A Study of Deuterium Distribution in Deuterated Polyolefins by Pyrolysis−Photoionization Mass Spectrometry

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ABSTRACT: The saturation of polydienes with deuterium produces labeled polyolefins that, when studied with the identical hydrogenated polydienes, have proven quite useful for the understanding of many of the basic properties of these materials. However, until now the only way to determine the amount of deuterium substitution on the labeled molecules has been to compare the densities of the hydrogenated and deuterated polymers, which gives no information on how the deuterium is distributed along the chains. The information is important, since it is clear from the density results that with some saturation catalysts (Pd) there must be some H−D exchange since there are more than two deuterium atoms per diene monomer on the labeled species, while for others (Wilkinson's) there appears to be no exchange. In this work, pyrolysis−photionization mass spectrometry has been used to examine the structure of the hydrogenated and deuterated polydienes in more detail. The deuterium distributions were determined using a modified Bernoullian model that takes into account the first two D's that were added by the saturation event. The most revealing data come from the tetramer $C_4H_{8-x}D_x$, which confirm the average level of deuteration as measured by density. For polymers saturated with Pd catalysts, the pyrolysis−photoionization mass spectra show that the deuterium was randomly distributed by the H−D exchange. Perdeuteriopolyisobutylene was also examined, as was its blend with hydrogenous polyisobutylene, which helped to confirm that exchange had occurred during the saturation of the polydienes using the catalyst rather than during the measurement step. The data for the polydiene deuterated using Wilkinson's catalyst confirmed that there was little, if any, exchange.

Introduction

Deuterated polymers, especially hydrocarbon macromolecules, are extensively used to study the basic physical properties of these materials. The contrast between the interactions of neutrons with the ^{1}H (proton) and D (deuteron) nuclei is the basis for much neutron scattering work and is perhaps that most noted example. In particular, small-angle neutron scattering (SANS) has been used to determine such basic features as the size and mixing of polymer coils in the melt state.[1] Neutron reflectivity has been applied to characterize the interfaces in polymer systems.[2] The reactions of deuterons with helium ions has been exploited in nuclear reaction analysis and forward recoil elastic scattering, again mostly to measure polymer interfaces.[3,4] Deuterated polymers have also been useful in infrared experiments to investigate the nature of chain folding in semicrystalline polyethylene.[5] Overall, the availability of deuterated polymers has been extremely valuable to the advance of polymer science.

In many cases, the deuterated polymers are made by the polymerization of deuterated monomers in just the way that normal, hydrogenous polymers are synthesized. However, this can be an expensive route due to the cost of the special monomers. Moreover, there are often isotope effects on the polymerization, which make it difficult to produce a deuterated polymer that exactly matches its hydrogenous analogue in all molecular characteristics such as molecular weight, molecular weight distribution, tacticity, etc. These are important, since generally the deuterated polymer is playing the role of a "labeled" species, which is physically identical to the unlabeled one. Without a close match between the labeled and unlabeled polymers, it can be difficult to know how much of the effects seen (in, say, miscibility or crystallization) are due to the variables being studied and how much derives simply from the differences between the deuterated and hydrogenous polymers.

In recent years, a new way of making deuterated polymers has been used which ensures a match between the labeled and unlabeled macromolecules.[6] This technique is available when the polymer to be studied can be made by saturating a polydiene, such as the hydrogenation of polybutadiene to produce model ethylene−butene copolymers. This has proven to be useful in making many versions of the commercially important polyolefins, especially when anionic methods are used to make a polydiene with very narrow molecular weight distribution. This synthetic scheme has become important in the production of labeled polymers since the saturation can be done on the same polydiene with either hydrogen gas or deuterium. Catalysts have been developed that can give full saturation without any degradation of the polymer molecular weight, so the hydrogenous and deuterated products of these reactions will be identical to each other in all characteristics such as molecular weight, sequence distribution, etc.[7,8] Moreover, these are less expensive to produce than polymers made by the polymerization of deuterated monomers, which all cost much more than D_2.

