PFG-NMR Studies of Linear and Dendritic Polymers

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Abstract Diffusion coefficients were measured by pulsed-field gradient NMR for low molecular weight linear polystyrenes in THF and for a broader molecular weight range of linear polystyrenes in chloroform and for PAMAM dendrimers up to generation 4 in methanol. Radii were calculated from the measured diffusion coefficients using the Stokes-Einstein relationship. The linear polystyrenes displayed a relationship between radius and molecular weight that followed the expected power law. From simple theoretical considerations, the dendritic polymers were expected to follow a logarithmic relationship between radius and molecular weight. The PAMAM dendrimers gave reasonable fits to both a power law and a logarithmic relationship from generation 0 to generation 3 (the power law gave a slightly better fit), but displayed a turnover with generation 4, which gave a smaller Stokes radius than generation 3. These results were compared with earlier results from poly (aryl ether) monodendrons, where the relationship was ambiguous between a power law and a logarithmic relationship.

Keywords: dendrimers, pulsed field gradient NMR, diffusion coefficients, scaling law, hydrodynamic radii

Cite This Article: James E. Hanson, Sibel Alkan, Hershel Lackey, and Judith B. Cain, "PFG-NMR Studies of Linear and Dendritic Polymers." *Journal of Polymer and Biopolymer Physics Chemistry*, vol. 6, no. 1 (2018): 26-30. doi: 10.12691/jpbpc-6-1-3.

1. Introduction

Pulsed-field gradient NMR (PFG-NMR) was first applied to polymers in 1967. [1] Use of PFG-NMR to characterize polymers accelerated in the last years of the 20th century and has provided a "new" method for the direct and simple measurement of diffusion coefficients for molecular species. [2-8] Since diffusion coefficients can be related to hydrodynamic radii by the Stokes-Einstein equation, [9,10,11] PFG-NMR is a useful method for rapidly determining such radii. We have previously used PFG-NMR to measure the diffusion coefficients of a series of pyrene labeled poly(aryl ether) monodendrons as part of a more comprehensive study of these materials including photophysical measurements. [12] In this report we employ PFG-NMR to measure the diffusion coefficients of commercially available PAMAM dendritic polymers and narrow molecular weight distribution polystyrenes, and combine the results with our previous data to analyze the molecular weight dependence of the hydrodynamic radius for low molecular weight linear and dendritic polymers. While there have been numerous papers published on the PFG-NMR of linear polymers and dendritic polymers, [13,14,15,16] there have been few reports that have directly compared results on both molecular architectures.

2. Materials and Methods

2.1. Materials

For experiments in THF, narrow molecular weight distribution polystyrene standards were obtained from Polysciences and used as received. The molecular weight distributions from the manufacturer were as follows: $M_p = 580$, $M_w/M_n = 1.18$; $M_p = 2960$, $M_w/M_n = 1.06$; $M_p = 11,300$, $M_w/M_n = 1.04$; $M_p = 39,000$, $M_w/M_n = 1.03$; $M_p = 370,000$, $M_w/M_n = 1.04$. Molecular weights quoted in the text are the M_p values provided. For measurements in chloroform, polystyrene molecular weight standards, polystyrene samples with narrow molecular weight distribution, were used as received from Aldrich. The reported M_w values were 2500, 4000, 13,000, 35,000, 50,000, 200,000 and 900,000. PAMAM Starburst © Dendrimers were obtained from the Aldrich Chemical Company and used as received. NMR solvents were obtained from the Aldrich Chemical Company or Acros Chemicals and used as received.

2.2. Methods

NMR measurements for polystyrene in THF and for PAMAM dendrimers were acquired at Unilever

Laboratories in New Jersey on a Bruker DMX-500 NMR with a 5mm inverse broad band probe with triple axis gradients or a Bruker DMX-400 NMR with a 5mm inverse broad band z-gradient probe using the bipolar LED sequence developed by Wu *et al*. [17] The diffusion coefficients were obtained from linear regression analysis of the natural logarithm of the intensity as a function of the gradient strength squared. Diffusion coefficients of the solvent and adventitious water were used as internal standards. NMR measurements for polystyrene in chloroform were acquired at VMI on a Varian Mercury plus 400 MHz NMR spectrometer equipped with a Highland Technologies Performa II Gradient Driver and an ATB gradient probe capable of generating 100 G/cm gradients. A Hahn double simulated echo with convection correction experiment was used for these diffusion measurements. [18]

