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^{129}Xe NMR Investigation of the Free Volume in Dendritic and Cross-Linked Polymers

D. R. Morgan and E. O. Stejskal

Department of Chemistry, North Carolina State University, North Carolina 27695

A. L. Andrady

Chemistry and Life Sciences, Research Triangle Institute, North Carolina 27709

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ABSTRACT: ^{129}Xe NMR spectroscopy was used to study the free-volume changes associated with cross-linking of linear polymers and extensive chain branching in dendritic tree molecules. Qualitative changes in the free volume in model networks of poly(oxypropylene) and in starburst dendrimers of poly(amidoamine) were studied as a function of the cross-link density and the generation, respectively. Consistent with the present understanding of these end-linked networks, the change in chemical shift of the xenon was found to correlate well with the reciprocal of the average molecular weight between cross-links of the end-linked networks. With dendrimers, the chemical shift of xenon varied linearly with the generation number. A modified form of the chain-end free volume theory applicable to dendritic molecules was used to interpret the data.

Introduction

The concept of free volume is central to the interpretation of many polymer characteristics including those of branched and cross-linked polymers. Yet, while the concept is based on a strong theoretical foundation, direct experimental assessment of free volume in polymer systems is difficult. Attempts to do so have involved spectroscopic characterization of probe molecules dispersed or bound within a polymer matrix. Absorbance spectroscopy,[1] fluorescent anisotropy measurements,[2,3] and electron spin resonance (ESR) line-width measurements[4,5] have been used for characterization of such systems. Probe-free techniques such as positron annihilation lifetime measurements have also been proposed for the study of free volume in polymers[6] but have met with limited success. Although local chain dynamics of polymers are well-known to be characterized by τ_1 and the segmental motions associated with the process are likely to be the same as those involved in viscoelastic relaxation, conventional NMR techniques do not provide a convenient means of probing polymer free volume. The recently developed ^{129}Xe NMR spectroscopy that uses xenon as a gaseous probe, however, has shown considerable promise as a simple and effective technique in free-volume studies. In this study, we have selected branched and cross-linked polymer systems that show structurally defined variations in free volumes for study using xenon NMR spectroscopy.

Conventional NMR analysis of polymers typically involves the atoms in the macromolecule, particularly carbon and hydrogen. For sufficient resolution and signal intensity, solid polymer samples are often analyzed using cross polarization and magic angle spinning (CPMAS). This technique is technically demanding, and the broad lines in the solid-state spectrum often obscure important information about the polymer. An alternative approach to studying a polymer is to perform NMR spectroscopy on gaseous xenon probe molecules dissolved in it, as these will relay molecular-level information about their environment. Xenon is particularly well suited for this purpose as it is inert, spherical symmetric, and soluble in many polymers. The main advantage of xenon as a probe molecule is its particular sensitivity to its molecular environment. Also, the high natural abundance (26.44%) and the large magnetogyric ratio (∼10% larger than carbon) of ^{129}Xe provide a strong signal. The solubility of xenon in polymers is on the order of 1 cm^3 gas/cc polymer at 1 atm, and xenon NMR studies are usually done at elevated pressures of xenon, typically between 2 and 10 atm.

Because the chemical shift of the xenon atom is proportional to its collision rate within the free-volume elements in the polymer matrix, it provides a measure of the fractional free volume. As the free volume decreases (because of deformation, annealing, or cross-linking), the chemical shift of xenon moves downfield to larger values. Most polymers produce a xenon resonance between 190 and 220 ppm downfield from xenon gas extrapolated to zero pressure.[7] At temperatures above T_g of the polymer, xenon readily diffuses between sites in response to fluctuations in the polymer-segment density. Rapid diffusion collapses the inhomogeneously broadened xenon resonance into a narrow line that is the average over the inhomogeneously broadened line.

The first published example of a spectrum of xenon absorbed in a polymer was by Sefcik and Schaefer.[8] The spectrum of xenon in poly(vinyl chloride) was approximately 100 ppm wide and had poor signal-to-noise ratio. Four years later, Stengle and Williamson[9] demonstrated that useful information could be obtained from a spectrum of xenon dissolved in a polymer. They demonstrated that for poly(ethyl methacrylate) a plot of the line width of the xenon resonance versus temperature showed a change in slope near the T_g. Spectra of xenon gas in a cross-linked or extensively branched polymer matrix have not been widely studied. Cross-linking an EPDM rubber (66.5% ethylene, 30.6% propylene, 2.9% ethylidene norbornene) is reported to produce changes in the xenon spectrum.[10] Before cross-linking with sulfur, the spectrum showed two overlapping regions, and upon cross-linking, the peaks farthest

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upfield (those associated with the largest free volume) greatly diminished in intensity. This comparison was qualitative in that the cross-linking was random and could not be easily and directly quantified.