One problem that remains with the use of deuterated polymers made by the saturation of polydienes is the determination of their level of deuteration. For example,

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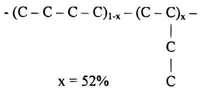
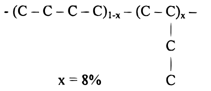
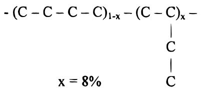
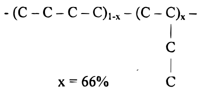
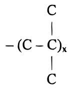
saturating polybutadiene with D_2 would give a polymer with an empirical formula of $C_4H_6D_2$ if no other reactions take place. However, the densities of many of these polymers are inconsistent with such a formula. Assuming that the molar volume of a polymer does not change with deuteration, the only way to explain the higher densities is a higher level of deuteration. The additional deuteriums on the polymers (beyond those from the saturation event) are placed there by exchange reactions between the hydrogens on the chain and the deuterium. Density measurements can thus be used to determine the level of deuteration, but to be more confident of this number it would be useful to have another way of determining deuteration level. ^{2}H NMR spectra of these polymers do show many peaks, indicating that there is a broad range of patterns of substitution; however, it is too complicated to interpret in terms of exactly which species are present. No other technique has yet been found that can independently measure the deuterium level.

In this paper we describe a pyrolysis mass spectrometric technique which can determine deuteration level and deuterium distribution in such polymers. Pyrolysis mass spectrometry has been widely applied for characterization of polymer structure and composition[9−13] including deuterated samples.[14] When combined with photoionization, the technique has been used to determine polymer microstructures and differentiate various polyolefins types.[15,16] With this technique, a polymer is pyrolyzed into to small oligomers (typically less than 400 Da) which are softly ionized by vacuum-ultraviolet photons and analyzed by mass spectrometry.[15] Because fragmentation in the ionization step is minimized, the mass distribution of oligomers can be obtained directly from the photoionization spectrum to determine the level of deuteration as well as the distribution of D along the polymer chain. Comparison of the measured distribution to a model for the exchange reaction provides microstructural information on the deuterated polymer.

Experimental Section

Synthesis of Polymers. The details of the synthesis and characterization of these model polymers have been given previously. Four of the samples (A−D in Table 1) are model ethylene−butene copolymers (EBs) that were made by the saturation of polybutadienes of varying vinyl content.[6] The polybutadienes were made anionically to produce polymers with narrow molecular weight distributions and well-defined chemical compositions. Each 1,2-addition in the butadiene polymerization translated into a butene moiety in the final hydrogenated polymer and each 1,4-addition into two ethylenes. Raising the polarity of the polymerization medium increased the level of vinyl incorporation. For polymers A, B, and D, the saturation was performed with heterogeneous palladium catalysts that provide essentially complete saturation without degrading the chains.[7] For polymer C this was done using Wilkinson's catalyst.[8] In each case, the saturation was done with deuterium as well as with hydrogen, allowing for the production of both labeled and unlabeled versions of each model polyolefin. These two catalysts were used to make the samples for this study because density measurements of the deuterium level in the past have indicated that H−D exchange occurs when saturating with Pd catalysts, but not when using Wilkinson's. The fifth polymer pair (E) is composed of two versions of polyisobutylene: one from the normal hydrogenous monomer and one from the perdeuterio monomer. These were made by living cationic polymerization techniques and supplied by Prof. Rudi Faust, University Massachusetts−Lowell.[17] This pair provides a case where the polymer is either fully hydrogenated or fully deuterated.

Table 1. Molecular Structures of Polymers Studied

Polyolefin Sample	Chemical Structure[a]	M_w (10^3 g/mol)[b]
A	 $-(C-C-C-C)_{1-x}-(C-\underset{\substack{\vert\\C\\\vert\\C}}{C})_x-$ x = 52%	85
B	 $-(C-C-C-C)_{1-x}-(C-\underset{\substack{\vert\\C\\\vert\\C}}{C})_x-$ x = 8%	65
C	 $-(C-C-C-C)_{1-x}-(C-\underset{\substack{\vert\\C\\\vert\\C}}{C})_x-$ x = 8%	140
D	 $-(C-C-C-C)_{1-x}-(C-\underset{\substack{\vert\\C\\\vert\\C}}{C})_x-$ x = 66%	114
E	 $-(C-\overset{\substack{C\\\vert}}{\underset{\substack{\vert\\C}}{C}})_x-$	85 (H version) 107 (D version)

[a] Determined by NMR. [b] Determined by SEC light scattering; for all of these polymers, M_w/M_n is less than 1.10.

Molecular weights and their distributions were determined by light scattering and size exclusion chromatography (SEC). Density was measured on a density gradient column.[18] A comparison of the densities of the H and D versions of a given polymer was used to find the level of deuteration in each material. Chemical microstructures were determined by ^{1}H and ^{13}C NMR. All of these polymers were found to have sequence distributions characteristic of random copolymers based upon the ^{13}C NMR results. The polymers used in this study are listed in Table 1, which also gives characterization data.

