Macromolecules **1999,** *32,* 4608−4614

Colligative and Viscosity Properties of Poly(propylene imine) Dendrimers in Methanol

Ivo B. Rietveld* and Jan A. M. Smit

Colloid and Interface Science Group, LIC, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Received January 5, 1999; Revised Manuscript Received April 28, 1999

ABSTRACT: The colligative properties of poly(propylene imine) dendrimers in methanol have been investigated with low-angle laser light scattering and vapor pressure osmometry. The molecular weights and second virial coefficients of the first five generations have been determined. The molecular weights have been found to agree with the theoretically expected values. Effective radii have been obtained from the second virial coefficient, viscosity, and the partial specific volume. Both pair interaction and viscous state of the particles are considered in terms of effective volumes. The fifth generation shows the most pronounced hard-sphere interaction probably reinforced by Coulombic repulsion. The viscosity behavior of these dendrimers is like nondraining spheres. All radii grow almost linearly with the generation number. Together with the exponential growth of their molecular weights, this excludes a power law dependence of molecular weight and radius; i.e., these dendrimers are not self-similar. This also explains the maximum in the viscosity.

Introduction

Dendrimers are nowadays well-known as highly and regularly branched oligomers mostly of spherical form. Since the pioneering work of Tomalia, many efforts have been put in synthesizing different types of dendrimers.[1−6] Because of their regular conformation and their high degree of monodispersity in comparison to other highly branched polymers, these molecules are very useful as model systems. Much effort has been put into molecular modeling calculations,[7−10] but until recently, it has been difficult to compare these results with experimental data, because of the limited availability of dendrimers. Experimental data have become available for the well-known starburst dendrimer of Tomalia[1,11] and the diaminobutane poly(propylene imine) dendrimer of De Brabander and Meijer produced by the Dutch company DSM. These latter dendrimers consist of a diaminobutane core to which four branches of poly(propylene amine) are attached (DABPA).[2,12] They are obtained by Michael addition of acrylonitrile to the amine endgroups of an earlier generation followed by hydrogenation of the resulting nitrile endgroups. The functionality of the amine branching points is 2. Thus, the first generation terminates with 4 amine groups at the outer shell, growing exponentially to 64 amine endgroups in the fifth generation. A fifth generation DABPA dendrimer can be seen in Figure 1. The dendrimers are polybases because of the presence of primary endgroups and tertiary amine groups.

In the case of poly(propylene imine) dendrimers, mostly SANS (small-angle neutron scattering) and viscosity measurements have been done in water and to a lesser extent in methanol, resulting in radii of gyration and the scaling exponent of this radius with the molecular weight.[13,14]

In this paper, the colligative properties are examined for poly(propylene imine) dendrimers in methanol using low-angle laser light scattering (LALLS) and vapor pressure osmometry (VPO). Using the virial coefficients, an effective radius as well as an interaction volume are determined. From the viscosity, the corresponding radius and the solvated volume are found, whereas the specific volume yields the “unsolvated” radius. A comparison is made with calculated and experimental radii of gyration. The relationship between the radius and the molecular weight is investigated. Methanol has been chosen because it is a good solvent for these dendrimers. Thereby, this solvent suppresses the charge formation on the dendrimers, due to their basic property, in comparison to that of water.

Working Equations

Results measured by LALLS as well as by VPO can be obtained from so-called Berry plots. In the case of light scattering, the equation is given by

$$\sqrt{K_{\mathrm{LALLS}}c/R_\theta} = \sqrt{1/M_\mathrm{w}} + A_{2,\mathrm{LALLS}}\sqrt{M_\mathrm{w}}c + \frac{1}{2}(3A_{3,\mathrm{LALLS}}\sqrt{M_\mathrm{w}} - A_{2,\mathrm{LALLS}}^2\sqrt{M_\mathrm{w}{}^3})c^2 \quad (1)$$

with K_{LALLS} as the optical constant, R_θ as the Rayleigh ratio, M_w as the weight average molecular weight, and A_2 and A_3 as the second and third virial coefficient, respectively. The coefficient of c^2 in eq 1 is expected to remain small as the mutual contributions of A_2 and of A_3 may cancel out each other. Therefore, “square root” plots following eq 1 are found to be more linear than the familiar Zimm plots.