The present study is on two polymer systems where the fractional free-volume changes in a predictable manner, namely, model poly(oxypropylene) networks and poly(amidoamine) (PAMAM) dendrimers. In a series of end-linked elastomeric networks of poly(propylene glycol), the cross-link density is calculated independently from the molecular weights of the prepolymer. These systems are prepared by stoichiometric reaction of a linear prepolymer with terminal hydroxy functionalities with a tri- or tetrafunctional isocyanate.[11,12] Dendritic polymers are among the most intriguing macromolecules synthesized in recent years.[13,14] They have a highly branched cascade structure[15,16] often referred to as starburst topology.[17] In the common divergent route, dendrimers are synthesized by stepwise condensation of trifunctional monomers about a multifunctional core molecule. This produces a layered spheroidal product the size of which depends on the number of layers or generations. As the functionalities available for subsequent reaction double with each condensation step (or generation), the larger dendrimers have a very large number of surface functionalities per macromolecule. Their unique molecular structure results in a cavity or a less-dense region in the core area of the spheroidal macromolecule.[18] It is reasonable to expect their free-volume fractions to increase with the generation number *G* of the dendrimers at least for low generations. The objective of the present investigation was to establish if xenon NMR can be used to characterize the range of free-volume fractions in the above systems.

Experimental Section

Materials. The PAMAM dendrimers (on an ethylenediamine core) were obtained in 20% methanol solution from Dendritech, Inc., (Midland, MI) and were stored in a refrigerator until use. The poly(propylene glycol) prepolymers were kindly donated by the Arco Chemical Company (Newtown Square, PA). The tris(*p*-isocyanatophenyl)thiophosphate cross-linking agent was kindly provided by Mobay Chemical Company. Natural abundance xenon gas was purchased from National Welders Company. All other chemicals and solvents were purchased from Aldrich Chemicals, Inc., and were used as received.

The methanol solvent in PAMAM dendrimer solutions was removed prior to NMR spectroscopic investigation, initially using a vacuum centrifuge operated at 40 °C. The centrifuged samples were exhaustively dried to constant weight using a vacuum pump at ambient temperature over several days or weeks in the case of higher-generation material.

Network Preparation. The average molecular weights of the poly(propylene glycols) are slightly different from the nominal molecular weights indicated by the manufacturer and were determined using standard titrimetric methods for determination of the hydroxy number. The samples were dried in a vacuum oven at ambient temperature for at least 48 h before use. Tris(*p*-isocyanatophenyl) thiophosphate, the trifunctional cross-linking agent, was provided in methylene chloride solution, and its concentration was determined by a standard titrimetric procedure using dibutylamine (ASTM D 4665-87 standard test method for polyurethane raw materials). Stoichiometric quantities of the polyol and cross-linking agent solution were mixed and gently heated with stirring to remove all of the methylene chloride. When the mixture began to increase in viscosity, it was poured into a Teflon-lined mold and allowed to cure at ambient temperature in a laboratory press under a pressure of 5000 psi for 24 h. The networks were removed from the mold and heated at 60 °C in a vacuum oven overnight to complete the reaction. Network samples were washed with toluene (and a series of toluene/methanol mixtures of increasing methanol concentration) to remove any unreacted polyol materials.

In the experiment designed to observe the kinetics of cross-linking, poly(propylene glycol) PPG 1025 was cross-linked using 2,4-toluene diisocyanate in the presence of the catalyst dibutyl tin dilaurate. An equimolar mixture of the polymer and cross-linking agent was mixed with about 0.1% by weight of the catalyst and allowed to cross-link under 1 or 7 atm of xenon gas.

Measurements. All solid state ^{13}C NMR spectra were acquired on a Chemagnetics CMC-200S spectrometer operating at a ^{13}C frequency of 50.144 MHz. The spectra were acquired under CPMAS conditions with a spinning rate of 3.5 kHz with the contact time for each sample determined separately to provide the maximum signal.

All ^{129}Xe spectra were acquired on a General Electric GN300 Omega spectrometer, with a 10 mm broadband probe tuned to the resonance frequency of 83.138 MHz. All spectra were single-pulse excitation spectra with no proton decoupling or sample spinning. Excitation pulse widths were 30°, and the pulse delay was 2 s. All chemical shifts are externally referenced to a solution of xenon in $CDCl_3$, which has been assigned the value of 217 ppm. The samples were contained in plastic sample containers. The reusable containers were attached to a vacuum/pressure line that allowed the samples to be evacuated and then pressurized with xenon gas to approximately 100 psi.

The preformed network samples, usually about 0.5−1 g, were placed under xenon pressure in the sample container for 2 days before acquisition of spectra.