Pyrolysis−Photoionization Mass Spectrometry. The experimental setup for pyrolysis−photoionization mass spectrometry is described in detail elsewhere.[15,16] Pyrolysis was performed directly in the source region of a reflectron time-of-flight (RETOF) mass spectrometer using an insertion probe and a temperature-programming system. Photoionization was performed with 118.2 nm (10.49 eV) radiation produced by frequency tripling the third harmonic of a Nd:YAG laser operating at 50 Hz. Mass spectra were continuously averaged at the laser repetition rate with a transient digitizer mounted in a personal computer. An averaged mass spectrum was recorded every 32 laser shots.

Similar to our previous polyolefin work,[16] 10 μg samples were loaded into the bottom of a Pyrex vial and heated at a rate of 4.2 °C/s to a final temperature of 450 °C. Figure 1 shows typical total ion current plots for (a) completely hydrogenated and (b) partially deuterated polybutadiene (polymer B in Table 1). Six averaged mass spectra from the peak of the total ion current were used for determination of deuteration levels and distributions. As indicated by the inset of Figure 1a, additives generally evolve at a lower temperature than the main pyrolysis peak and therefore do not significantly compromise the mass spectra used for analysis.

Because the sample location within the vial and the vial location within the probe assembly varied slightly from sample to sample, the temperature recorded by the thermocouple inside the probe assembly was not an exact measure of the sample temperature. Therefore, the peak maximum of the total ion current plot varied on the order of ±10 °C from run to run. In fact, the temperature shift between the main pyrolysis peaks in Figure 1a,b is within this uncertainty. To compensate for this effect, the pyrolysis photoionization mass spectra used for data analysis (and shown in subsequent figures) were

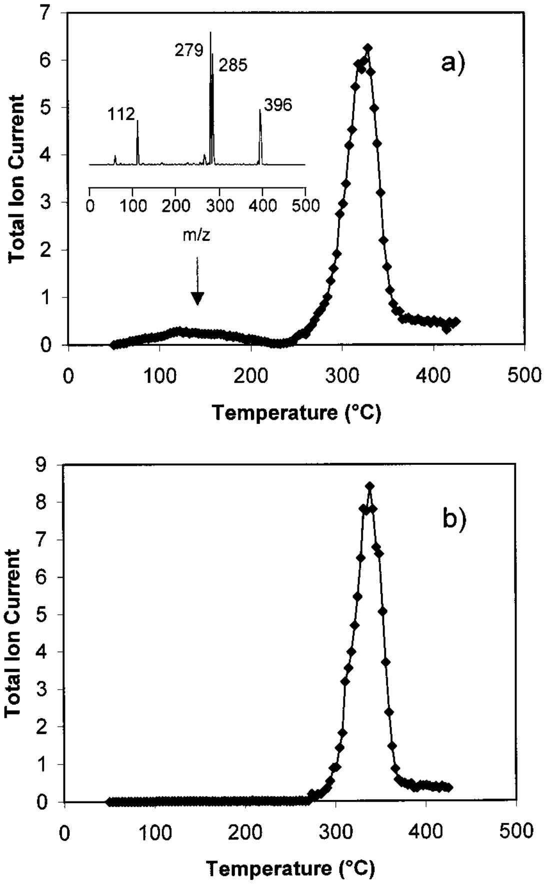


Figure 1. Total ion current plots for pyrolysis−photoionization mass spectra of polymer B: (a) hydrogenated and (b) partially deuterated. The inset shows the mass spectrum for the low-temperature desorption products at 132 °C.

obtained by integrating the ion signal over a 4 s interval around the observed peak maximum in the total ion current.

Results and Discussion

Several pairs of hydrogenated and partially deuterated polyolefins were analyzed by pyrolysis−photoionization mass spectrometry. Figure 2 shows the mass spectra at 270 °C for polymer A from Table 1: a completely hydrogenated polybutadiene (Figure 2a) and a deuterated polybutadiene with a 35.9% deuteration level as determined by density measurement (Figure 2b). The most intense series of pyrolysates for the hydrogenated polybutadiene is the alkene series (*m*/*z* = 42, 56, 70, 84, ...). The intense pentene (70) and butene (56) peaks are likely from enhanced cleavage of the polymer backbone at α- and *β*-positions to the branch site. For the deuterated polybutadiene, the signal for each of the alkene products is distributed over several *m*/*z* units corresponding to different levels of deuteration. For example, the most intense peak in the pyrolysis mass spectrum for the hydrogenated polybutadiene is *m*/*z* = 70, which corresponds to C_5H_{10}. The most intense peak in the pyrolysis mass spectrum for the deuterated polybutadiene is *m*/*z* = 73, which corresponds to $C_5H_7D_3$.

