Macromolecules **2007,** *40,* 5787−5790

Cross-Link Density of a Dispersed Rubber Measured by ^{129}Xe Chemical Shift

Wallace O. Parker, Jr.,*,[†] Angelo Ferrando,[‡] Dino Ferri,[‡] and Valentino Canepari[‡]

Physical Chemistry, Refining & Marketing Division, Eni S.p.A., via Maritano 26, 20097 San Donato Milanese, Italy, and Polymer Research Center "C. Buonerba", Polimeri Europa, via Taliercio 14, 46100 Mantova, Italy

Received April 3, 2007; Revised Manuscript Received June 1, 2007

ABSTRACT: ^{129}Xe NMR chemical shifts of adsorbed xenon (natural isotopic abundance) were used to probe the free volume in a cross-linked rubber, polybutadiene (PB), alone and occluded within high impact polystyrene (HIPS). Shift dependency on cross-link density, or N_m (average number of monomer units between chemical cross-links) determined by the classical solvent swelling method, was detailed for high-cis-1,4-PB. A decrease in N_m from 262 to 4 caused the shift to increase 4 ppm. A curve inflection, evident at 218 ppm (and $N_m = 30$), corresponded to a free volume with an average spherical diameter of 0.49 nm using the empirical (shift-pore size) relation known for zeolites. This diameter is essentially equal to that of the PB chain (0.48 nm) at its T_g (glass transition temperature). T_g plotted against N_m showed the same inflection (at $N_m = 25$), corroborating a regime with more severe interchain contacts when the free volume diameter is inferior to the chain diameter. The empirical relation between ^{129}Xe shift and N_m observed for pure PB was used to estimate the cross-link density of PB dispersed in HIPS as a function of cure time. Cross-linkage was greatly slowed after 8 h of curing, when N_m estimated by NMR spectroscopy was 10.

Introduction

Molecular structure−property relationships are paramount for effective production and marketing of specialized plastics such as high-impact polystyrene (HIPS) used in automobile bumpers. HIPS is a rigid biphasic material (moldable thermoplastic) designed to accept mechanical shock without being fractured.[1] It is a grafted copolymer made by bulk polymerization.[2] The impact resistance of rigid polystyrene (PS) is toughened by chemically dispersing small amounts (<10%) of a reinforcing rubber phase, such as polybutadiene (PB).

The performance of HIPS is profoundly influenced by the amount of cross-links created in PB during the curing process. Unfortunately, there is no simple method to determine this cross-link density. Solvent swelling is widely used to estimate cross-link densities in one-phase amorphous polymers. However, this method cannot be applied to HIPS because the rubber phase is bonded to polystyrene, making possible only a generic "swelling index" for comparative purposes. Thus, a simple spectroscopic method was sought.

The ^{129}Xe chemical shift of adsorbed xenon depends on the density of the containing medium, in terms of the free volume space for interaction of Xe with atoms of the medium. ^{129}Xe NMR spectroscopy has been used to probe the morphologies of polymers and polymer blends[3−5] and to assess the free volume elements in polymers.[6−10] It has been shown that cross-linking in polymers causes downfield Xe shifts[3,11] as the free volume decreases. However, only one report was found following the shift as a function of known N_m,[6] and this involved a monophase system.

The aim of this work is to estimate the amount of cross-linkage (average number of monomer units between cross-links, N_m) in the dispersed PB phase of HIPS by NMR. First, the relation between ^{129}Xe NMR shift and N_m is drawn for monophasic PB, with N_m determined by solvent swelling.[12] This shift relation is then used to guide the reticulation conditions of the rubber phase in HIPS, which is critical for producing this highly utilized biphase material.

Experimental Section

Chemical cross-links were introduced into linear PB (Aldrich, cis-1,4 configuration >98%, $M_w = 2 \times 10^6$) by dissolution of PB in CHCl$_3$, addition of variable amounts of dicumyl peroxide (0.16−25.06 wt %), lyophilization of solvent, compression into a thin disk, and heating at 145 °C for 45 min.