Results and Discussion

Although solid-state NMR with CPMAS does not yield direct information on the free volume of cross-linked networks, it is interesting to characterize the four networks used in the present study using the technique. In Figure 1, the backbone carbons in the polyoxypropylene units and the methyl carbons are clearly seen in the spectrum of the network with the lowest cross-link density, labeled $M_C = 3025$. As the chain mobility is increasingly restricted with increasing cross-link density, both bands broaden as the average molecular mass between cross-links M_c decreases. However, as might be expected, there is no significant dependence of the chemical shifts on cross-link density of the network. With the network labeled $M_C = 725$, which has the highest cross-link density and therefore the highest fractional content of the cross-linking moiety (0.45 g cross-linking agent/g polyol), it is possible to discern the weak signals from the aromatic carbons from phenyl functionalities in the cross-linking agent. These weak bands in the region of 160−120 ppm are not readily visible in the spectra for the other networks in Figure 1, under the conditions used here.

The figure also shows the corresponding data from ^{129}Xe NMR analysis of the same networks. In these spectra, the single band of interest is that for xenon. Gaseous xenon under a pressure of 100 psi yields a strong band at about 8 ppm. When sorbed in these poly(oxypropylene) networks, xenon shows a chemical shift in the range of 217.2−222.2, depending on the cross-link density of the network, with the signal shifting downfield with decreasing cross-link density of the system. The change in chemical shift for xenon indicate the free-volume element in which the gas molecules reside decreases significantly with the extent of cross-linking. It is instructive to obtain a semiquantitative

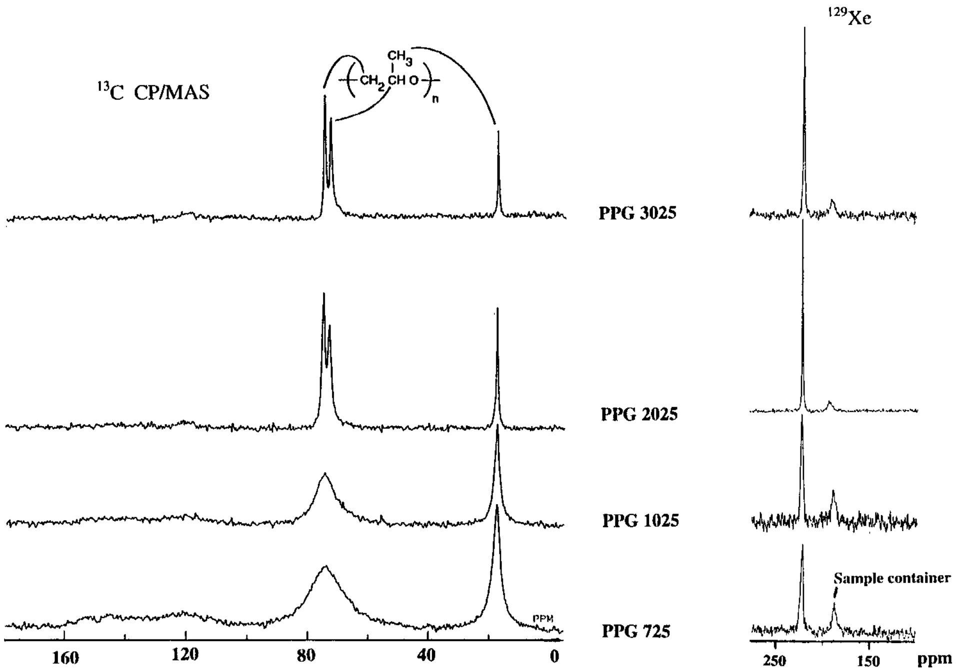

Figure 1. Solid-state ^{13}C NMR spectra and ^{129}Xe NMR spectra for end-linked poly(oxypropylene) networks cross-linked with tris(*p*-isocyanatophenyl)thiophosphate. The M_c values for the networks are given in Table 1.

relationship between the chemical shift data for xenon and the expected free volume in the networks.

Under equilibrium conditions, the fractional free volume *f* is a function of the temperature and can be defined as follows[19]

$$f = (v - v_o)/v_g \tag{1}$$

where v is the specific volume, v_o is the volume occupied by the macromolecule, v_g is the volume of the system at its T_g. The fractional free volume *f* is the volume fraction available for accommodation and transport of the xenon molecules within the network. For the present networks, made by stoichiometric end-linking of polyols of narrow molecular weight distribution, *f* may be written as follows, analogous to the Fox and Loshaek treatment.[19] The expression treats the network as a binary system of network chains and cross-linking junctions.