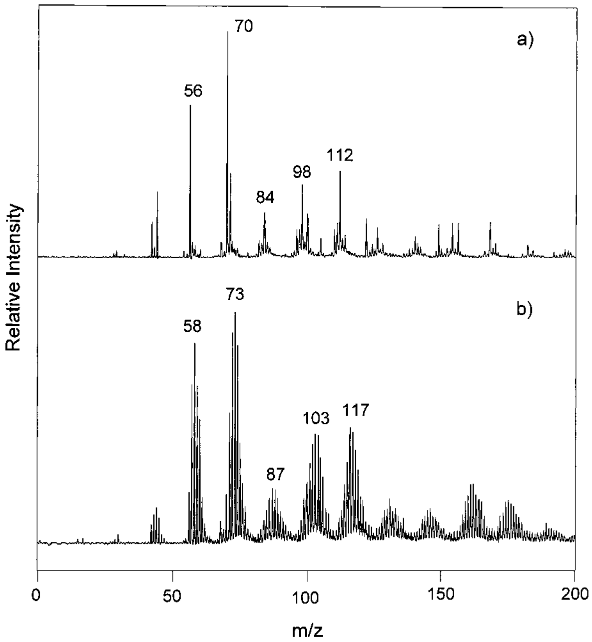


Figure 2. Pyrolysis photoionization mass spectra at 270 °C for polymer A: (a) hydrogenated and (b) partially deuterated.

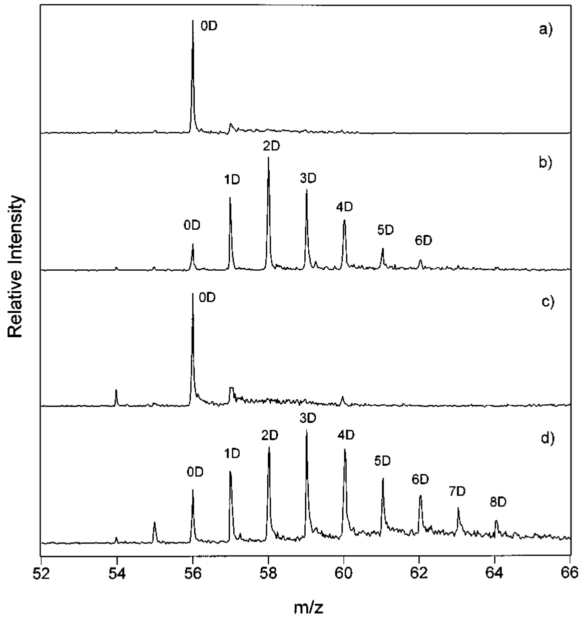


Figure 3. Pyrolysis−photoionization mass spectra of the C_4 distributions for polymer A at 270 °C, (a) hydrogenated and (b) partially deuterated, and for polymer B at 305 °C, (c) hydrogenated and (d) partially deuterated.

The butene pyrolysates ($C_4H_xD_{8-x}$) were chosen for quantitative characterization of deuterium content and microstructure. These distributions exhibit high signal intensity and are low enough in mass that the adjacent pyrolysate distributions (C_3 and C_5) do not overlap in the analysis of deuterated samples. Also, the hydrogenated samples exhibit a single dominant peak in the C_4 pyrolysate distribution (*m*/*z* = 56) whereas the C_5 and larger pyrolysate distributions exhibit a more complicated series of peaks. The simple peak pattern for the butene pyrolysates facilitates the modeling procedure (see below) which adjusts the calculated distribution to account for competing pyrolysis pathways.