3. Results

Two sets of measurements were performed on polystyrene. The diffusion coefficients for a number of narrow molecular weight distribution polystyrene (PS) molecular weight standards were measured in THF-d_8 by PFG-NMR, for comparison with dendritic polymers. The plot of the natural log of the intensity vs. the square of the gradient is shown in Figure 1, and the results are listed in Table 1. All but the lowest MW sample ($M_p = 580$) of the polystyrene standards had polydispersities less than 1.10, yet the data at higher molecular weights were noticeably less linear (r^2 from 0.90 to 0.99) than the essentially monodisperse dendritic polymers (with all r^2 from 0.98 to 0.99). Diffusion coefficients were also measured for a set of polystyrene standards in chloroform. These results are listed in Table 2.

The diffusion coefficients for five generations (G0 – G4) of commercially available poly(amido-amine) (PAMAM) dendrimers were measured in methanol-d_4 by PFG-NMR. The plot of the natural log of the intensity vs. the square of the gradient is shown in Figure 2, and these results are listed in Table 3. The measured diffusion coefficient for the generation 4 PAMAM dendrimer was reproducibly greater than that measured for the generation 3 dendrimer, including measurements on two separately purchased samples.
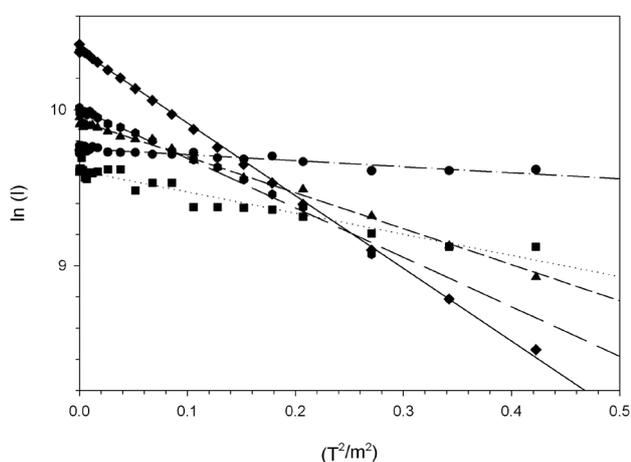
Figure 1. Plot of natural log of intensity vs. gradient squared for polystyrenes in THF ($M_p = 580$ ◆, ———; $M_p = 2960$ O, — — ; $M_p = 11.6$K ▲, -·-; $M_p = 39$K ■·········· $M_p = 370$K ●, — —)
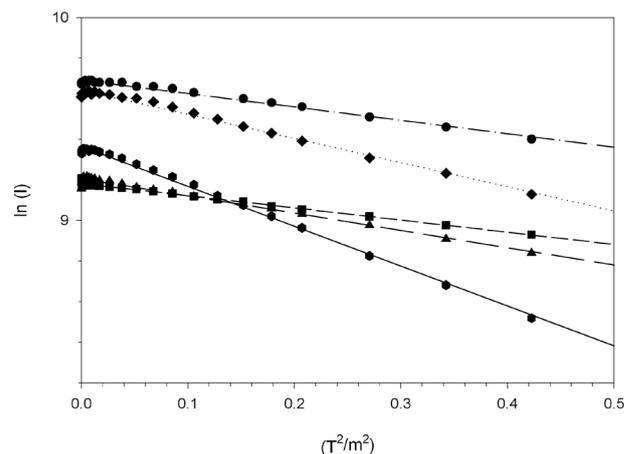
Figure 2. Plot of natural log of intensity vs. gradient squared for PAMAM dendrimers in methanol (Generation 0, O , ———; generation 1, ◆, — ; generation 2, ▲, — — — — ; generation 3, ■,·········; generation 4, ●, — —)

Table 1. Diffusion Analysis of Narrow Molecular Weight Distribution Polystyrenes in THF

M_p, $(M_w/M_n)^a$ (D)	D^b, r^2 (cm^{2}sec^{-1})	R_{Stokes}^c (Å)^b	V_{Stokes}^d (Å^3)^c	ρ_{Stokes}^e (D/Å^3)^d
580, (1.18)	7.3 x 10^{-6}, 0.99	6.6	1,200	0.48
2960, (1.06)	4.9 x 10^{-6}, 0.99	9.8	3900	0.75
11300, (1.04)	3.4 x 10^{-6}, 0.99	14	14,000	0.81
39000, (1.03)	2.1 x 10^{-6}, 0.93	23	51,000	0.76
370000, (1.04)	6.1 x 10^{-7}, 0.90	78	2,000,000	0.18

a. M_p from the manufacturer as described in the experimental section, $M_w/M_n < 1.05$.
b. Calculated from NMR data as described in the experimental section.
c. Calculated from equation (1) using, $k_B = 1.381$ x 10^{-23} J/K, T = 298 K, $\eta = 4.56$ x10^{-4} Pa-sec for THF [19].
d. Calculated from R_{Stokes} given above, $V_{Stokes} = 4\pi/3$ $(R_{Stokes})^3$.
e Calculated from V_{Stokes} given above and MW, $\rho_{Stokes} = MW/ V_{Stokes}$.