$$f = f_C - (A_x\,\Gamma_3)/N \tag{2}$$

where f_C is the free-volume fraction of the polymer chains, Γ_3 is the number of trifunctional cross-links per unit volume, N is Avogadro's constant, and A_x is a material constant. The cross-link density represented by Γ_3 is proportional to $(1/M_c)$ where M_c is the number-average molecular weight between two cross-links. With end-linked stoichiometric networks, M_c is the same as the average molecular weight of the prepolymer (or the average M_n) used to prepare the networks. Therefore, provided the chemical shift of xenon is a linear function of the free volume of the system, it must correlate with $1/M_c$ for the four networks. Figure 2 shows a plot of the present data, showing excellent linearity. Andrady[20] previously showed the T_g of these same networks to be a linear function of $1/M_c$, suggesting that the glass-transition temperature and the xenon chemical shifts for these networks will also show a high degree of correlation. As the M_c is related to the cycle rank and to the cross-link density (the number of junction points per unit volume of network), the results suggest that the xenon NMR data are correlated with these network parameters as well. The finding is important in that it allows for the first time the interpretation of chemical shifts of xenon dissolved in the cross-linked networks in terms of the free volume of a network. The data on the four networks investigated are shown in Table 1.

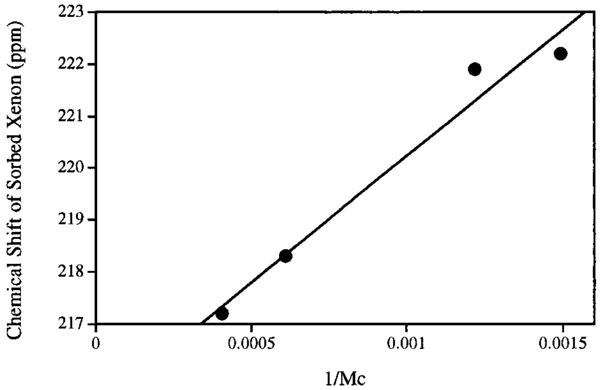

Figure 2. Dependence of the xenon chemical shift (ppm) on the reciprocal of the number-average molecular weight between cross-links in the end-linked poly(oxypropylene) networks.

The main limitations of this qualitative interpretation, however, is that it does not take into account the effects of compositional variation in the networks due to their chemical modification by the cross-linking agents. The series of networks shown in Figure 2 have different cross-link densities as well as different compositions in terms of the weight fraction of the tris(*p*-isocyanatophenyl)thiophosphate cross-linker in them. Some unknown component of the change in T_g of the networks has to be ascribed to this change in composition. It is interesting to study a polyurethane network system where the composition remains about the same while the cross-link density changes with time. This is obtained with a polyol and isocyanate mixture during the latter stages of cross-linking. To study such a

Table 1. Xenon NMR Results for Poly(propylene glycol) Networks

network designation[a]	M_n of prepolymer[b]	chemical shift for prepolymer (ppm)	chemical shift for networks (ppm)	line width (Hz)	T_g (K)	swelling ratio[21]
PPG 725	670	213.9	222.2	225	281	0.464
PPG 1025	820	214.0	221.9	220	262	0.406
PPG 2025	1640	214.4	218.3	81	241	0.286
PPG 3025	2470	214.4	217.2	91	235	0.216

[a] The nominal average molecular weight of the prepolymers are indicated by this designation. [b] Based on GPC measurements on the prepolymer carried out at Arco Chemical Company. The figures indicate the nominal molecular weight of the prepolymer.

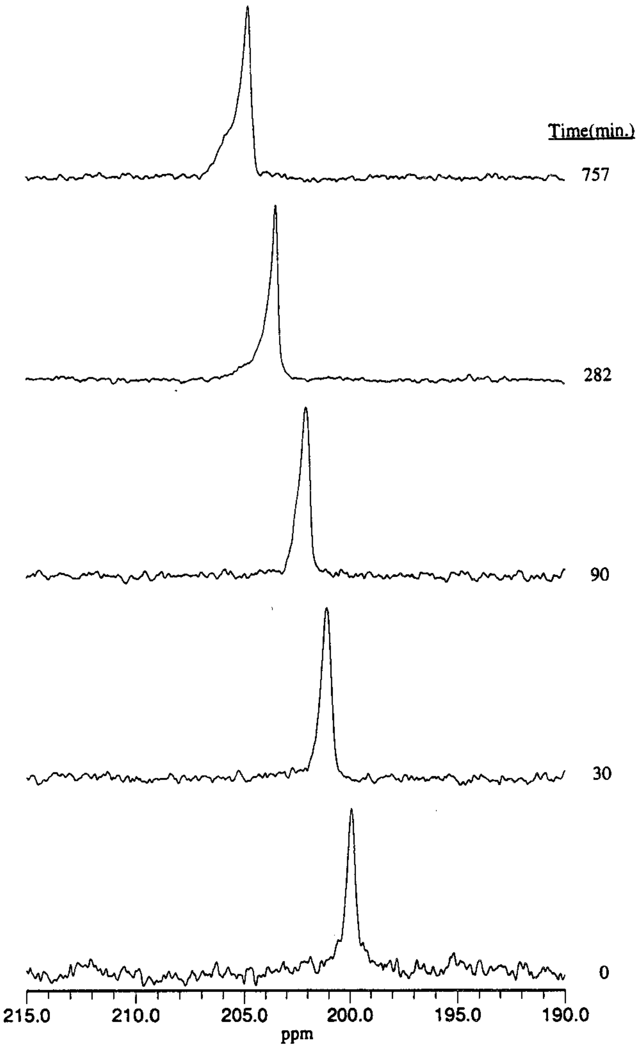

Figure 3. Change in xenon resonance signal during the cross-linking of a poly(oxypropylene)diol prepolymer sample (M_n = 820) by 2,4-toluene diisocyanate, in the presence of about 100 psi of xenon gas.