HIPS was produced by mixing PB with styrene followed by polymerization in continuous mass at Polimeri Europa Mantova as described previously.[13] The total dispersed phase in HIPS was 31 wt % (caused by a total of 8.5 wt % PB) and consisted of "salami" particles (see transmission electron micrograph in the TOC graphic) with a number-average diameter of ca. 2 μm. PB of HIPS ($N_m \approx 30$ from production, $M_w = 2.7 \times 10^5$, 38% cis-1,4 and 51 wt % trans by solution state ^{1}H NMR) were cross-linked by curing at 250 °C under vacuum for various times.[13]

N_m was calculated for monophasic PB from the increase in disk diameter after swelling in toluene (for 2 days) using the Flory formula:[12]

$$\nu_e = \frac{\ln(1 - \upsilon_2) + \upsilon_2 \chi \upsilon_2^{\,2}}{V_1\left(\sqrt[3]{\upsilon_2} - \frac{1}{2}\upsilon_2\right)} \tag{1}$$

where ν_e is the lattice chain density (i.e., number of cross-links per volume), $\upsilon_2 = (D_d/D_w)^3$ is the ratio between dry (D_d) and wet diameters (D_w), χ is the polymer−solvent interaction parameter (for PB−toluene = 0.34), and V_1 is the solvent molar volume (for toluene = 106.54 cm^3/mol). This value and the molar density δ_m (for PB = 0.0187 mol/cm^3) gave the average number of monomer units between chemical cross-links.

$$N_m = \delta_m/\nu_e \tag{2}$$

---

* Corresponding author. E-mail: wallace.parker@eni.it.
[†] Eni.
[‡] Polimeri Europa.

10.1021/ma070793a CCC: $37.00

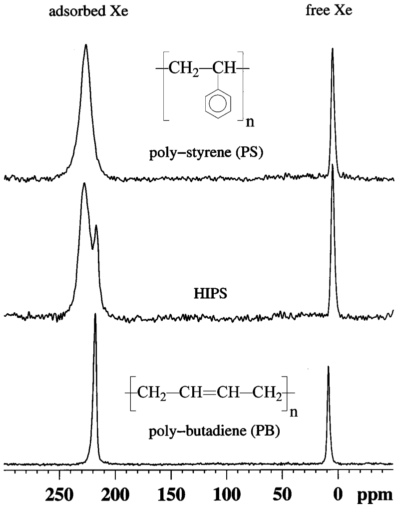

Figure 1. ^{129}Xe NMR spectra of Xe adsorbed in cross-linked PB (N_m = 43), HIPS (cured 2 h), and PS.

The glass-transition temperature (T_g) was measured with a Rheometrics rheometer (model 800) by applying rectangular torsion (sample dimension = 2 × 8 × 35 mm). Temperature scans were made at 1 Hz while heating 1 °C/min, as previously.[13]

Xenon gas (2 mmol), at natural abundance ^{129}Xe (26%), was adsorbed on ca. 400 mg of shredded samples (degassed under vacuum, 25 °C, 12 h), contained in glass tubes (10 mm o.d.), by cold finger transfer to give a final pressure of ca. 2 bar at 25 °C. After flame-sealing, samples were equilibrated at 25 °C for 4 days. ^{129}Xe NMR spectra (83 MHz) were collected with a Bruker AMX-300 spectrometer using 70° (20 μs) pulse, 10 s delay, and 8000 scans. Shifts were referenced externally to Xe (g) at low pressure (0 ppm) via a secondary standard of Xe in decane (175.4 ppm).[14] Free (nonadsorbed) Xe within the tube gave a signal at 6.0 ± 0.5 ppm in HIPS and at 10.0 ± 0.5 ppm in PB samples. ^{129}Xe shift of adsorbed Xe was pressure independent. T_1's of adsorbed Xe were 15−30 s.

Results and Discussion

Preliminary ^{129}Xe NMR spectra of HIPS showed two signals for adsorbed xenon. Comparison of spectra for Xe adsorbed in authentic PB and PS samples revealed that the larger shift (226.7 ppm) arose from the PS phase (Figure 1). A greater chemical shift is expected for Xe within the PS phase with less fractional free volume. Xe is exchanging slowly (compared to the NMR time scale) between the separate PS and PB phases since two narrow peaks are seen, each at its pure phase positions, with a separation of ca. 8 ppm or 600 Hz. If a minimum product of 20 is used in the slow exchange limit (exchange time × 600 Hz = 20), then a Xe atom remains at least 33 ms in one phase before exchanging to another with an interphase exchange rate less than 30 s^{-1}.

It is possible that the upfield ^{129}Xe signal in HIPS does not reflect the entire PB phase. There was a large size distribution for the dispersed PB particles, mainly from 0.7 to 2.9 μm (see TOC graphic). Since interphase exchange rates are expected to increase as the domain size decreases, we cannot rule out some Xe exchanging in the intermediate regime (between the smallest domains with high surface area) to give unresolved signals. Integral areas were not utilized here, only shifts.

As expected, the signal line width is greater for Xe in the more rigid PS phase (850 Hz) of HIPS compared to that in the elastomeric PB phase (400 Hz).