Osmotic pressure data can be treated in a similar way

$$\sqrt{\frac{\Pi}{RTc}} = \sqrt{\frac{K_{\mathrm{VPO}}\Delta R_\Omega}{c}} = \sqrt{1/M_\mathrm{n}} + \frac{1}{2}A_{2,\mathrm{VPO}}\sqrt{M_\mathrm{n}}c + \left(A_{3,\mathrm{VPO}}\sqrt{M_\mathrm{n}} - \frac{1}{4}A_{2,\mathrm{VPO}}^2\sqrt{M_\mathrm{n}^3}\right)c^2 \quad (2)$$

with Π as the osmotic pressure and M_n as the number-average molecular weight. Π is measured with VPO as the difference in resistance (ΔR_Ω) between the solution droplet (with concentration c) and the solvent, involving the calibration constant K_{VPO}. Ideally, this constant depends on temperature, solvent, and apparatus.

10.1021/ma9900075 CCC: $18.00

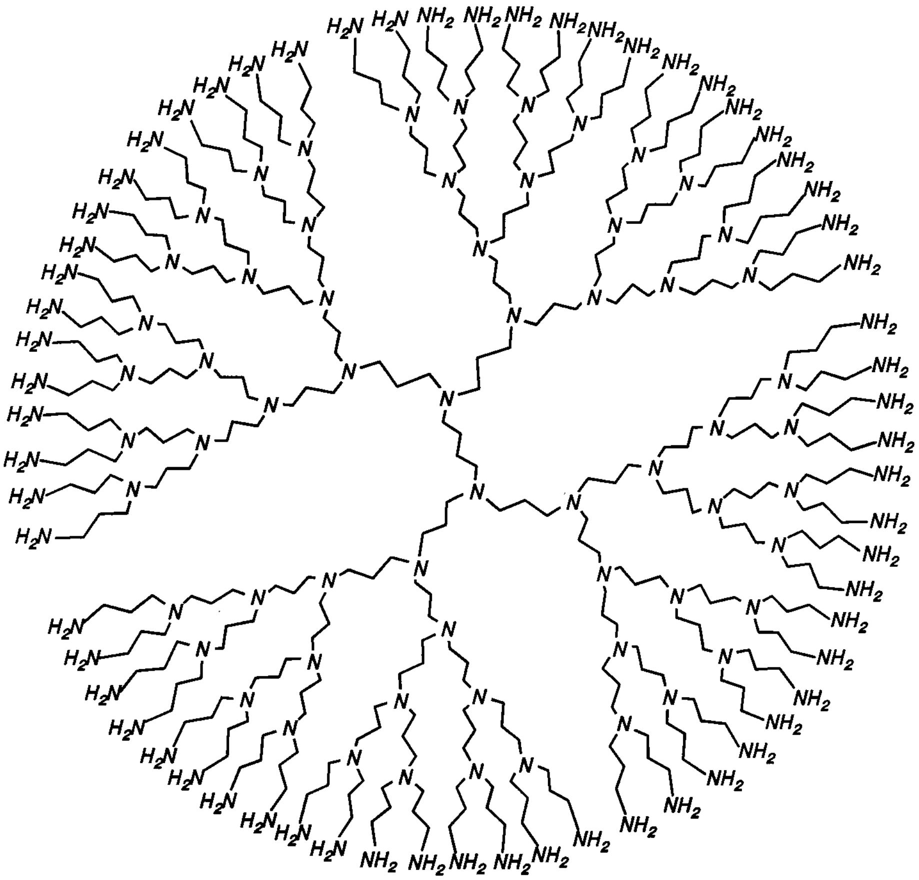

Figure 1. Representation of the fifth generation of an ideal poly(propylene imine) dendrimer.

When heterodispersity among the particles is absent, the coefficient A_2 can be interpreted as describing the binary interaction between equal particles. Then for pairwise interaction between dendrimer molecules, one may write

$$M^2A_2 = \frac{1}{2}N_AV_u = 4N_AV_{HS} \tag{3}$$

where N_A represents Avogadro's number and V_u stands for the particle excluded volume. According to a quasi-hard-sphere model, $V_u = 8V_{HS}$, which is just 8 times the interaction volume of a single dendrimer molecule.

Furthermore, the hydrodynamic size of a dendrimer molecule can be modeled as a rigid Einstein sphere

$$M[\eta] = 2.5N_AV_\eta \tag{4}$$

Here $[\eta]$ is the limiting viscosity number, whereas V_η is the volume of a solvated dendrimer sphere.

Finally, the thermodynamic volume V_v is defined as

$$Mv_{sp} = N_AV_v \tag{5}$$

in which v_{sp} is the specific partial volume.

The left-hand sides of eq 3–5 contain experimental quantities from which the effective volumes can be determined. If as before[7,8,13] dendrimer molecules are considered to be spherical, effective radii can be obtained. Hence, one may adopt an effective interaction radius, denoted here as R_{HS}, a viscosity radius R_η, and the thermodynamic radius R_v.