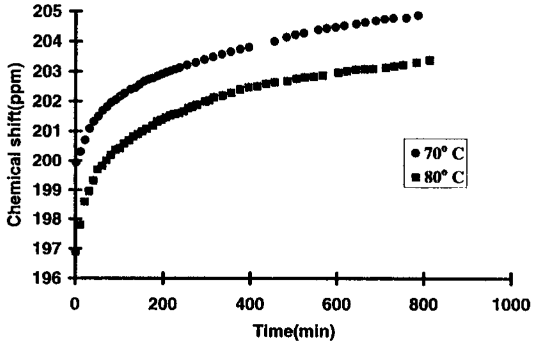

Figure 4. Change in the chemical shift of xenon sorbed in the prepolymer−isocyante mix as the reaction progressed at 70 and at 80 °C.

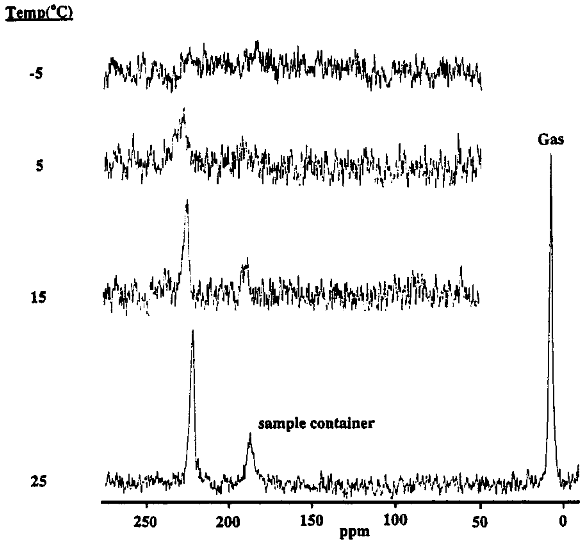

Figure 5. Changes in the ^{129}Xe NMR spectra for the network with M_c = 670 at several temperatures above and below the known T_g of the network.

system, an equimolar mixture of 1,4-toluene diisocyanate and poly(propylene glycol) of M_n = 820 was degassed and exposed to xenon at a pressure of about 100 psi. Xenon NMR spectra of the system were collected at 70 and 80 °C as a function of time, in an attempt to monitor the spectral changes during cross-linking (Figure 3). As expected, there was a downfield shift in the xenon signal with time or as cross-linking progressed, with the signal approaching an asymptote at about 12 h, when the observations were discontinued (see Figure 4). The initial gradient of the plot of chemical shift versus time yielded estimates of the rate of curing as observed by this technique. The rate approximately doubled on increasing the temperature by 10 °C (from 70 to 80 °C).

The temperature dependence of the free volume in the networks may also be studied using this technique. In the glassy state where the fractional free volume in the system is low, the amount of xenon sorbed is too small to yield a signal. In the neighborhood of T_g, the dependence of free volume on the temperature is linear.

$$f = f_g - \alpha\,(T_g - T) \quad \text{for } T > T_g$$
$$f = f_g - \alpha_1\,(T - T_g) \quad \text{for } T < T_g \qquad (3)$$

For most polymers, the value of f_g is assumed to be around 0.025, and the sorbed xenon signal at T_g is expected to be quite small. The stacked spectra in Figure 5 show that the upfield sorbed xenon peak appears at temperatures over 5 °C in the case of a network with M_c = 670. Published data for this type of polyurethane network of M_c = 670 determined[21] using dynamic mechanical analysis is about 8 °C, in good agreement with our observations. The xenon NMR technique provides a useful means of detecting the glass-to-rubber transition of cross-linked polymers. Using a gaseous probe molecule for this purpose is particularly useful in understanding the gas transport properties of the system. However, when extrapolating these findings to different gaseous systems, the dependence of the data on the van der Waal radius of the xenon atom must be taken into account.

