the intermediate molecular mass hybrid copolymers in benzene (expanded dendrimer form, Figure 4a) are statistically larger than linear polystyrene and achieve a value of approximately one. The average value for polystyrene with masses between 28 and 110 kDa was found to be 0.424 ± 0.049 and within the range quoted for polystyrene in the literature.[28] It is difficult to assign this increased Huggins constant to indicating hard sphere interactions between the molecules, due to thermodynamic interactions. However, it is clear that the hydrodynamic (and thermodynamic) molecular interaction is different to virgin polystyrene in the intermediate molecular mass region.

The situation is different for the solvent chloroform (collapsed dendrimer form, Figure 4b). Although the Huggins constant is larger, there is no clear difference between the hybrids and polystyrene. Thus, as expected based on the above data, the intermolecular hydrodynamic and thermodynamic interactions are similar between the two.

Conclusion

Intrinsic viscosity measurements were useful in finding the conformation and solubility parameter of the hybrid copolymer in different solvents. The dendrimers were found to change volume by the same relative amount as linear polystyrene and their hybrid copolymers in a variety of solvents. Furthermore, the maximum in the intrinsic viscosity occurred at approximately the same solvent solubility parameter for all compounds and is indicative of similar thermodynamic behavior (for the range of solvents chosen).

The dendrimers show the usual intrinsic viscosity maximum with molecular mass in a good solvent, THF, suggesting that each generation adds linearly to the hydrodynamic radius. The trend is different in a poorer

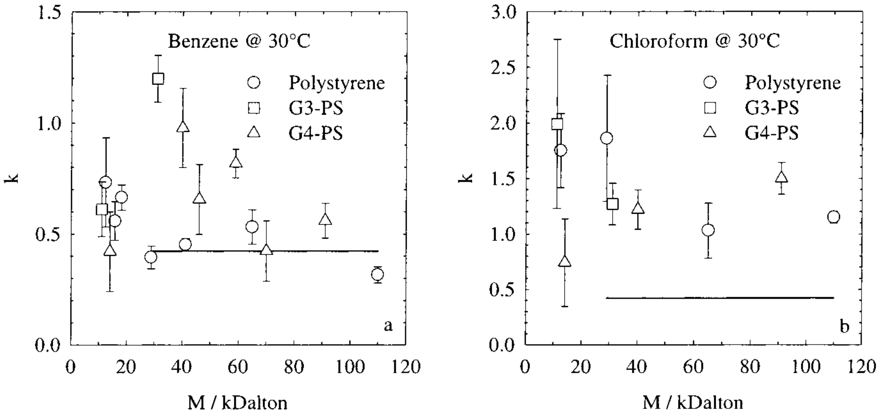


Figure 4. Huggins constant for the linear polystyrenes and hybrid block copolymers as a function of molecular mass. (a) Data for the solvent benzene. The horizontal line represents the average value of the Huggins constant for linear polystyrene with molecular mass between 28 and 110 kDa (0.424 ± 0.049). (b) Data for chloroform. The horizontal line is the same as in Figure 4a. The Huggins constant will be 1.0 according Batchelor's theory[42] for hard spheres.