Compared to the above-defined radii, the radius of gyration (R_G) is of most interest because it can be introduced without any interference of a model and indicates most appropriately the size of a molecule in a specific solvent. So instead of eq 4, one may probe the validity of an equation of the form

$$M[\eta] = C_\eta N_A R_G^3 \tag{6}$$

For Einstein spheres ($R_\eta^2 = {}^5/_3R_G^2$), C_η turns out to be 22.5. Generally, C_η remains constant in self-similar structures such as polymer chains, when the hydrodynamic interactions between the segments of the molecule are strong (nonfree-draining case).

In addition, eq 3 can be generalized to

$$M^2A_2 = C_AN_AR_G^3 \tag{7}$$

For solid spheres, $C_A = 36$, whereas for linear polymers in a good solvent, $C_A = \pm 5$. In addition, C_A is expected to be constant for a homologous series of self-similar structures. It becomes smaller as the mutual interaction potential between the spheres becomes less repulsive.

In this paper, the different radii, including the radius of gyration, will be considered as functions of the generation number G. In addition, the molecular weight can be expressed in this way

$$M = a_1 + a_2 2^G \tag{8}$$

For DABPA dendrimers, $a_1 = -140$ and $a_2 = 228$. Besides, it has been customary in the literature to express the radii as a function of the molecular weight to the power of the exponent ν. This ν appearing in the

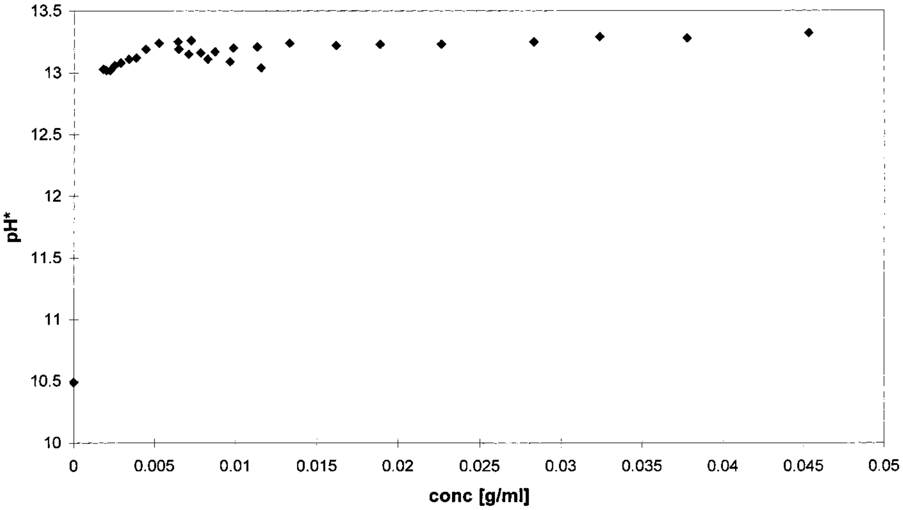

Figure 2. pH* (=$pH_{glass\ electrode}$ + 2.34) of the second generation dendrimer in methanol as a function of concentration.

power law for the radius of gyration has been the object of many studies.[7,8,15]

Experimental Section

The DABPA dendrimers were purchased from DSM in different generations ranging from 1 to 5. The following specifications were given by the producer: a water content varying from 4.5 to <0.1 wt %, a toluene content of <0.1 wt %, and a cobalt content of at most <8 ppm. Methanol p.a. was purchased from Baker and used without further purification.

The samples were prepared as follows. All generations were dried for 3 days under vacuum at 40 °C to remove as much solvent as possible. Then they were dissolved in methanol and measured. The concentrations ranged from 1 to 8 wt %. Only the fourth and fifth generations were filtered twice with a 0.1 μm Millex VV filter before measuring. This was done to remove the turbidity from the solutions, for which the cause is not clear yet. Concentrations were determined by weighing. The concentration of filtered solutions was checked after the measurements by evaporation of the solvent and determination of the residual mass. Sample preparation was performed under a nitrogen atmosphere to keep the water content as low as possible.

The water content of the dendrimers was determined before and after drying using infrared spectrometry. No water could be detected after the drying treatment. The measurements were performed on a BIO-RAD FTS 175.

The densities of the solutions of the dendrimers in methanol were determined with the Anton Paar precision density meter DMA 02C. The measurements were performed at 25 °C for various concentrations of the different generations of dendrimer.

pH measurements of solutions of all five generations of dendrimer in methanol were performed using a glass electrode. These measurements were done according to Klooster.[16] The glass electrode was calibrated with the standard buffer pH solutions of 7.00 and 10.00. Subsequently, the electrode was left overnight in methanol to equilibrate. After the measurements were done, the calibration of the electrode was checked again. The measurements were performed under nitrogen atmosphere. pH values of the glass electrode measured in methanol can easily be converted to real methanol pH* values by adding a value of 2.34.[16] By using the autoprotolysis constant of 16.7 for methanol,[16] the methanolate concentration in dendrimer solutions due to the basic activity of the dendrimer can be calculated approximately.