Figures 3 and 4 show the pyrolysis−photoionization mass spectra in the *m*/*z* region of the butene pyrolysate ($C_4H_xD_{8-x}$) for four pairs of polyolefin samples. Figure 3a,b shows the mass spectra for a completely hydrogenated and a partially deuterated polybutadiene containing 52% branched monomer (polymer A in Table 1). Figure 3c,d shows the mass spectra for a completely

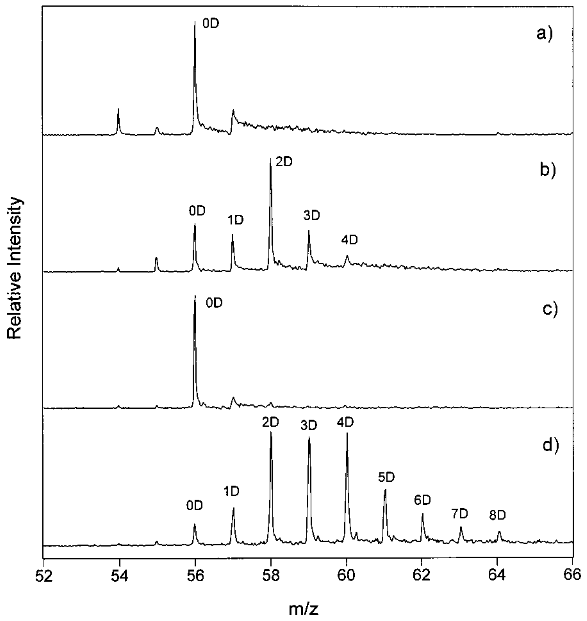


Figure 4. Pyrolysis photoionization mass spectra of the C_4 distributions for polymer C at 315 °C, (a) hydrogenated and (b) partially deuterated, and for polymer D at 294 °C, (c) hydrogenated and (d) partially deuterated.

hydrogenated and a partially deuterated polybutadiene containing 8% branched monomer (polymer B in Table 1). Figure 4a,b shows the mass spectra for a completely hydrogenated and partially deuterated polybutadiene containing 8% branched monomer (polymer C in Table 1). Figure 4c,d shows the mass spectra for a completely hydrogenated and partially deuterated polybutadiene containing 66% branched monomer (polymer D in Table 1). The most intense peak for all four completely hydrogenated polybutadienes is due to the butene pyrolysate. Fairly broad and even distributions of deuterium atoms are observed for the deuterated polyolefins A, B, and D. In contrast, for the deuterated polyolefin C, the peak at $m/z = 58$ corresponding to substitution of two deuterium atoms has an increased intensity. This difference in peak distribution indicates that H−D exchange occurred with the Pd-catalyzed deuteration in polymers A, B, and D but was insignificant for the polymer C saturated using Wilkinson's catalyst.

If pyrolysis−photoionization mass spectrometry is used to determine the distribution of deuterium throughout the polyolefin chain, it is important to determine whether exchange between hydrogen and deuterium atoms occurs during the pyrolysis step. Figure 5 shows the pyrolysis−photoionization mass spectra for polymer E from Table 1, including a completely hydrogenated polyisobutylene (Figure 5a), a completely deuterated polyisobutylene (Figure 5b), and a mixture of the hydrogenated and deuterated polyisobutylenes (Figure 5c). Pyrolysis of polyisobutylene produces highly branched alkenes which fragment upon 10.49 eV photoionization to produce peaks at $m/z = 57$, 97, and 113. The polyisobutylenes were amorphous polymers that could be mixed together fairly efficiently with a microspatula. As shown in Figure 5c, the mass spectrum for the polyisobutylene mixture is essentially a summation of the mass spectra obtained for the individual polymers. Therefore, any hydrogen/deuterium exchange between polymer chains or between the polymers and the pyrolysis apparatus was negligible. The results of this experiment indicate that the distribution of deuterium atoms in the polymer chain should be reflected in the pyrolysates.

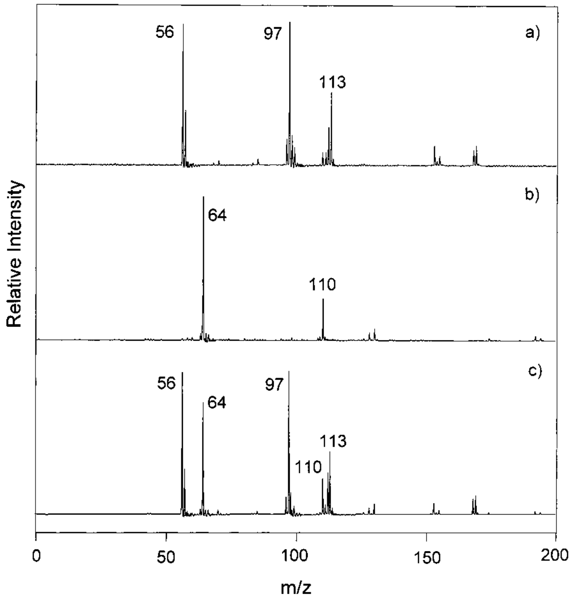


Figure 5. Pyrolysis photoionization mass spectra of polymer E at 225 °C: (a) hydrogenated, (b) completely deuterated, and (c) a mixture of the hydrogenated and deuterated samples.