Taken together, these results illustrate for the first time that the free volume estimates experimentally derived from xenon NMR data are in qualitative agreement with those expected on the basis of network structure and the T_g. The technique allows the use of xenon as a probe molecule to obtain an experimental T_g for polymers pertinent to gas transport in the system. The implicit assumption in the interpretation of data, that the presence of the xenon gas does not alter the free volume of the system, is a reasonable one for these networks. The approximate amount of xenon sorbed by the networks was estimated gravimetrically to be less than 0.3% by weight. At this level of sorption, it is reasonable to assume that the free volume of the networks is unaltered by the gas sorbed.

Dendritic Molecules. The de Gennes and Hervet model[18] of dendrimer structure tacitly assumes that the branches elongate as the generation numbers increase and that the terminal functional groups lie at the surface of the spheroidal molecule during all stages of growth. This led them to focus on space-filling considerations at the surface, implying that the free volume is associated primarily with the core of the dendritic molecule. As might be expected, the density of poly(amidoamine) dendrimers used in this study was shown to decrease with the generation number up to generation 4 and thereafter increase up to generation 8.[22] Recent simulation of dendrimer structure based on kinetic growth in a self-avoiding walk algorithm by Lescanec and Muthukumar,[23] however, suggest that some terminal groups may possibly sample the interior of the molecule. The free volume in this case will be distributed between the core and surface areas of the macromolecule. Chiral tree molecules with cavities have been reported previously[24,25] and have been characterized using appropriate markers. It is the topology of the core that determines the cavity volume in the dendritic polymer and is invariably responsible for the dramatic changes in physical properties[26] with the generation number.

For linear macromolecules, the free volume of the system depends on the average molecular weight because of the higher relative mobility of chain ends.[27] If the excess free-volume contribution by a single chain end is represented by θ, excess free volume per unit volume of the system is inversely proportional to its molecular weigh and is given by $(2\theta N/M)\rho$. The glass-transition temperature of a linear polymer of molecular weight M (g/mole) will be lower than that of a chain of infinite molecular weight by an amount proportional to this excess volume.

$$[T_g(\infty) - T_g(M)] = (2\rho\theta N\alpha^{-1})\ 1/M \qquad (4)$$

where ρ represents the density, α is the free-volume expansion coefficient, and N in Avogadro's number. With dendritic systems, however, $(2\theta N/M)\ \rho$ is not a constant, and the excess free volume or the T_g is not expected to be a function of $1/M$ as suggested by eq 4. As the molecular weight increases, the number of chain ends z of dendritic molecules increase rapidly. The excess free-volume term is given instead by assigning the free-volume increment to each of the chain ends.[28]

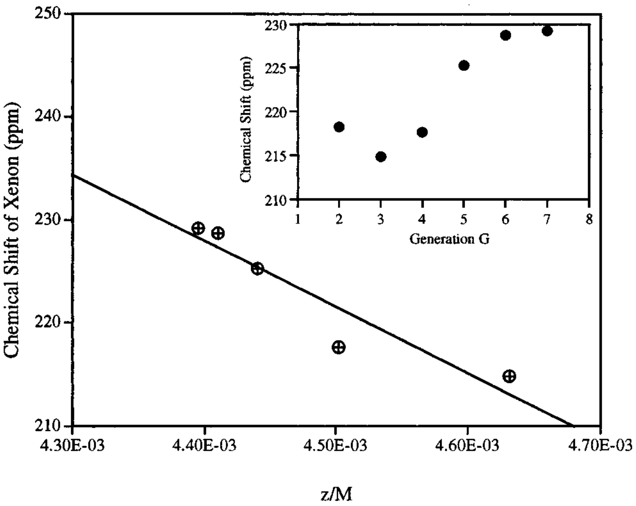

Figure 6. The dependence of the chemical shift (ppm) of xenon sorbed in poly(amidoamine) (PAMAM) dendrimers on the z/M value of the dendrimer. The inset figure shows the change in chemical shift (ppm) with the generation number.

$$\text{Excess free volume per unit volume} = (\rho\theta N\alpha^{-1})z/M \qquad (5)$$

where z represents the number of chain ends per molecule. If the chemical shift of the xenon signal is assumed to be directly proportional to the excess free volume in the system, it will vary linearly with z/M for dendrimers of different molecular weight. The linearity of the plot in Figure 6 shows that for the PAMAM dendrimers used here a linear relationship is obtained. Equation 5 can be written in terms of T_g of the dendrimers. The linear relationship between T_g and z/M of several other dendritic systems has been reported.[28] However, the term $\rho\theta N\alpha^{-1}$ need not necessarily be constant for the dendrimers as at least θ is likely to change with the generation number as well. The data suggest that the change is either too small to affect the linearity or is offset by changes in other parameters, such as the density of the system.

