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Deuterium NMR of Deuterated Probes Dissolved in Stretched Polyethylene

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ABSTRACT: Deuterium NMR spectra of deuterated organic probes (including benzene-d_6, chloroform-d, acetone-d_6, pyridine-d_5, and o- and p-xylene-d_{10} dissolved in stretched polyethylene (PE) are reported for two polymer samples, viz., low-density PE and cross-linked middle-density PE. All spectra exhibit quadrupole splittings due to the finite average quadrupole interaction of the various deuterons. Their behavior is typical of ordered systems in which the probe molecules undergo fast diffusion (on the NMR time scale) between different solvation sites such as, e.g., in liquid crystals. The magnitude of the splitting was studied as a function of probe concentration, temperature, and the degree of stretching, λ. The observed quadrupolar splitting of all probes studied is quite small (less than 5% of the solid-state value) and shows a sigmoidal dependence on the probe concentration. For the low-density PE sample the splitting has a perfect linear dependence on the elongation factor. In unidirectionally stretched PE the asymmetry parameter of the quadrupole Hamiltonian η is zero, but in samples stretched successively in two perpendicular directions $\eta \neq 0$.

I. Introduction

In the present work we describe deuterium NMR measurements of deuterated compounds dissolved in stretched polyethylene (PE). Since the stretching process introduces a degree of ordering, the resulting material is anisotropic, and consequently the deuterium NMR spectrum exhibits splitting due to quadrupole interaction. This splitting and its dependence on external parameters such as the extent of stretching, solute concentration, etc. may provide information on the polymer itself, as well as on the interactions between the polymer and the probe molecules.

The product of ethylene polymerization is very dependent on the type of initiator used and the reaction conditions: it can yield a polymer with linear chains (high-density PE) or one with a certain degree of branching (low-density PE).[1] Both types, however, are partly crystalline; i.e., they contain regions where the hydrocarbon chains are parallel and regularly spaced, interspersed with less ordered, or amorphous, areas. Linear PE may approach 95% crystallinity, but branching interferes with the stacking of the chains, resulting in smaller crystallites and a lower degree of crystallinity—typically ca. 50%.

Spiess and his collaborators have extensively investigated the NMR properties of linear PE in the solid state, including, more recently, the use of perdeuterated material.[2] Taking advantage of the large difference in the relaxation times of nuclei in the amorphous and crystalline regions, separate spectra for the two types of domains could be recorded, using appropriate pulse sequences with careful adjustment of the pulse timing. A temperature study led to information on the modes of chain reorientation in the amorphous regions.

When a PE sample is cold-drawn, it stretches in the direction of the applied stress; X-ray, optical, and NMR studies indicate that in such samples the polymer chains, both in the amorphous and crystalline regions, tend to orient parallel to the direction of the stretch.[2,3] The anisotropic properties of stretched low-density polyethylene have been extensively used in order to study linear dichroism of dissolved organic molecules.[4,5] More recently, the electron spin resonance spectra of probe molecules containing free radicals (either stable or generated in situ) dissolved in stretched PE have also been measured.[6] The results of these studies are normally interpreted in terms of the distribution of the probe molecules in the PE lattice; it is now generally believed that solutes cannot penetrate crystalline domains, being instead associated with more or less ordered amorphous regions.[6,7] In the present work we employ a similar approach using the deuterium NMR of deuterated probes dissolved in the PE. Due to the fast diffusion of these molecules (on the NMR time scale) between the various sites of the polymer,[8] the resulting magnetic parameters represent weighted averages over all the sites.

The NMR spectrum of a deuteron due to a molecule diffusing rapidly in an anisotropically ordered environment consists of a doublet whose spacing $\delta\nu$ is

$$\delta\nu = \nu_Q[{}^1\!/_2(3\cos^2\theta - 1) + {}^1\!/_2\eta\sin^2\theta\cos 2\phi] \qquad (1)$$

where ν_Q and η are parameters depending on the geometry of the molecule, the deuterium principal quadrupole tensor, and the average ordering parameters of the molecules.[9] The angles θ and ϕ are the polar and azimuthal angles of the magnetic field with respect to the principal coordinate system of the phase. In uniaxial samples such as PE stretched along one direction, the asymmetry parameter, η, vanishes. If the sample history is more complex, e.g., if the PE film is successively stretched in different directions, a finite value of η may be observed. The magnitude of $\delta\nu$ for the probe molecules and its angular dependence thus reflect the anisotropic environment of the host molecules, and by studying its dependence on external parameters such as probe concentration, temperature, and degree of stretching, some specific information on the PE may be obtained. This approach was recently used by Deloche and Samulski to study orientational order in strained elastomers.[10]