The deuteration levels for the polyolefins analyzed by pyrolysis−photoionization mass spectrometry were determined from the average of six mass spectra (total of 192 laser shots) at the peak of the total ion current for each polyolefin. As in our previous work,[15] a modeled distribution was fit to the experimentally determined distribution. The modeled distribution was calculated from an assumed deuteration level of the polymer and then adjusted for the contributions of dialkene formation during pyrolysis ($M - 2$) and ^{13}C isotopic substitution ($M + 1$) to the ion current.

The C_4 distribution ($m/z = 56-65$) for each polyolefin sample was modeled using Bernoullian statistics. With this model, the possible sites for deuteration are viewed as a linear sequence. For example, the probability that the eight sites are occupied in the manner H−D−H−D−D−H−H−H is $(P_H)^5(P_D)^3$ where P_D is the level of deuteration and $P_H = 1 - P_D$. The total probability of formation for an oligomer with the formula $C_4H_5D_3$ is obtained by summing the probabilities of all possible sequences. In this manner, the relative distribution of oligomers $C_4H_xD_{8-x}$ where $x = 0-8$ can be calculated for an assumed value of P_D. The oligomer distribution is then adjusted for dialkene formation (ion current at $M - 2$ relative to each oligomer m/z) and ^{13}C isotopic substitution (ion current at $M + 1$ relative to each oligomer m/z) to obtain the modeled distribution expected in the mass spectrum. The fit of the modeled distribution to the mass spectral data is assessed by the percentage of ion current modeled:

$$\%\ \text{ion current modeled} = \left(1 - \sum_{m=54}^{65} |\%\ m_{\text{expt}} - \%\ m_{\text{model}}|/2\right) \times 100\% \quad (1)$$

where $\%\ m_{\text{expt}}$ is the normalized experimental peak area and $\%\ m_{\text{model}}$ is the peak probability determined by the model. The optimum value of P_D gives the highest percentage of ion current modeled.

Table 2. Results from Modified Bernoullian Modeling of the Pyrolysis Photoionization Mass Spectra

polyolefin sample	density measurement (% D)	pyrolysis measurement (% D)	P_{2D}	ion current modeled (%)
A	35.8	30.3 ± 1.2	0	96.2
B	43.4	39.7 ± 1.2	0.007	89.9
C	25.1	25.0 ± 2.0	0.610	94.0
D	40.6	41.7 ± 1.2	0.010	93.8

Bernoullian statistics assume that individual deuterons are randomly incorporated into the polymer. Random incorporation is expected when H/D exchange is significant as in the case of polymers A, B, and D. However, the addition of D_2 across a double bond results in the addition of exactly two deuterons per monomer. If H/D exchange is not significant, then the distribution of deuterons will favor the formation of $C_4H_6D_2$ by pyrolysis. This effect is apparent in the pyrolysis–photoionization spectrum of polymer C (Figure 4b). To allow for this possibility, a second adjustable parameter, P_{2D}, was included in the model. For each Bernoullian distribution determined by an assumed value of P_D, the peak corresponding to two deuterium substitutions ($C_4H_6D_2$ at m/z 58 plus its $M + 1$ and $M - 2$ contributions at m/z 59 and 56, respectively) was multiplied by a second value (P_{2D}). The parameters P_D and P_{2D} were then adjusted to provide the best fit to the mass spectrum based upon the percentage of ion current modeled.

For polymers having a strictly random distribution, P_{2D} is zero and % D is given by P_D. If the distribution is nonrandom, P_{2D} is nonzero and % D must be determined in another way. In this work, % D was calculated from the best fit spectrum by

$$\%\,\mathrm{D} = \frac{\sum_{i=56}^{64} A_i\left(\frac{i-56}{8}\right)}{\sum_{i=56}^{64} A_i} \times 100\% \qquad (2)$$

where A_i is the calculated peak area at a given m/z and $(i - 56)/8$ is the fraction of deuterium in the formula $C_4H_xD_{8-x}$ where $i = 64 - x$. This calculation is only approximate in that it assumes (1) the relative contributions of $M - 2$ and $M + 1$ are the same across the oligomer series and (2) the $M - 2$ contributions of C_4H_8 and C_4H_7D and the $M + 1$ contribution of C_4D_8 are negligible. The validity of these assumptions can be tested by comparing % D calculated by eq 2 with P_D calculated from the Bernoullian model for polymers having a random distribution (i.e., P_{2D} equals zero). Table 2 shows that polymers A, B, and D fall into this category. For each of these polymers, the % D calculated by eq 2 matches that given by P_D within experimental error.