Static light scattering data were obtained using the LALLS photometer KMX-6 of Chromatix at a temperature of 25 °C and a measuring angle of 6−7°. The dn/dc of the samples at 25 °C were determined with the laser differential refractometer KMX-16 of Chromatix. This resulted in the following mean dn/dc value for all generations: 0.230 ± 0.003. The third and fifth generations were also measured at 45 °C, to compare the LALLS results with the VPO measurements.

VPO measurements were performed using a Gonotec vapor pressure osmometer consisting of the Osmomat 070 cell unit and the Osmomat 070/090 control unit-B. The operating temperature was 45 °C due to apparatus requirements. The calibration constant determined with sucrose−octaacetate (M_n: 678.61) in methanol was 0.0615 ± 0.0007 mol Ω^{-1} L^{-1}. Sucrose−octaacetate was purchased from Schuchardt (München) and was dried under vacuum before use. It is mentioned in the literature as a useful calibration substance.[17] The molecular dependence of the calibration constant[17−22] was checked with poly(ethylene glycol) of varying molecular weights and poly(vinyl pyridine).

Viscosity measurements were performed with a Ubbelohde 0a and a Schott AVS 310 viscometer at 25 °C.

Results and Discussion

The pH* (= $pH_{glass\ electrode}$ + 2.34) as a function of concentration stabilized above 5 g/L at a value of 13.3 ± 0.1 at least up to 50 g/L (see Figure 2). The pH at higher concentrations has not been determined. All of the generations showed this same plateau value. Using the autoprotolysis constant of methanol of 16.7 results in a concentration of 4×10^{-4} mol/L of methanolate in the concentrations of the dendrimers measured with LALLS and VPO. The presence of a small amount of methanolate shows that, although charges on the dendrimers are suppressed to a high degree, some remaining charges may give rise to weak electrostatic repulsion between the molecules.

Both the LALLS and the VPO experiments were more difficult to perform than commonly experienced with dilute solutions of polymers. The molecular weights of the dendrimers are found near the lower detection limit of light scattering. The number concentration of these particles has to be relatively high to obtain enough scattering intensity. For this reason, the use of the Berry plots was preferred instead of Zimm plots.

In the case of VPO, methanol is not the most suitable solvent. It is difficult to get stable results, and great care has to be taken to avoid the presence of water in the system. In addition, calibration with polymer standards yielded an unacceptable variation of K_{VPO} with the molecular weight. The problem is known from the literature.[17−22] For the poly(ethylene glycol) standards used, this behavior is probably also partially due to their

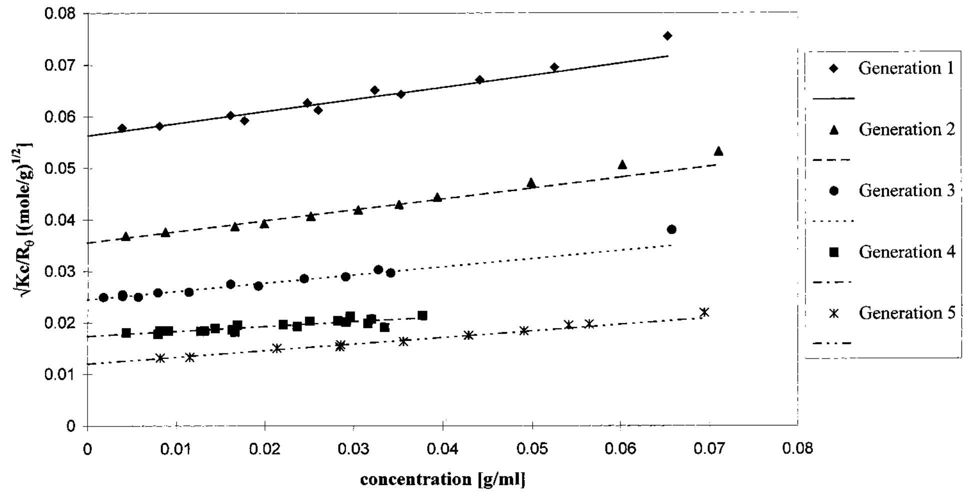

Figure 3. Berry plot of LALLS measurements.