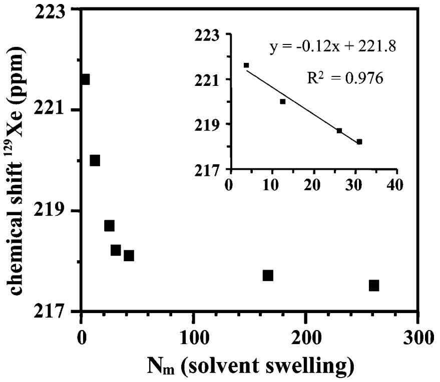

Figure 2. Plot of N_m (average number of monomers per cross-link) vs ^{129}Xe chemical shift for Xe adsorbed in high-cis PB with varying amounts of cross-links. N_m values (3.8, 12.5, 26, 31, 43, 167, and 262) were determined by solvent swelling. Inset shows linearity in the range above 218 ppm.

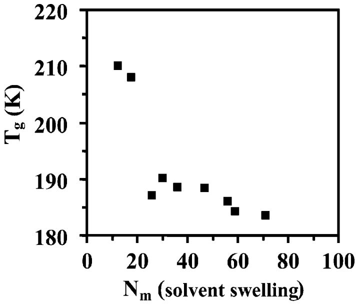

Figure 3. Plot of N_m vs T_g for linear high-cis 1,4-PB with varying degrees of cross-linkage.

Polybutadiene. The shift value (217.5 ppm) observed for Xe adsorbed in pure (monophase) PB with the least amounts of cross-links (N_m = 262) agrees with the literature,[8] ca. 216 ppm considering a 2 ppm correction for bulk susceptibility.[8] Some workers reference shifts internally to "free" xenon (set at 0 ppm). This referencing method was rejected here since the shift of free Xe varies according to pressure and chemical exchange with the adsorbed phase.

^{129}Xe NMR shift dependency on the degree of chemical cross-linkage was detailed for monophasic high-cis PB's with known N_m (solvent swelling). As anticipated, the ^{129}Xe shift increased with increasing cross-link density (decreasing N_m). A maximum shift excursion of ca. 4 ppm was realized, which is much greater than the experimental precision (±0.2 ppm). Strikingly, there are two linear regimes apparent in the plotted data (Figure 2), with an inflection evident near N_m = 30 and chemical shift = 218 ppm. This inflection, observed at room temperature, is not due to the glass transition for cross-linked PB (for N_m = 30, T_g = 190 K). The origin of this inflection is addressed below. Clearly, Xe experienced enhanced compression (more pronounced shift) when the distance between cross-links was less than 30 monomer units. From a practical application point of view, HIPS with extensively cross-linked PB (N_m < ca. 25) does not exhibit desirable anti-impact properties.

Quantitative empirical relationships between experimental observables sensitive to free volume in polymers, such as ^{129}Xe NMR shift, gas permeability, solubility parameters, and positron annihilation lifetimes, have been reported recently.[7−10] Since correlations of ^{129}Xe shift with N_m and T_g with N_m[15] exist, a parallel between T_g and ^{129}Xe shift was anticipated. Any reduction in free volume will cause an increase in both T_g and Xe shift. Importantly, the T_g plot for 1,4-PB (Figure 3) shows an inflection near N_m = 25, similar to that in Figure 2. When there are less than 25 monomer units between cross-links, the free volume (diameter) is less than the thickness of the polymer chain. Ulterior cross-linkage beyond this point causes entry into another regime where polymer chain contacts are more intense.

This gives a more solidlike behavior, as evidenced by the ca. 20 °C jump in T_g.

On the basis of chemical shift, we would like to have information about the environment around the large Xe atom dissolved in the polymer, such as the average size of the void space containing xenon. As yet, chemical shift functions for Xe−polymer interactions are unknown. Xe chemical shift cannot be calculated from first principles knowing the chemical structure of the polymer. However, the temperature dependence of Xe shift (not analyzed here) can be calculated from polymer parameters, using a model describing the van der Waals dispersion interaction between Xe and neighboring polymer chains.[8]

The size of the void space (for a given shape) occupied by xenon in zeolites can be estimated on the basis of an empirical relation reported by Demarquay and Fraissard.[16] In fact, eq 3 is the *only* widely used relation between void size and Xe shift. It relates the diameter of a spherical zeolite void (d_s) with Xe shift (δ). Voids smaller than the van der Waals diameter of Xe (0.44 nm) are not considered. Quantum mechanical calculations have shown that Xe NMR shielding response is more pronounced at shorter distances from neighboring atoms. This is the theoretical basis for the empirical correlation expressed in eq 3 for a given type of wall atom.