Table 2 compares the deuteration levels obtained by density measurement and pyrolysis photoionization mass spectrometry. The pyrolysis uncertainties are given as the 95% confidence limits from measurements of three separate samples. The uncertainties of the density measurements are on the order of ±2%. For polymers C and D, the deuteration levels determined by the two methods agree within experimental error. For polymers A and B, the pyrolysis measurements are somewhat lower than the density measurements.

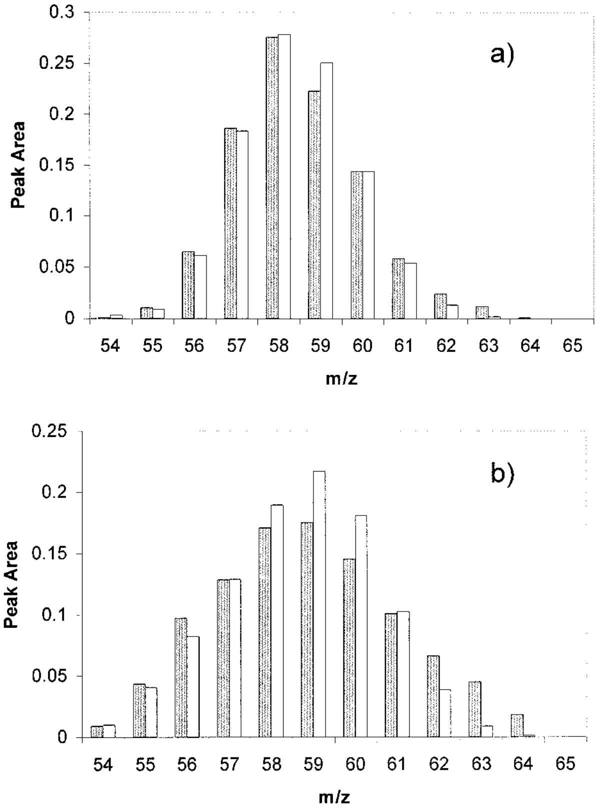


Figure 6. Comparison of measured (shaded region) and calculated (open region) C_4 distributions of (a) polymer A and (b) polymer B. Each plot is the average of three separate data sets.

What factors influence pyrolysis–photoionization measurements and which are most likely to affect the results presented here? First, pyrolysis of the polyolefins is not completely random. Pyrolysis–photoionization mass spectra of ethylene/α-olefin copolymers exhibit enhanced intensities of ions corresponding to bond cleavages near the branches of the polyolefin chain.[16] For polymers A–D, D_2 addition across all double bonds should lead to equal amounts of deuterium substitution on the branch and along the backbone. However, the amount of H/D exchange along the backbone may be different than on the branches. If, for example, the C_4 pyrolysates are formed preferentially from the backbone, then the level of deuterium substitution in these pyrolysates may not accurately reflect substitution on the branches. Second, differences in the photoionization efficiencies of hydrogenated and deuterated polyolefins could alter the relative peak areas in the mass spectra. This is not believed to be an important factor since the ionization potentials are very close, within ~0.02 eV. Third, pyrolysates may undergo further fragmentation leading to smaller m/z ions in the mass spectrum and a lower apparent value for deuterium substitution. In the analysis, the amount of dialkene formation is determined from the pyrolysis mass spectrum of totally hydrogenated polymer. Although it is unlikely that the rate of dialkene formation from the deuterated polymer is significantly different from the hydrogenated polymer, a kinetic isotope effect could bias the results.

Density measurements may also be subject to systematic error. As illustrated in Figure 1, the hydrogenated sample of polymer B contained some lower temperature desorption products that were not present in the deuterated sample. These additives and other