II. Experimental Section

NMR Measurements. Most deuterium NMR experiments were done at 41.45 MHz using a Bruker WH-270 superconducting spectrometer. The spectra were obtained by Fourier transformation of the FID signals following short radio-frequency pulses at the deuterium resonance frequency. Toward the end of the work some spectra were recorded on a new Bruker CXP-300 spectrometer (at 46.07 MHz), utilizing a $(90°_x–\tau–90°_y–\tau–\text{acquisition})_n$ pulse sequence, with $\tau = 0.1$ ms. The temperature was controlled with a BST 100/700 unit whose absolute reading was calibrated with a Fluke 2190A digital thermometer; unless otherwise indicated, the data refer to ambient temperature, which corresponds to 27 ± 2 °C. The angular dependence measurements were done at 13.8 MHz using a Bruker WH-90 iron core spectrometer.

Low-Density Polyethylene Film. Suprathen 200 (thickness 200 μm) from Kalle and Co. A.G. (West Germany) was used. This material is supplied in large rolls, from which 5-cm-wide strips were cut with their long dimension parallel to the direction of the roll. Samples were then prepared by cold-drawing parallel

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to the long dimension of the strips, at room temperature, either by hand or by machine, an Instron Universal Testing Instrument, Floor Model (TT), at the rate of 2 cm/min. When the samples were hand-drawn, a neck forms, and further stretching continuously increases the extent of the neck region, but not the degree of stretching. This was checked by marking, in ink, lines 1 cm apart on the unstretched film. After hand-drawing, the distance between the lines was quite uniform and indicated that the degree of elongation, λ = (final length)/(initial length), was approximately 4.3. When the samples were machine-drawn, no necking was observed, and samples of any desired λ value up to 4.5 could be obtained. For $\lambda > 2.5$, an initial gap of 5 cm between the clamps of the Instron was used, and the value of λ was determined from the distance between two lines 4 cm apart. For samples with low degrees of elongation ($\lambda < 2.5$) it is more difficult to get uniform stretching, and therefore a larger initial gap (12 cm) was used. Ink lines 1 cm apart were marked, and a uniformly stretched region was selected for the NMR measurements. In all cases the useful region was cut into 3–5-cm pieces, which were stacked, rolled, and tied at both ends with thin strips of stretched PE. These PE "cigarettes" had their long axis parallel to the stretching direction.

The probe solutions were prepared as follows: PE cigarettes were weighed and then placed into 10-mm-o.d. NMR tubes. The deuterated probe was then added and the precise amount determined by weight difference. The tubes were capped, "sealed" with Parafilm, and equilibrated for 1–2 days. Some loss occurred during this period, especially for the more volatile liquids like acetone and chloroform, but this could be monitored by reweighing the tubes just before and after the NMR experiment. In the above arrangement the stretch axis is parallel to the (vertical) direction of the NMR tube and of the magnetic field of the superconducting spectrometer. In order to determine the angular dependence of the splitting, samples were prepared in which the strech direction was perpendicular to the NMR tube axis. A hand-stretched sample was cut into 5-mm stripos, and these were stacked, rolled, and tied with sewing string. The flat cylinder obtained was introduced into the NMR tube so that its axis (and therefore the draw axis) was horizontal. Thus, in the iron core magnet of the WH-90 spectrometer, the rotation pattern could readily be obtained by turning the sample tube about its long axis. The plastic sample holder had radial markings at 10° intervals from which one could read the value of the angle θ.

Cross-Linked Middle-Density PE Film. Cryovac D-925 (thickness 25 μm) from W. R. Grace (Canada) was used. This PE is biaxial because during its manufacture it underwent two successive stretching processes: first a transverse stretch due to the blow extrusion and then a longitudinal stretch due to the rolling process. Subsequent to the stretching processes the PE was cross-linked by radiation. It was used without any further stretching. Rolled cylinders were prepared in a way similar to the one described above, from long strips, cut so that their short axes formed an angle of 0, 45, or 90° with the direction of the roll. As before, when inside the spectrometer, the short axis of the strip is parallel to the magnetic field of the superconducting magnet. In another experiment, several thicknesses of film were cut with a cork borer into disks of 7.5 mm diameter; these were joined together through their centers with a needle and thread. The resulting stack was put vertically in the NMR tube, so that H was parallel to the normal to the plane of the PE sheet.

Probes. Commercial perdeuterated compounds enriched to more than 95 atom % deuterium were used without further treatment.

III. Results and Discussion

In this section we describe the deuterium NMR results obtained from the various deuterated solute/polyethylene systems studied. The most extensive measurements were made for benzene-d_6 dissolved in low-density PE and we therefore discuss this system first, isolating the influence of several variables.