$$d_s = 2[(499.1/\delta) + 0.146] \tag{3}$$

Let us neglect for a moment the difference in electronic shielding surfaces for a zeolite (oxygen vertices) and PB (methylene group) and use the zeolite correlation as other workers have done.[7,9,10] However, a priori we expect that xenon will interact more (stay closer and have a greater shift) with hydrocarbon chains than with oxygens on the zeolite walls.[17] From eq 3, the chemical shift of 218 ppm at the inflection point in the plot of Figure 2 corresponds to a spherical void diameter (d_s) of 0.49 nm. This value is very close to the van der Waals diameter of the polymer chain (0.48 nm) for linear 1,4-PB at its T_g (173 K), calculated by Miller et al.[8] from ^{129}Xe NMR shifts and a van der Waals shift model. Also, it is not far from the estimated van der Waals diameter of xenon (ca. 0.44 nm), where a stronger shift response is expected. However, the common inflection in shift and T_g plots (near $N_m = 30$) shows that there was a jump down in effective void volume.

Above T_g, where all NMR measurements were made, the size and shape of the free volume (micropores) fluctuate rapidly in time due to efficient polymer chain motions. These motions (e.g., trans−gauche isomerization) are required to accept the large Xe atom. When the diameter of the void volume is comparable to (or less than) the polymer chain diameter (ca. 0.48 nm), then polymer chain contacts are more severe. This causes a jump in shift and T_g (Figures 2 and 3, respectively).

The application of eq 3 to dense hydrocarbons (i.e., cross-linked rubber) may appear overly optimistic. But, other workers found it valid for systems with pore walls clearly chemically different from those of an aluminosilicate. The zeolite correlation (eq 3) yielded reasonable sizes for the nanopores in crystalline $[Co(en)_3]Cl_3$[18] and for the microcavities in amorphous perfluorinated polymers.[10]

In the only other report of ^{129}Xe shift vs reticulation density in polymers,[6] a continuous linear relationship was observed. Morgan et al. studied the free volume changes associated with (cross-linkage) end-linking of poly(oxypropylene) chains and branched starburst dendrimers. Shift measurements were made at 298 K, just above the glass-transition temperatures (235−281 K). They found a linear 5 ppm increase in xenon chemical shift (from 217.2 to 222.2 ppm) as M_c decreased from 2470 to 670 (N_m = 42 to 11) for end-linked networks in poly(oxypropylene). The slope for this correlation is −0.16 ppm per monomer unit between cross-link. The results of the present work gave a slope of −0.12 ppm per monomer for $N_m = 4-30$ and a slope of −0.003 ppm per monomer for $N_m = 30-260$.

If a change in slope occurs when the apparent void volume diameter hosting xenon approaches the polymer chain diameter, then an inflection should occur also in the plot for poly(oxypropylene). The average chain diameter for poly(oxypropylene) is ca. 0.4 Å greater than that for PB.[19] Since the change in slope occurred near $N_m = 30$ for PB, a change in slope for poly(oxypropylene) is expected above $N_m = 30$. In other words, the regime with very small slope was not evidenced by Morgan et al. (Figure 2 in ref 6) because they did not examine samples with high N_m (>40).

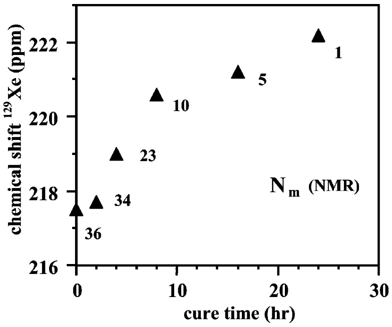

Figure 4. Plot of cure time (250 °C) vs ^{129}Xe chemical shift for Xe dissolved in the PB phase of HIPS. N_m values, shown near symbol, were calculated from the relation in Figure 2 for monophase PB.

Polybutadiene Dispersed in HIPS. The shift for xenon dissolved in PB in HIPS was 4−9 ppm upfield from that of Xe in PS (226.5 ± 0.4 ppm). N_m values for PB dispersed in HIPS, cured for different times (Figure 4), were estimated from the linear relation in Figure 2 (shift = $-0.12N_m + 221.8$) found for the "highly compressed" regime above the 218 ppm inflection. This relation was applicable because before curing PB had $N_m \approx 30$. Since Xe shift strongly depends on the local environment, the N_m shift correlation obtained for pure PB is expected to give a reasonable estimate of N_m for PB in the dispersed phase of HIPS. More specifically, PS dispersed inside the spherical rubber occlusions (see "salami particles", TOC graphic) should have no appreciable influence on xenon shift.