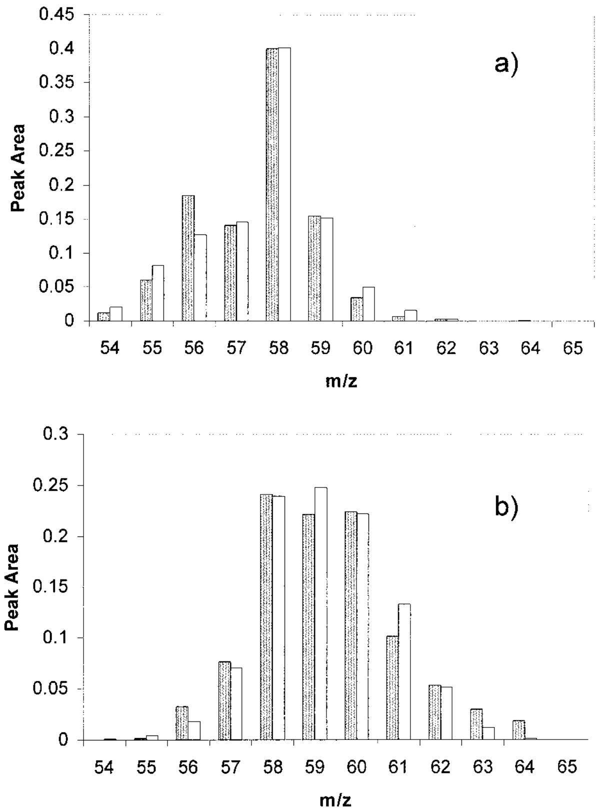


Figure 7. Comparison of measured (shaded region) and calculated (open region) C_4 distributions of (a) polymer C and (b) polymer D. Each plot is the average of three separate data sets.

(nonvolatile) impurities may alter the density measurements and hence the deuteration levels that are calculated. While we performed replicate measurements on the samples available to us, replicate samples could not be studied to asses the effects of impurities.

Microstructure

The pyrolysis photoionization mass spectra also give information on the deuterium distribution throughout the polymer. Visual inspection of the mass spectra in Figures 3 and 4 suggests that the deuterium distribution for polymer C is fundamentally different from A, B, and D. Polymer C shows a strong bias toward formation of $C_4H_6D_2$ that is consistent with addition of D_2 across the double bond in each monomer without much additional H/D exchange. This bias is reflected in the modeling results in Table 2 which show that P_{2D} is large for polymer C but virtually zero for polymers A, B, and D. The strong bias toward D_2 addition for polymer C is also consistent with the calculated deuterium content of 25.0%, which is the expected value if no additional H/D exchange occurs. In contrast, polymers A, B, and D exhibit much higher deuterium contents, and the pyrolysates indicate random deuterium distributions. In each case, it appears that H/D exchange not only increases the deuterium content above 25% but also completely randomizes the locations of the original deuterons that added across the carbon double bonds.

Figures 6 and 7 compare the experimental and calculated C_4 distributions of the four partially deuterated polymers. For polymers A, C, and D, the agreement is high as indicated by the percent ion current modeled in Table 2. For polymer B, the agreement is somewhat less, and Figure 6b shows that the measured distribution is wider than the calculated distribution. This suggests that the H/D exchange rate is not quite uniform. If some regions of the polymer exchange extensively while others exchange sparingly, then the distribution will be wider than expected for a given deuterium content averaged over the entire length. At this time, there is no way to test this hypothesis since pyrolysis−photoionization is the only currently available method that provides microstructure information on deuterium substitution.

As stated previously, % D calculated by eq 2 and P_D from the Bernoullian fit should be the same for polymers having a random deuterium distribution. An unexpected result of this work is that % D and P_D for the polymer containing a nonrandom distribution, polymer C, are also equal. This result indicates that there is some residual H/D scrambling during saturation, but no more than $(1 - P_{2D})$ of the deuteriums in the $C_4H_6D_2$ products or about 40%. In any event, it is clear that the sample saturated with Wilkinson's catalyst (polymer C) shows only H/D exchange between or within the polymer chains ("scrambling"), while for those saturated with Pd (polymers A, B, and D) there was also exchange between D_2 and the polymer.

Conclusion

Pyrolysis−photionization mass spectroscopy has been shown to be an excellent technique to examine the microstructure of polyolefins and particularly to determine the distribution of deuterium in labeled polymers. Two samples showed a very narrow distribution of deuterium substitution per monomer: the one made with perdeuterio monomer (PIB) and that made by saturating polybutadiene using Wilkinson's catalyst, which presumably did not foster H−D exchange. For the three labeled polymers made by saturating polybutadiene with Pd catalysts, the high level of D substitution per monomer measured by density (3−4) was confirmed by pyrolysis−photionization mass spectroscopy. The distributions of D per monomer were determined using a modified Bernoullian model that takes into account the first two D's that were added by the saturation event. This work helps clarify the structures of these labeled polymers and so makes them more useful for the study of the basic physical properties of polyolefins.

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