Table 1. Molecular Weights: Theoretical and Determined with LALLS and VPO[a]

generation	theoretical (g/mol)	M_w (LALLS) ($\times 10^2$ g/mol)	M_n (VPO), uncorr ($\times 10^2$ g/mol)	M_n (VPO), corr ($\times 10^2$ g/mol)
1	317	3.2 ± 0.1	3.2 ± 0.1	3.2 ± 0.1
2	773	7.9 ± 0.2	7.8 ± 0.2	7.8 ± 0.2
3	1687	16.7 ± 0.3	16.6 ± 0.8	16.7 ± 0.7
4	3514	33.2 ± 1.2	30.9 ± 1.3	32.6 ± 1.5
5	7168	69.4 ± 2.2	59 ± 5	69 ± 6

[a] For VPO, both uncorrected and corrected values have been given. In the latter, the small amount of methanolate has been taken into account.

Table 2. Second Virial Coefficients Determined by LALLS and VPO[a]

generation	A_2 (LALLS) 25 °C ($\times 10^{-3}$ mol mL g^{-2})	A_2 (VPO), uncorr 45 °C ($\times 10^{-3}$ mol mL g^{-2})	A_2(VPO), corr 45 °C ($\times 10^{-3}$ mol mL g^{-2})
1	13 ± 2	10 ± 1	10 ± 1
2	7.5 ± 0.5	8.5 ± 0.8	7.8 ± 0.7
3	3.9 ± 0.2	5.3 ± 0.6	4.7 ± 0.5
4	1.6 ± 0.2	2.9 ± 0.3	2.7 ± 0.3
5	1.5 ± 0.1	2.3 ± 0.3	2.2 ± 0.3
3 (45 °C)	4 ± 1		
5 (45 °C)	1.4 ± 0.1		

[a] The light scattering results of the third and fifth generations measured at 45 °C have been given as well. For VPO, the same correction as in Table 1 has been applied.

surface activity in methanol. Because the theoretically expected molecular weights of the first three generations were found with sucrose–octaacetate as a calibration standard, it was also used for the two higher generations.

Freshly prepared dendrimer solutions showed an insoluble fraction visible in the form of spherical sediments, which was most pronounced for the fourth and fifth generation. It has been ascribed to the presence of nitrile-terminated dendrimers remaining after incomplete hydrogenation[13,14] during synthesis. IR measurements with the fourth and fifth generations could not confirm this. The occurrence of this phenomenon made determination of the concentrations rather laborious.

The light scattering data have been analyzed with eq 1. It can be seen in Figure 3 that these Berry plots give fairly straight lines, allowing an easy determination of slopes and intercepts. The resulting molecular weights can be found in Table 1. The second virial coefficients have been assembled in Table 2.

For the VPO data in the first instance, the usual plotting method of Π/cRT against c has been used for interpretation. The resulting molecular weights are given in Table 1. It can be seen from these values that especially for the higher generations there is a decrease in molecular weight compared to the light scattering results.

Two causes can be given for this effect. The first is the variation of the calibration constant as a function of the molecular weight of the measured substance as discussed above. The second cause is the presence of the methanolate ion. When calculating the number-averaged molecular weight of the dendrimers taking the amount of ions into account, one finds that the fourth and fifth generations will show a smaller molecular weight, which is comparable to the decrease found in VPO. Similar calculations for the weight-averaged molecular weights determined with light scattering show that these molecular weights are not influenced by the presence of methanolate. Therefore, the VPO data has been corrected for the presence of the ions in the following way. Their contribution can be subtracted from the measured signal by ignoring any interactions between the particles and expressing the osmotic pressure of the ions as $\Pi/RT = K_{VPO}\Delta R_{\Omega} = N/V = c/M$, where N/V is directly obtained from the pH measurements.

The subtraction of the ions makes the resulting line of the VPO data more curved, as the subtracted amount will be larger for smaller concentrations (it is divided by a smaller dendrimer concentration in the Zimm plot). Therefore, the analysis of the curve will become more difficult using the normal way of plotting. Furthermore, if the light scattering data show a distinct curvature due to higher virial coefficients, this effect will be present in the curve of the osmotic pressure versus concentration as well. Finally, using eq 2 for the corrected osmotic data makes the analysis procedure more consistent. The resulting corrected molecular weights can be found in Table 1. The second virial coefficients obtained with VPO are given in Table 2.

Limiting viscosity numbers were obtained from the viscosity measurements. The values are collected in Table 3 as well as the specific partial volumes that have been calculated from the density measurements.