1. Benzene-d_6 in Low-Density PE. (a) Concentration and Orientation Dependence.

When small amounts of benzene are added to hand-stretched PE film, the liquid is completely absorbed. The NMR spectrum from the dissolved C_6D_6 consists of a broadened quadrupole doublet whose intensity, peak width, and splitting depend on the amount of benzene added. Examples of spectra are shown in Figure 1. These spectra were recorded with the magnetic field in the direction of the stretch and correspond to the maximum observed splitting. When the magnetic field is rotated with respect to the draw axis, a "rotation pattern" is obtained, typical of a uniaxial ($\eta = 0$) system. Examples of spectra and the dependence of $\delta\nu$ on θ are depicted in Figure 2 for a sample with 0.11 C_6D_6:PE (w/w) (i.e., 0.11 g C_6D_6 per g of PE). This behavior is of course that expected for a unidirectionally stretched PE.

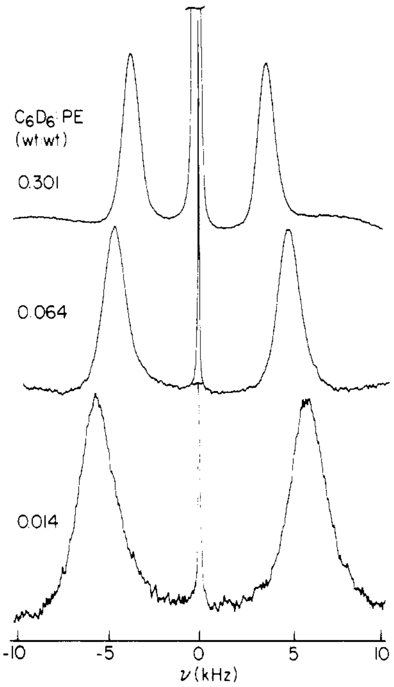

Figure 1. Deuterium NMR spectra of benzene-d_6 absorbed in hand-stretched low-density PE. The benzene:PE ratio (w/w) is indicated next to each spectrum ($t = 27 \pm 2$ °C).

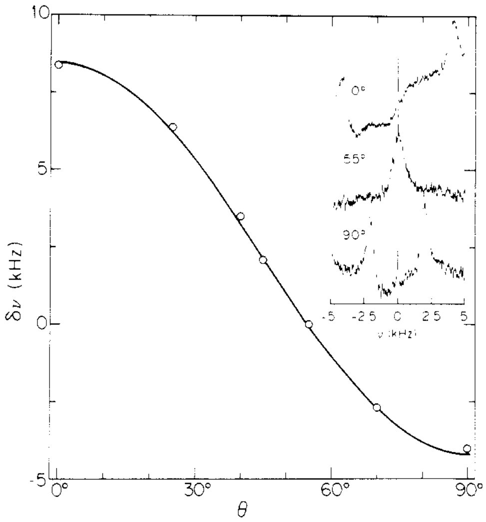

Figure 2. Plot of $\delta\nu$ vs. θ, the angle between the draw axis and the magnetic field, for a sample of benzene-d_6 in hand-stretched low-density PE (0.11 w/w). The full curve is calculated from eq 1 using $\nu_Q = 8.46$ kHz and $\eta = 0$. Inset: a few representative spectra ($t = 27 \pm 2$ °C).

In the spectra shown in Figure 1 a sharp but weak center line may be observed. However, above ca. 0.15 w/w of benzene a new center line, shifted by some 3.5 ppm upfield

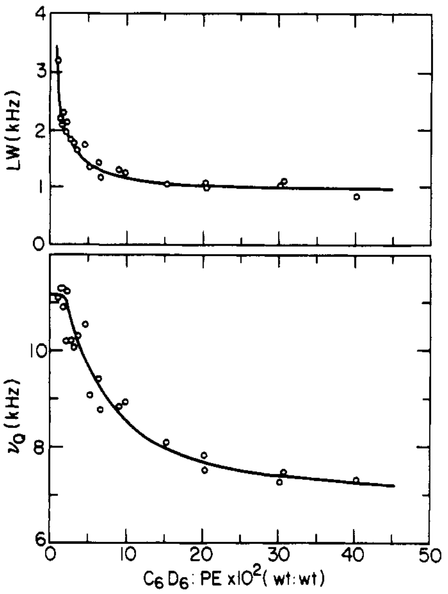

Figure 3. Experimental $|\nu_Q|$ and line width values obtained from spectra like those of Figure 1 as a function of the benzene:PE ratio.

from the first one, shows up. Its appearance approximately coincides with observation of bulk liquid in the test tube, and its intensity increases upon further addition of benzene. This signal is therefore identified with isotropic liquid benzene not absorbed in the PE while the center line observed at low benzene contents is apparently due to benzene vapor. We can define a "solubility" of the probe in the PE as the weight/weight ratio corresponding to point at which the signal due to the isotropic liquid starts to appear.