Table 2. Diffusion Analysis of Narrow Molecular Weight Distribution Polystyrenes in chloroform

M_w^a (D)	D^b (cm^{2}sec^{-1})	R_{Stokes}^c (Å)^b	V_{Stokes}^d (Å^3)^c	ρ_{Stokes}^e (D/Å^3)^d
2500	5.0 x 10^{-6}	8.1	2,200	1.1
4000	3.6 x 10^{-6}	11	5,600	0.72
13000	2.2 x 10^{-6}	18	24,000	0.53
35000	2.0 x10^{-6}	21	59,000	0.90
50000	1.6 x 10^{-6}	26	74,000	0.68
200000	8.9 x 10^{-7}	46	410,000	0.49
900000	2.8 x 10^{-7}	140	11,500,000	0.078

a. M_w from the manufacturer as described in the experimental section.
b. Calculated from NMR data as described in the experimental section.
c. Calculated from equation (1) using, $k_B = 1.381$ x 10^{-23} J/K, T = 298 K, $\eta = 5.36$ x10^{-4} Pa-sec for chloroform [19].
d. Calculated from R_{Stokes} given above, $V_{Stokes} = 4\pi/3$ $(R_{Stokes})^3$.
e Calculated from V_{Stokes} given above and MW, $\rho_{Stokes} = MW/ V_{Stokes}$.

Table 3. Diffusion Analysis of PAMAM Dendrimers in Methanol

sample	MW (D)	D^a, r^2 (cm^{2}sec^{-1})	R_{Stokes} (Å)^b	V_{Stokes} (Å^3)^c	ρ_{Stokes} (D/Å^3)^d	GRI^e (Å)
G0	517	3.1 x 10^{-6}, 0.99	13	9,200	5.6 x 10^{-2}	-
G1	1,429	1.9 x 10^{-6}, 0.99	21	39,000	3.7 x 10^{-2}	8
G2	3,256	1.3 x 10^{-6}, 0.98	31	120,000	2.7 x 10^{-2}	10
G3	6,909	9.5 x 10^{-7}, 0.99	42	310,000	2.2 x 10^{-2}	11
G4	14,215	1.1 x 10^{-6}, 0.99	36	200,000	7.1 x 10^{-2}	(-6)

a. Calculated from NMR data as described in the experimental section.
b. Calculated from equation (1) using, $k_B = 1.381$ x 10^{-23} J/K, T = 298 K, $\eta = 5.47$ x10^{-4} Pa-sec for methanol [19].
c. Calculated from R_{Stokes} given above, $V_{Stokes} = 4\pi/3$ $(R_{Stokes})^3$.
d. Calculated from V_{Stokes} given above and MW, $\rho_{Stokes} = MW/ V_{Stokes}$.
e. Generation radial increment

Table 4. Diffusion Analysis of Pyrene Labeled Poly(aryl Ether) Monodendrons in THF and Acetonitrile [4]

sample	MW (D)	D^a (cm^{2}sec^{-1})	R_{Stokes} (Å)^b	V_{Stokes} (Å^3)^c	ρ_{Stokes} (D/Å^3)^d	GRI^e (Å)
THF						
G0Py	309	13 x 10^{-6}	3.7	210	1.47	-
G1Py	521	9.7 x 10^{-6}	4.9	490	1.06	1.2
G2Py	945	7.8 x 10^{-6}	6.1	950	0.99	1.2
G3Py	1,795	4.8 x 10^{-6}	10	4200	0.43	3.9
G4Py	3492	3.4 x 10^{-6}	14	11,500	0.30	4.0
CH$_3$CN						
G0Py	309	18 x 10^{-6}	3.3	150	2.06	-
G1Py	521	14 x 10^{-6}	4.1	289	1.80	0.8
G2Py	945	12 x 10^{-6}	4.9	490	1.92	0.8
G3Py	1,795	11 x 10^{-6}	5.4	660	2.72	0.5

a. Calculated from NMR data as described in [12]
b. Calculated from equation (1) using, $k_B = 1.381 \times 10^{-23}$ J/K, T = 298 K, $\eta = 4.56 \times 10^{-4}$ Pa-sec for THF, $\eta = 3.69 \times 10$-4 for acetonitrile [19].
c. Calculated from R_{Stokes} given above, $V_{Stokes} = 4\pi/3$ (R_{Stokes})^3.
d. Calculated from V_{Stokes} given above and MW, ρ_{Stokes} = MW/ V_{Stokes}.
e. Generation radial increment