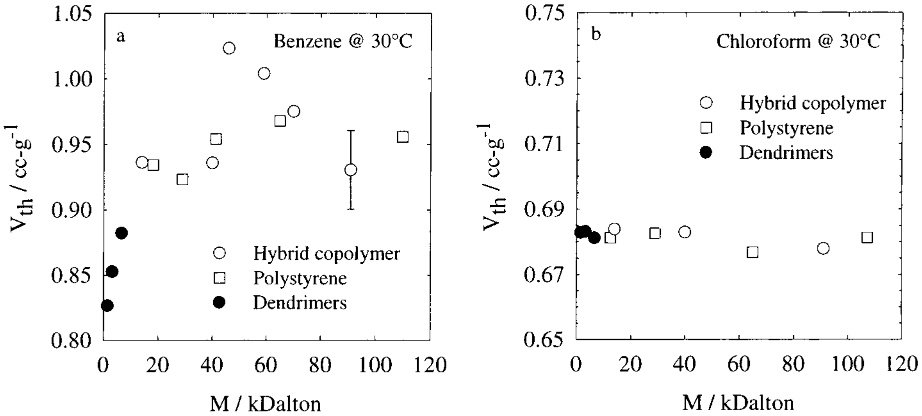


Figure 5. Thermodynamic (partial molar) volume vs molecular mass for the dendrimers, polystyrene and hybrid copolymers in (a) benzene at 30 °C and (b) chloroform at 30 °C, note the expanded scale in this figure. An example error bar is shown for the G4-PS-91K sample in benzene. The error is less in chloroform.

solvent, chloroform, and it is found that the intrinsic viscosity is molecular mass independent. This suggests a collapsed architecture with constant molecular density and a radius that scales with $M^{1/3}$. Other solvents show different behavior and a clear conclusion cannot be made as to their hydrodynamic volume.

An intrinsic viscosity reduction was found at intermediate molecular masses for the hybrid copolymers compared to linear polystyrene when the dendrimer is in the expanded form only. The reason for this reduction is hypothesized to be due to the polystyrene wandering within the relatively open dendritic structure. We do not believe it is due to major solubility differences of the two components in this solvent (benzene) as observed by Gitsov and Fréchet for poly(ethylene oxide) systems.[9] The thermodynamic (partial molar) volume behavior was found to be typical for all systems (see Figure 5) and so the polymer–solvent interactions are similar for this quantity in addition to the interactions measured by the solubility parameter. However, the molecule–molecule hydrodynamic/thermodynamic interactions measured by the Huggins coefficient were affected.

A fairly sharp intrinsic viscosity rise for the hybrid copolymers was seen when the molecular mass achieved 60–70 kDa in a solvent that expands the dendrimer. We believe the model of Skvortsov et al. explains this phenomenon where they show a coil–flower (coil–stretch) transition when a polymer chain is tethered close to a low-energy region. In other words, the dendrimer is a high-energy region, and when the linear polymer is long enough it too can undergo a transition to locate as many segments as possible in the surrounding solvent (low-energy region). If the dendrimer is collapsed, the intrinsic viscosity is similar to virgin polystyrene regardless of the molecular mass. Thus, polystyrene cannot readily penetrate the dendrimer internal structure and so has a similar intrinsic viscosity to virgin polystyrene.

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Appendix 1

Here we consider two possibilities that affect the intrinsic viscosity for a nondraining sphere. We take the molecular density equivalent to the bulk density. Assuming an attached hydrodynamic layer of thickness, *d*, made of solvent molecules, is present around the collapsed molecules one can rewrite eq 1 as

$$[\eta] = {}^{5}/_{2}\{1 + d/R\}^{3}V$$

where R is the molecular radius and V is the bulk specific volume. The effect of the absorbed layer is to increase the effective hydrodynamic volume. One finds d/R equal to 0.063 using the data for chloroform and independent of molecular mass (generation number) suggesting that d increases with generation number. This does not seem reasonable as one would expect the layer thickness to remain constant.

Should the solvent show hydrodynamic slip at the molecular surface then the intrinsic viscosity can be written[43]

$$[\eta] = {}^{5}/_{2}\{[R\kappa + 2\eta]/[R\kappa + 5\eta]\}V \approx {}^{5}/_{2}\{1 - 3\eta/R\kappa\}V \quad \text{(small slip)}$$

where κ is a slip coefficient ($\kappa \rightarrow 0$, free slipping; $\kappa \rightarrow \infty$, no slip) and η is the solvent viscosity. The approximation is the result for a small amount of slipping. It is clear that slip will result in the "Bulk" calculated curve in Figure 1b being further from the chloroform data and does not serve to reconcile the difference.