A plot of the chemical shift of the xenon versus the generation number is also indicated in Figure 6 and, interestingly, shows some linearity for samples with generation numbers from 3 to 7. A deviation from linearity is seen in the case of the generation 2 dendrimer where the chemical shift of xenon is higher than that of the generation 3 dendrimer. The lower-generation PAMAM molecules, particular generations 2 and 3, are unlikely to have the spheroidal structure characteristic of the higher-generation molecules, and such deviations are expected. This is analogous to the reversal of the trend in density reported for PAMAM dendrimers where the density increases after generation 4 is reached. The technique of xenon NMR is particularly advantageous for use with dendrimers as the C-13 and proton NMR spectra with overlapping resonances, are often too complicated to interpret. Table 2 lists the chemical shift data for xenon in dendrimers.

Table 2. Chemical Shift Data for PAMAM Dendrimers

generation number G	calculated functionality per molecule Z	calculated molecular weight M (g/mole)	$Z/M \times 10^{-3}$	xenon chemical shift (ppm)
2	16	3 256		
3	32	6 909	4.63	214.8
4	64	14 215	4.50	217.6
5	128	28 826	4.44	225.2
6	256	58 048	4.41	228.7
7	512	116 493	4.44	229.2

Exhaustive removal of methanol solvent under vacuum preceded the xenon NMR analysis of the above samples. With dendrimers, it is difficult to envision solvent-induced conformational changes analogues to those seen for linear polymers, other than perhaps simple isotropic changes in volume. It is likely that dendrimers behave as free-draining systems with the methanol readily accessing the interior of the larger molecules. With the higher-generation samples, removal of residual methanol was difficult and required pumping over a period of several weeks until the chemical shift was constant. Extensive hydrogen bonding in the surface moieties probably effectively entraps any methanol in the interior of dendrimers. Any methanol within the dendrimer provides quite a different environment for the dissolved xenon gas than that of the free bulk methanol. Approximately 20 wt % solutions of various dendrimers in methanol, when studied using the xenon NMR technique, yielded a xenon resonance at around 158 ppm, far downfield from than that for xenon solutions in methanol (about 150 ppm). We speculate that this chemical shift is very likely to be concentration dependent.

The generation 3 PAMAM dendrimers used in this study are known to undergo glass transition at around -20 °C, on the basis of dynamic mechanical analysis.[29] The very significant increase in chain flexibility at temperatures higher than the T_g should generally result in a larger expansion coefficient for the free-volume fraction, compared to that when $T < T_g$. Figure 7 shows a series of xenon NMR spectra for the PAMAM dendrimer of generation 3 at several different temperatures both above and below its approximate T_g. As we expected, with decreasing temperature, the chemical shift for xenon moves downfield because of gradual constraints on the motion of the gas atoms within the dendritic interior. As in the case of linear polymers hitherto investigated, the sub-T_g resonance bands for xenon are extremely broad, reflecting the very small free-volume fraction available in the glassy state. As suggested by eq 3 for linear polymers, the free volume of dendrimer as measured by the chemical shift of dissolved xenon is also a linear function of the temperature, indicating that the relevant expansion coefficient is constant in the range of temperatures studied. The linearity is excellent ($r^2 = 0.99$), and the negative temperature coefficient obtained for PAMAM (generation 3) was 0.143 ppm/°C. In linear polymers, any temperature-induced phase separation or crystallization is expected to cause deviations from linearity. In the case of dendritic molecules with highly branched tree structures, no crystallinity or phase separation is expected.

Conclusions

A new analytical technique, ^{129}Xe NMR spectroscopy, was used to study the free volume changes associated with cross-linking (specifically end-linking) of poly(oxypropylene) chains, as well as in extensively branched starburst dendrimers. The findings illustrate the potential of the technique to study free-volume changes in complex polymer systems in general.

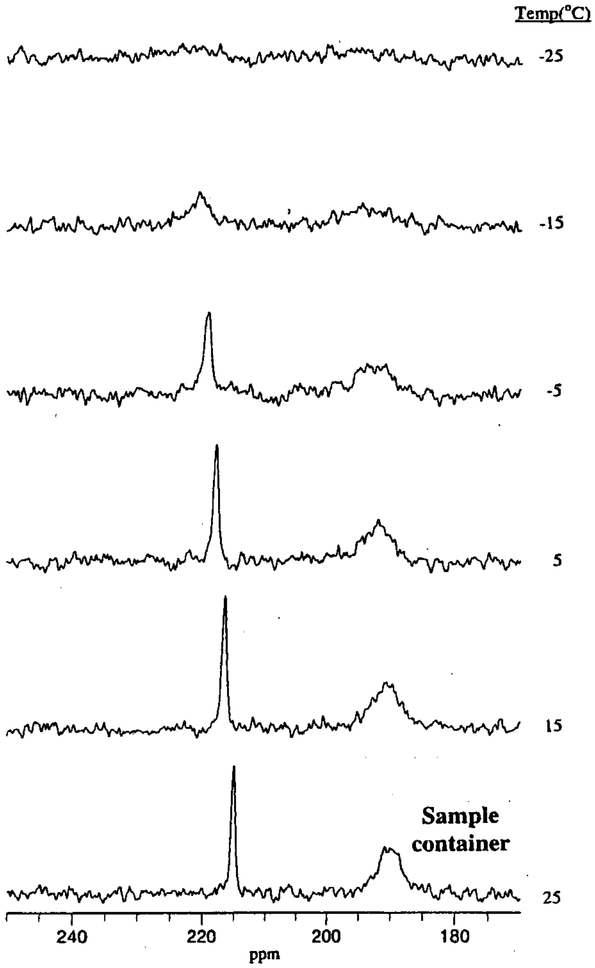

Figure 7. Temperature dependence of the resonance signal for xenon sorbed in PAMAM dendrimer of generation 3.