Table 3. Limiting Viscosity Numbers and Specific Partial Volumes of the Dendrimers in Methanol Solution[a]

generation	$[\eta]$ ($cm^3\ g^{-1}$)	v_{spec} ($cm^3\ g^{-1}$)	$N_A R_G{}^3/M$ ($cm^3\ g^{-1}$)
1	5.50 ± 0.06	0.981 ± 0.002	0.238
2	6.23 ± 0.09	0.959 ± 0.004	0.342
3	6.76 ± 0.05	0.960 ± 0.002	0.368
4	7.0 ± 0.1	0.954 ± 0.003	0.368
5	7.11 ± 0.06	0.924 ± 0.005	0.338

[a] For comparison, the last column contains the volume $N_A R_G{}^3/M$, where the R_G from Table 5 has been used.

Table 4. Product of Molecular Weight and Second Virial Coefficient of LALLS and VPO, Respectively

generation	$M_w A_{2,LALLS}$ ($cm^3\ g^{-1}$)	$M_n A_{2,VPO}$ ($cm^3\ g^{-1}$)
1	4.2 ± 0.6	3.2 ± 0.2
2	6.0 ± 0.4	6.1 ± 0.5
3	6.5 ± 0.4	7.9 ± 0.9
4	5.4 ± 0.8	8.9 ± 0.9
5	10.6 ± 0.6	15.1 ± 2.5

For the first three generations, the molecular weights (M_{th}, M_w, and M_n) are the same within the experimental error (Table 1). This means that the polydispersity of these samples is fairly low. These dendrimers are well-defined, and every shell is almost complete.[23] The fourth and fifth generations show a slight decrease in value in comparison to the theoretical value. This result may indicate that the dendrimers have not completely reacted, because they lack monomer units in the outer shell or even larger branches, causing a somewhat lower mean weight. This assumption is confirmed by electron spray mass spectrometry, where a weight of about 7000 was found for the fifth generation.[23]

As a general trend, VPO yields higher values of A_2 than those obtained by LALLS (Table 2). The causes for this are not clear, as temperature does not seem to play an important role considering the second virial coefficient measured with light scattering at 45 °C for the third and fifth generation. The product of A_2M (Table 4) allows a still better comparison between LALLS and VPO. In the case of LALLS A_2M_w is independent of K_{LALLS}, whereas A_2M_n from VPO does not depend any more on K_{VPO}. Again, it is seen that the VPO results turn out to be larger than the LALLS results.

The second virial coefficient of the fourth generation measured by LALLS is lower than expected. It is equal to the value of the fifth generation. It is probably caused by the spherical sediments present in the solution as described earlier, which were very hard to remove from solutions of the fourth generation. This aggregation contributes a negative influence to the second virial coefficient, reducing the total measured value. Why this only occurs in solutions of the fourth generation is not clear.

In Table 5, values of different types of radii have been compiled. The theoretical radii of gyration referring to a good and a bad solvent have been reported recently by Scherrenberg et al.[13] They were obtained by molecular dynamics simulation originating from rather homogeneous density profiles within the molecule.[13] Experimental (SANS) radii of gyration recently measured by us[24] are also shown. They agree reasonably with the values obtained recently by SAXS in methanol[25] (only the third and fourth generations could be compared). Finally, Table 5 also gives the data for the other radii, i.e., R_{HS}, R_η, and R_v, which are calculated from, respectively, eqs 3, 4, and 5.

The binary interaction between two dendrimers is described using the value of R_{HS}. The general trend emerging from Table 5 is that the interaction radii are equal or somewhat larger than those of the good solvent and the SANS radii of gyration. More precisely, deviations from their global rule are seen for the fourth and fifth generation. Obviously, R_{HS} for the fourth generation (LALLS) turns out to be too small (see also the relatively small slope of the plot of the fourth generation in Figure 3). In addition, R_{HS} may be larger than expected by occurrence of Coulomb repulsion between the molecules. This effect is more prominently present in the fifth generation, as can be deduced from the pH behavior. As all generations level off at the same pH and weight concentration, the charge of the larger generations will be higher. However, globally it can be said that the dendrimers have an interaction radius that is about the same as the experimental radius of gyration, which in turn comes close to the theoretical radius found for a swollen structure. Thus, the latter is a strong indication that methanol is a good solvent and may be a better solvent than water, in which the radii of gyration appear to be somewhat smaller.[13]

The thermodynamic radii are significantly smaller than the good solvent radii of gyration indicating the ability of methanol to interpenetrate the dendrimer molecules. Roughly, methanol molecules occupy 30−40% of the swollen dendrimer volume.