Cross-linkage was relatively rapid up to about 8 h and N_m = 10, when the creation of new cross-links became much more difficult. N_m values below 10 would cause a substantial increase in T_g (e.g., Figure 3), especially considering that the PB used in HIPS contains 50 wt % of the trans isomer. This would slow chain movements and hinder the intermolecular interactions necessary for cross-linkage. HIPS samples with $N_m \leq 10$ are easily crazed, being unable to resist impact.[13]

Conclusions

Based on a empirical ^{129}Xe chemical shift vs reticulation density correlation for pure (monophase) PB, the amount of cross-linkage in a dispersed PB phase was estimated. Pure PB showed two linear regimes in the correlation (shift = 222−217 ppm and N_m = 4−262) with different slopes. The transition between the two regimes occurred at ca. N_m = 30 and 218 ppm, when the diameter of the estimated free (spherical) volume hosting Xe was comparable to the polymer chain diameter. Thermal glass transitions showed the same inflection (at ca. N_m = 25), confirming a regime of higher contact (less void volume) between polymer chains when the void diameter is inferior to the chain diameter. ^{129}Xe NMR spectroscopy monitored the degree of PB cross-linkage within HIPS, allowing noninvasive control of the curing process to avoid over-reticulation. This work extends the quantitative relationship between xenon chemical shift and free volume in polymers.

Acknowledgment. C. J. Jameson provided enlightening concepts on the Xe shielding response in nanometer void spaces.

References and Notes

(1) (a) Maestrini, C.; Castellani, L.; Merlotti, M.; Vighi, M. *Polymer* **1992**, *33*, 1556−1558. (b) Alfarraj, A.; Nauman, E. B. *Polymer* **2004**, *45*, 8435−8442.

(2) (a) Echte, A. In *Rubber-Toughened Plastics*; Riew, C. K., Ed.; American Chemical Society: Washington, DC, 1989. (b) Harper, C. A. *Handbook of Plastics, Elastomers & Composites*; McGraw-Hill: New York, 2002.

(3) Mansfeld, M.; Flohr, A.; Veeman, W. S. *Appl. Magn. Reson.* **1995**, *8*, 573−586.

(4) (a) Mansfeld, M.; Flohr, A.; Veeman, W. S. *Appl. Magn. Reson.* **1995**, *8*, 573−586. (b) Walton, J. H. *Polym. Polym. Compos.* **1994**, *2*, 35−41.

(5) Simonutti, R.; Bracco, S.; Comotti, A.; Mauri, M.; Sozzani, P. *Chem. Mater.* **2006**, *18*, 4651−4657.

(6) Morgan, D. R.; Stejskal, E. O.; Andrady, A. L. *Macromolecules* **1999**, *32*, 1897−1903.

(7) Merkel, T. C.; Toy, L. G.; Andrady, A. L.; Gracz, H.; Stejskal, E. O. *Macromolecules* **2003**, *36*, 353−358.

(8) Miller, J. B.; Walton, J. H.; Roland, C. M. *Macromolecules* **1993**, *26*, 5602−5610.

(9) Nagasaka, B.; Educhi, T.; Nakayama, H.; Nakamura, N.; Ito, Y. *Radiat. Phys. Chem.* **2000**, *58*, 581−585.

(10) Golemme, G.; Nagy, J. B.; Fonseca, A.; Algieri, C.; Yampolskii, Y. *Polymer* **2003**, *44*, 5039−5045.

(11) Kennedy, G. J. *Polym. Bull. (Berlin)* **1990**, *23*, 605−608.

(12) Flory, P. J.; Rehner, J. *J. Chem. Phys.* **1943**, *11*, 521−526.

(13) Canepari, V. Study of Cross-linkage Using NMR Methods: Application to Anti-Impact Styrene Systems. Doctoral Thesis in Mechanical Engineering, Univ. Brescia, Italy, 2002.

(14) Stengle, T. R.; Reo, N. V.; Williamson, K. L. *J. Phys. Chem.* **1981**, *85*, 3772−3775.

(15) Andrady, A. L.; Sefcik, M. D. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2453.

(16) Demarquay, J.; Fraissard, J. *Chem. Phys. Lett.* **1987**, *136*, 314−318.

(17) Sears, D. N.; Jameson, C. J. *J. Chem. Phys.* **2004**, *121*, 2151−2157.

(18) Ueda, T.; Eguchi, T.; Nakamura, N.; Wasylishen, R. E. *J. Phys. Chem. B* **2003**, *107*, 180−185.

(19) Zang, Y.-H.; Carreau, P. J. *J. Appl. Polym. Sci.* **1991**, *42*, 1965−1968.

MA070793A