4. Discussion

The results from our previous studies [12] on poly (aryl ether) monodendrons in two solvents, THF and acetonitrile, are provided in Table 4 for comparison with the data reported here. In our previous study, we were able to measure diffusion coefficients up to generation 4 in THF and up to generation 3 in acetonitrile, lack of solubility prevented measurement of a diffusion coefficient for the generation 4 monodendron.

The diffusion coefficients D can be related to hydrodynamic radii (Stokes radii, R_{Stokes}) by the Stokes-Einstein relation,

$$D = \frac{k_B T}{6\pi\eta R_{Stokes}} \qquad (1)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η the viscosity of the solvent. [9,10,11] Perdeuteration may change the viscosity of a solvent by as much as 10%, leading to corresponding changes in R_{Stokes} calculated from equation 1. [20,21] Since we are interested in trends in R_{Stokes} as a function of molecular weight rather than precise values, this potential offset is relatively unimportant. The Stokes-Einstein relation has been the subject of considerable study over the years, and corrections have been reported for molecules that are oblate or prolate spheroids rather than spheres, [9,10,11] and the numerical factor of 6 is strictly valid only for particles that are significantly larger than the solvent. Smaller particles may require a smaller factor, which has a lower limit of 4 in hydrodynamic theories. [9,10,11] For our PAMAM and polystyrene data, equation (1) is expected to be valid for all of the molecules, which will be roughly spherical and larger than the solvent. Equation (1) was used to determine radii R_{Stokes} from the diffusion data, and these values are reported in Table 1 – Table 4. Molecular densities have been used to correlate the properties of polymers in solution as well. [22] To obtain these densities, the Stokes radii were converted to volumes V_{Stokes} through the appropriate geometric formula $V = 4/3 \pi R^3$. The densities were then obtained by dividing the molecular weight by the molecular volume. The

volumes and densities are also provided in Table 1 – Table 4.

At high molecular weights, the radii of linear polymers are known to scale with the number of monomer units in the chain N by a power law relationship R = N^v. [23-28] This radius is a root-mean-squared radius derived from the end-to-end distance for a polymer chain in a self-avoiding random walk conformation, which at high molecular weights is directly related to the radius of gyration, which is then directly related to the hydrodynamic radius. [23-28] The deGennes model [29] of dendritic polymers predicts that each new generation should add a constant thickness to the spherical polymer, so that R would increase linearly with generation. Since, the number of monomers and the molecular weight increase exponentially with generation, the result is a predicted logarithmic relationship between R and the number of monomers, R = k log N, where k is a constant controlled by the molecular details of the dendrimer.

Since dendritic polymers might increase linearly in radius with generation, in our previous work we utilized the concept of a "generational radial increment" or GRI for dendritic polymers. [12] This is a regular increase in molecular radius with generation, which would naively be expected for dendrimers which add a layer of regular thickness with each generation. The GRI is the difference between the radii of two dendritic polymers which differ by a single generation. These generational radial increments are also included in Table 3 and Table 4.

Figure 3 shows log-log plots of R_{Stokes} as a function of molecular weight for the linear polystyrenes, PAMAM dendrimers, and poly(aryl ether) monodendrons. It is apparent from the plots that there are differences in the radius-MW relationship between linear and dendritic polymers. The linear polystyrenes in THF can be fit well ($r^2 = 0.99$) to a power law relationship, with an exponent of 0.49. The predicted power law (with exponent of 0.57) is followed if the data is restricted to the higher molecular weights (above 10 kD). Empirically, the lower molecular weight data also follow a power law with an exponent near 0.3. The data in chloroform does not fit as well to the power law, with an exponent of 0.45 for the full range of values from 2.5 to 900 kD ($r^2 = 0.97$). Again, if data is restricted to the higher molecular weights (in this case, above 20kD), the fit is improved ($r^2 = 0.98$) and the exponent is as expected (0.57). Empirically, the lower MW data also follow a power law with an exponent around 0.5. As can be seen from Figure 3(a), the two sets of polystyrene data are essentially co-linear, and the fits match very closely.