The viscosity radii have been found to be distinctly larger than the radii of gyration; i.e., the ratio R_G (good solvent)/R_η (measured) turns out to be 0.81 on the average for all generations. This behavior corresponds to nondraining spheres for which $R_G{}^2 = {}^3/_5 R_\eta$. This relationship has also been found for aqueous solutions of poly(propylene imine) dendrimers.[13] Hence, we may tentatively test eq 6. In Table 3, $[\eta]$ is seen to increase monotonically with generation reaching a maximum level at the fourth and fifth generations. On the other hand, the ratio $N_A R_G{}^3/M$ was also calculated as a function of generation, using the theoretical values of R_G (good solvent) and of the molecular weight. This ratio is seen to pass through a flat maximum (Table 3). The origin of this type of maxima found with dendrimers is still in full debate.[26−30] The reasons for the occurrence of the maximum should be clear. R_G grows linearly with the generation (Figure 4), whereas M does so with 2^G (eq 8). Therefore, the volume of a dendrimer grows faster as a function of generation until a certain genera-

Table 5. Calculated Radii of Gyration for Good and Bad Solvent,[13] Experimentally Determined Effective Radii of the Virial Coefficients, Viscosity, Partial Specific Volume, and Radius of Gyration in Methanol[24]

generation	R_G (calcd)[13] good solvent [nm]	R_G (calcd)[13] bad solvent [nm]	R_{HS} (LALLS) [nm]	R_{HS} (VPO) [nm]	R_η [nm]	R_v [nm]	R_G (meas.)[24] methanol [nm]
1	0.50	0.49	0.51	0.47	0.65	0.50	
2	0.76	0.60	0.78	0.78	0.92	0.67	0.74 ± 0.2
3	1.01	0.74	1.02	1.09	1.21	0.86	0.97 ± 0.06
4	1.29	1.00	1.21	1.42	1.54	1.08	1.4 ± 0.2
5	1.59	1.25	1.94	2.18	1.98	1.37	

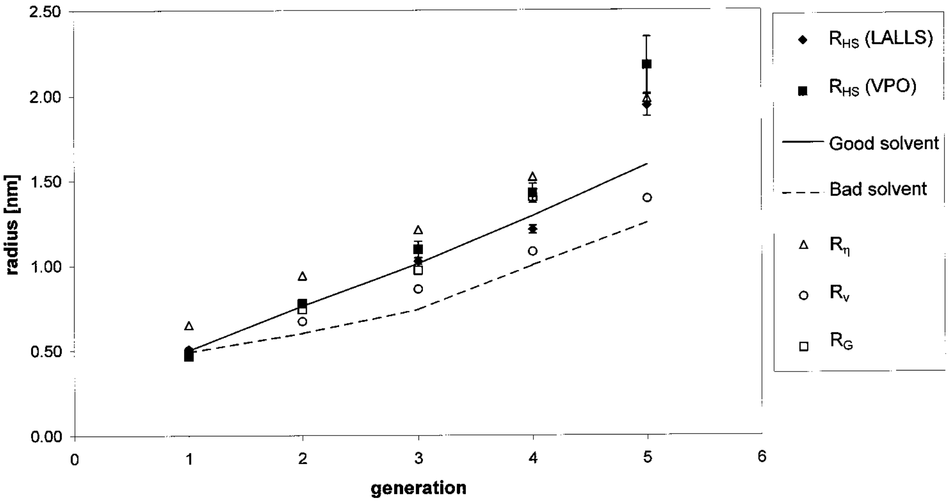

Figure 4. Different radii as a function of the generation number of the dendrimers.

tion where the molecular weight will take over. This causes a minimum in density and a maximum in its reciprocal volume. For C_η, we find 20.0 ± 2.0, which reflects the above-mentioned relationship between R_G and R_η again. Therefore, any draining effect should be visible by variation of the value of C with generation number G. Within the accuracy of the experiment, this could not be observed. Moreover, a significant draining effect should lead to $R_\eta < R_G$, which is certainly not the case.

Contrary to the above findings, C_A appearing in eq 7 is not a constant for all five generations. The light scattering results indicate soft-sphere interaction ($C_A \approx 17$) for the first three generations and hard-sphere interaction for the fifth generation ($C_A \approx 32$). The VPO results give the same trend for the lower generations. Thus, for the whole series of dendrimers, there is not a simple proportionality $\eta \sim MA_2$ (eqs 6 and 7) as found for polymers.

In Figure 4, the different radii have been plotted against the generation number. The experimental radii (SANS and viscosity) as well as the theoretical good solvent radius increase almost linearly with the generation number with the exception of the fifth generation, where electrostatic repulsion probably interferes. The above-mentioned linearity together with the exponentially growing molecular weight (eq 8) cannot be strictly reconciled with the scaling laws usually adopted, in which the log R−log M plot is assumed to be linear. The observation of Valachovic that the dendrimer radii do not scale with the molecular weight[11] also appears to be true in our case. In fact, dendrimers do not possess the self-similarity needed to make the scaling laws valid. Moreover, they are relatively small, branched molecules for which it is known that scaling theory fails.