Data from networks are generally consistent with the classical understanding of the manner in which the free volume of polymers changes on cross-linking. This strongly suggests that the xenon-probe NMR constitutes a simple nondestructive means of studying the free volume in cross-linked systems. The suppression of the xenon resonance signal at temperatures below the glass-transition temperature is qualitative evidence that the xenon probe samples the system at a macromolecular level.

The simple dependence of the chemical shift on the generation number of PAMAM dendrimers is interesting, in that it possibly reflects a simple relationship between the free volume and the generation number. The technique, however, cannot directly address the important issue of the free-volume distribution within the dendritic structure, as it does not presently provide sufficient information on the free-volume distribution. Yet the observation that the chemical shift data for entrapped xenon can be interpreted in terms of a modified chain-end approach to free volume is important. This observation, although suggestive of free volume being mostly associated with chain ends as in linear polymers, is not definitive. The volume of the dendrimer, and hence that of any core volume element, is also likely to increase with both z and M.

References and Notes

(1) Yu, W. C.; Sung, C. S. P.; Robertson, R. E. *Macromolecules* **1988**, *21*, 355.
(2) Jarry, J. P.; Monnerie, L. *Macromolecules* **1979**, *12*, 925.
(3) Noel, C.; Laupretse, F.; Friedrich, C.; Leonard, C.; Halary, J. L.; Monnerie, L. *Macromolecules* **1986**, *19*, 201.
(4) Smith, P. M.; Boyer, R. F.; Kumler, P. L. *Macromolecules* **1979**, *12*, 61.
(5) Cameron, G. G.; Miles, I. S.; Bullock, A. *Br. Polym. J.* **1987**, *19*, 129.
(6) Malhotra, B. D.; Pethrick, R. A. *Macromolecules* **1983**, *16*, 1175.
(7) Walton, J. H. *Polym. Polym. Compos.* **1994**, *2* (1), 35.
(8) Sefcik, M. D.; Schaefer, J. *Polym. Prepr.* **1983**, *24*, 85.
(9) Stengle, T. R.; Williamson, K. L. *Macromolecules* **1987**, *20*, 1428.
(10) Kennedy, G. J. *Polym. Bull.* **1990**, *3*, 605.
(11) Andrady, A. L.; Llorente, M. A.; Mark, J. E. *J. Chem. Phys.* **1980**, *74* (2), 2282.
(12) Llorente, M. A.; Andrady, A. L.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 621.
(13) Tomalia, D. A. *Sci. Am.* **1995**, *272* (5), 62.
(14) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466.
(15) Engel, R. *Polym. News* **1992**, *17*, 301.
(16) Tomalia, D. A. *Adv. Mater.* **1994**, *6*, 529.
(17) Krohn, K. *Org. Synth. Highlights* **1991**, 378.
(18) de Gennes, P.-G.; Hervet, H. J. *J. Phys. Lett* (*Paris*) **1983**, *44*, 351.
(19) Chompf, A. J. *Polymer Networks. Structure and Mechanical Properties*; Plenum Press: New York, 1971.
(20) Fox, T. G.; Loshaek, S. *J. Polym. Sci.* **1955**, *15*, 371.
(21) Andrady, A. L.; Sefcik, M. D. *J. Polym. Sci. Polym. Phys. Ed.* **1983**, *21*, 2453.
(22) Rees, L. M. *Science* **1985**, *230*, 1163.
(23) Lescanec, R. L.; Muthukumar, M. *Macromolecules* **1990**, *23*, 2280.
(24) Naylor, A. M.; W. A. Goddard, III; Keifer, G. Tomalia, D. A. *J Am. Chem. Soc.* **1983**, *111*, 2339.
(25) Jansen, J. F. G. A.; Meijer, E. W. *J. Am. Chem. Soc.* **1995**, *117*, 4417.
(26) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Frechet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401.
(27) Turner, D. T. *Polymer* **1978**, *19*, 789.
(28) Wooley, K. L.; Hawker, C. J.; Pochan, J. N.; Frechet, J. M. J. *Macromolecules* **1993**, *26*, 1514.
(29) Andrady, A., unpublished data.

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