Appendix 2

We present two simple models in an attempt to explain the intrinsic viscosity–molecular mass behavior. The first model for the hybrid copolymers' intrinsic viscosity can be developed by assuming the intrinsic viscosity is related to the hydrodynamic volume (v_h, units of volume) and molecular mass via

$$[\eta] = 2.5v_{h}/N_{A}M$$

The molecular mass, M, of the hybrid copolymer is merely $M_1 + M_2$ and using the above equation one arrives at

$$1/[\eta] = \phi_{1}/[\eta]_{1} + \phi_{2}/[\eta]_{2}$$

where the ϕ_i and $[\eta]_i$ are the molecular volume fraction and intrinsic viscosity of the linear polymer tail (1) and dendrimer (2), respectively. We call this the volume fraction model, and it is eq 2 in the text. Assuming the intrinsic viscosity for each component within the hybrid copolymer is not perturbed from the virgin value, one must still determine or assume a molecular volume fraction in order to predict the intrinsic viscosity.

We have measured the partial molar volume for the polymers used in this study, given in Figure 5, and will use this to estimate the above volume fractions from

$$\phi_{2} = V_{\mathrm{th},2}M_{2}/V_{\mathrm{th}}\mathrm{M}, \quad \phi_{1} = 1 - \phi_{2}$$

with the subscripts representing the individual components and the quantities with no subscripts are the total hybrid copolymer's. The thermodynamic volume for pure polystyrene is approximately constant as is the hybrid copolyme's, while it is quite low for G4 as reflected by its smaller bulk value (~0.84 cm^3/g determined by Hay et al.[36]).

Another simple model is to assume the hydrodynamic volumes are additive or v_h is equal to $v_{h1} + v_{h2}$ where the subscripts are the same as above. When this is done one finds

$$[\eta] = w_{1}[\eta]_{1} + w_{1}[\eta]_{2}$$

This is denoted as the mass fraction model and is eq 3 in the text.

Appendix 3

The free volume within the dendrimer is calculated through several techniques. We first note the free volume, v_f, is defined through the partition function for a molecule in the liquid as[44–46]

$$v_{\mathrm{f}} = c^{3}\{v_{\mathrm{molq}}{}^{1/3} - v^{*1/3}\}^{3} \tag{A1}$$

where c is a numerical factor representing molecular packing and intermolecular interaction effects, v_{molq}, a molecular volume and v^*, a characteristic or hard-core volume. Here we take $c = 2$ as suggested previously.[44] In the first case, we take v_{molq} as v_h, the hydrodynamic volume (see Table 2), and v^* as the van der Waals volume, v_W. The volume increments of Edward[47] were used to determine the volume contributions of the dendrimers' hydroxyl core ($v_w(\mathrm{C}) = 13.4$ Å^3), the $-CH_2-C_6H_3-(O-)_2$ branching unit ($v_w(\mathrm{BU}) = 93.9$ Å^3) and the $-CH_2-C_6H_5$ end group ($v_w(\mathrm{E}) = 92.1$ Å^3);see Scheme 1. The total van der Waal's volume for any generation dendrimer, g, is given by

$$v_{\mathrm{W}} = v_{\mathrm{W}}(\mathrm{C}) + [2^{g} - 1]\, v_{\mathrm{W}}(\mathrm{BU}) + 2^{g}v_{\mathrm{W}}(\mathrm{E})$$

In this way we find the free volumes given in Table 3.

In the second technique, we still assume eq A1 holds true, yet let v^* be the dendrimers–hydrodynamic volume in chloroform, v_h(chloroform). The supposition in this technique is that the dendrimer is completely collapsed when in chloroform. Results are shown in Table 4.

Note it is important to use an equation such as A1 rather than $v_f = v_{\mathrm{molq}} - v^*$ since eq A1 yields a fractional free volume (v_f/v_{molq}) for liquid benzene of 0.0502 and the simple subtraction method a value of 0.457 (benzene: $v_{\mathrm{molq}} = 148$ Å^3, based on the bulk density; $v^* = v_W = 80.3$ Å^3). Clearly the former value is more realistic. The subtraction method is useful for systems having large free volumes such as in gaseous systems.

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