Conclusions

LALLS and VPO measurements confirm that the investigated dendrimers are reasonably monodisperse samples with the expected molecular weights. The second virial coefficients have been determined. Although they are on the same order of magnitude, the values for VPO are generally somewhat higher than those of light scattering. This binary interaction in methanol can be described in terms of an effective interaction radius, which is similar to the radius of gyration of the swollen molecule. This is an indication that methanol is a good solvent. The increase of the effective volumes or radii of the second virial coefficients for the fifth generation is not only due to the relatively dense outer shell but is probably also enhanced by electrostatic repulsion.

From the comparison between the radius of gyration and the thermodynamic radius, it can be concluded that methanol also interpenetrates the inner part of the dendrimer.

The viscosity behavior for all generations is comparable to what one expects for nondraining spheres. There is some onset for a maximum of the limiting viscosity number as function of the generation number, which can be explained by a minimum in density as a function of generation. A power law dependence of R and M is not applicable for these dendrimers due to the lack of self-similarity between the different generations.

Acknowledgment. We thank F. A. Varkevisser for his support with the light scattering experiments and M. Kwaterski for performing some measurements. I.R. thanks DSM, Geleen, The Netherlands for financial support.

References and Notes

(1) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17*, 117−132.
(2) De Brabander, E. E. M.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1308−1311.
(3) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413−2420.
(4) Mekelburger, H. B.; Jaworek, W.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1571−1576.
(5) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1176−1178.
(6) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638−7647.
(7) Lescanec, R. L.; Muthukumar, M. *Macromolecules* **1990**, *23*, 2280−2288.
(8) Murat, M.; Grest, G. S. *Macromolecules* **1996**, *29*, 1278−1285.
(9) Mansfield, M. L.; Klushin, L. I. *J. Phys. Chem.* **1992**, *96*, 3994−3998.
(10) Mansfield, M. L.; Klushin, L. I. *Macromolecules* **1993**, *26*, 4262−4268.
(11) Valachovic, D. E. Structural Characterization and Polyelectrolyte Behavior of Poly(amido amine) Dendrimers Investigated by Light and Neutron Scattering Methods. Dissertation, University of Southern California, Los Angeles, CA, 1997.

(12) De Brabander, E. E. M.; Nijenhuis, A.; Mure, M.; Keulen, J.; Reintjes, R.; Vandenbooren, F.; Bosman, B.; De Raat, R.; Frijns, T.; Van de Wal, S.; Castelijns, M.; Put, J.; Meijer, E. W. *Macrom. Symp.* **1994**, *77*, 51−62.
(13) Scherrenberg, R.; Coussens, B.; Van Vliet, P.; Edouard, G.; Brackman, J.; De Brabander, E. *Macromolecules* **1998**, *31*, 456.
(14) Ramzi, A.; Scherrenberg, R.; Brackman, J.; Joosten, J.; Mortensen, K. *Macromolecules* **1998**, *31*, 1621−1626.
(15) De Gennes, P. G.; Hervet, H. J. *Phys. Lett. (Paris)* **1983**, *44*, 351.
(16) Klooster, N. Th. M. Polyelectrolytes in Nonaqueous Solvents: The Behaviour of Polyacrylate in Methanol. Dissertation, Leiden University, Leiden, The Netherlands, 1982.
(17) Burge, D. E. *J. Appl. Polym. Sci.* **1979**, *24*, 293−299.
(18) Bersted, B. H. *J. Appl. Polym. Sci.* **1973**, *17*, 1415−1430.
(19) Bersted, B. H. *J. Appl. Polym. Sci.* **1974**, *18*, 2399−2406.
(20) Brzezinski, J.; Glowala, H.; Kornas-Calka, A. *Eur. Polym. J.* **1973**, *9*, 1251−1253.
(21) Morris, C. E. M. *J. Appl. Polym. Sci.* **1977**, *21*, 435−448.
(22) Van Dijk, J. A. P. P.; Smit, J. A. M. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 197−208.
(23) Hummelen, J. C.; Van Dongen, J. L. J.; Meijer, E. W. *Chem. Eur. J.* **1997**, *3*, 1489−1493.
(24) Rietveld, I. B. forthcoming thesis.
(25) Prosa, T. J.; Bauer, B. J.; Amis, E. J.; Tomalia, D. A.; Scherrenberg, R. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 2913−2924.
(26) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138−175.
(27) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
(28) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401−2406.
(29) Cai, C.; Chen, Z. Y. *Macromolecules* **1997**, *30*, 5104−5117.
(30) Cai, C.; Chen, Z. Y. *Macromolecules* **1998**, *31*, 6393−6396.

MA9900075