The radii of the PAMAM tridendrons very closely follow a power law ($r^2 = 0.99$) with an exponent of 0.44 from G0 to G3, then grow smaller for G4. The data can also be fit to a logarithmic relation ($r^2 = 0.98$). The data of Dubin et al, where carboxylate terminated PAMAM dendrimers were studied by quasi-elastic light scattering in aqueous buffer, also gives a better fit to a power law than a logarithmic. [30] Dubin et al did not see the "turnover" observed here for G4, where a higher molecular weight dendrimer gave a smaller R_{Stokes}, most likely as a result of different solvation in water and methanol. A similar turnover was seen in the molecular volumes determined by DeSchryver for poly(aryl ether)

didendrons by fluorescence depolarization in acetonitrile. [17,18,31]

The poly(aryl ether) monodendrons also follow different relationships in different solvents. In THF, there is a small linear increase with generation between G0 and G2, and a larger linear increase with generation between G2 and G4. As a whole, the THF data gives a better fit to a power law with an exponent of 0.57 ($r^2 = 0.99$) than to a logarithmic ($r^2 = 0.95$) relationship. However, the two segments, G0-G2 and G2–G4, could be considered logarithmic. In acetonitrile, there is a larger linear increase between G0 and G2, and a smaller increase between G2 and G3 suggestive of the turnover seen in the PAMAM dendrimers. The acetonitrile data gives a slightly better fit to a logarithmic relationship ($r^2 = 0.98$) than a power law with exponent 0.26 ($r^2 = 0.95$). [12] Because the dendritic polymer data is limited in number of data points and extent of molecular weight, it is difficult to make a conclusive determination of the best model for the relationship between radius and molecular weight.
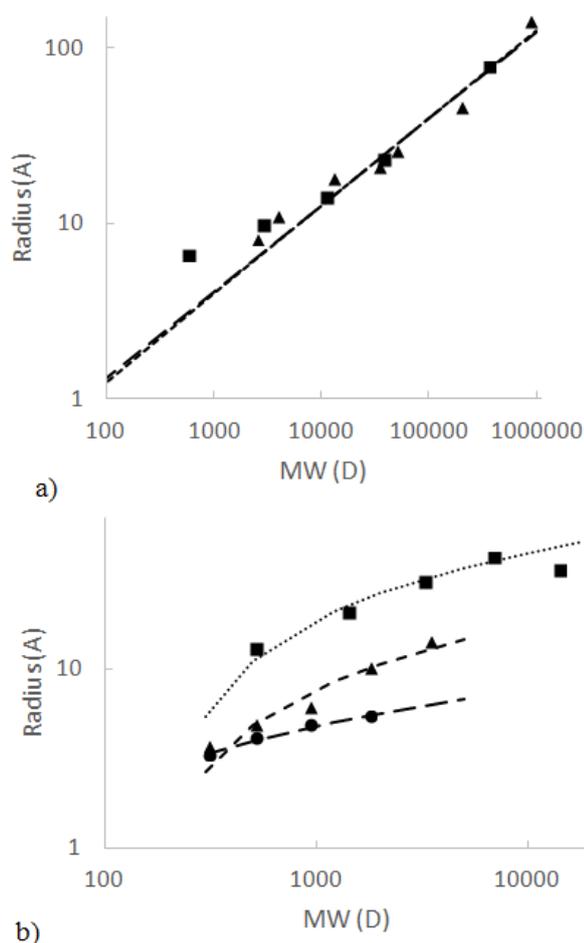
Figure 3. Plots of radius vs. molecular weight: a) Polystyrenes in THF and chloroform, lines are exponential fits to data with MW>10,000 D, both have an exponent of 0.57 and r^2>0.97 b) PAMAM dendrimers in methanol, poly(aryl ether) monodendrons in THF and acetonitrile. Lines are logarithmic fits to data, all r^2>0.95. Scale is identical on both plots.

5. Conclusion

These results confirm that the relationship of radius to molecular weight in dendritic polymers is complex. It cannot always be modeled with either a power law or logarithmic relationship, and is highly dependent on solvent. Dendritic polymers can show a turnover in their radii, where higher MW materials give smaller hydrodynamic radii. [32] Linear polystyrene with molecular weight above ~10-20 kD in a good solvent followed the expected power law relationship between molecular weight and radius.

Acknowledgements

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