Plots of the quadrupole splitting and width of the doublet components vs. the concentration of added benzene are shown in Figure 3. At low benzene contents (<0.02 w/w) the splitting assumes a limiting value of 11.2 kHz while above the "saturation" point (where the signal of liquid benzene first appears), ν_Q changes slowly, and approaches an asymptotic value of 7.0 kHz. In between the splitting follows a "titration-type" curve with a "half-wave" concentration of ca. 0.07 w/w. This behavior may be understood in terms of a distribution of solvation sites in which the first to be occupied are more higly ordered than those occupied at higher benzene concentrations. However, it is also possible that increasing the amount of solute swells the PE lattice and therefore results in an overall decrease in the probe order. Unfortunately, our data are not sufficient to differentiate between these alternatives.

(b) Temperature Dependence. A few samples were run as a function of temperature, down to −50 °C. As the temperature is lowered, there is an increase in line width; the quadrupolar splittings remain constant down to ca. −10 °C and then start to decrease slowly. Spectra cannot be taken above room temperature since heating of the sample leads to irreversible shrinking and swelling of the PE.

(c) Degree of Stretching. As described in the Experimental Section, the PE film could be machine-drawn in a continuous range of elongation ratios λ. From several such films, samples were prepared with approximately 0.25 w/w C_6D_6 (in this concentration range ν_Q is practically independent of the exact concentration; vide supra). Examples of spectra and plots of the splitting ν_Q and line width (LW) as function of the elongation parameter are shown in Figures 4 and 5. Perhaps the most striking result of these experiments is the perfect linear dependence of ν_Q on λ (Figure 5), including the result of the hand-stretched sample (filled circle). The quadrupolar splitting is therefore a good linear measure of the degree of stretching of a PE sample.

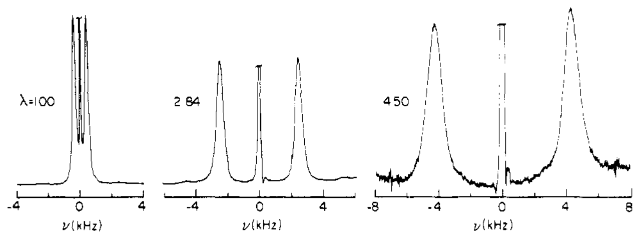

Figure 4. Deuterium NMR spectra of benzene-d_6 saturated in low-density PE, for different degrees of stretching, as indicated by the elongation factor λ.

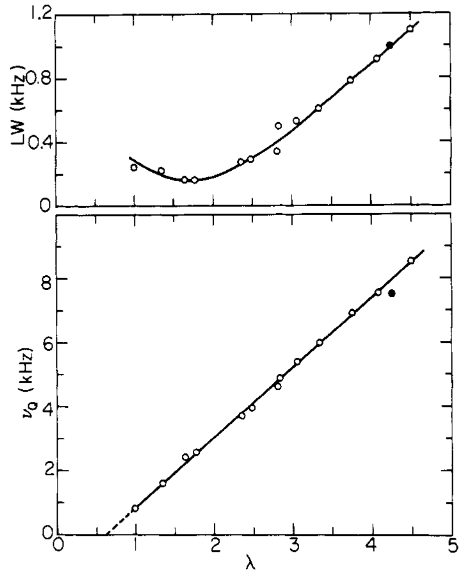

Figure 5. Plot of $|\nu_Q|$ and line width (LW) for the samples described in Figure 4. The solid circle corresponds to the hand-stretched samples.

Assuming, as is generally accepted,[6,7] that the probe molecules dissolve in the amorphous rather than in the crystalline regions of the PE, the increase in ν_Q with λ reflects an increase in the ordering of the amorphous part of the polymer. On a molecular level, the stretching process results in uncoiling and disentangling of the polymer chains, producing amorphous domains in which the PE molecules have a certain degree of alignment with an average orientation parallel to the stretching direction.[11] Probe molecules dissolved in such domains will experience a cylindrically symmetrical potential in much the same way as in (polymeric) nematic liquid crystals. It appears from the experimental results that at least in the range of λ accessible in the present experiments, the orientational order is linear with the elongation index. In "unstretched" samples a small splitting in the deuterium spectrum of dissolved C_6D_6 may still be observed. Clearly the commercially obtained film is not isotropic, and a small degree of orientation is introduced in the manufacturing process. Our data (see Figure 5) indicate an initial elongation of 1.6, with the preferred chain orientation parallel to the direction of the original roll. No splitting is resolved when the magnetic field is perpendicular to the roll direction, consistent with the observed line width and the expected decrease in the absolute value of $\delta\nu$ by a factor of 0.5. Taking into account the orientation already present in the commercial film, the maximum elongation used in our experiments actually corresponds to a factor of more than 7.

Table I
Solubility and ν_Q Values in Hand-Stretched[a] Low-Density PE Saturated with Organic Probes

probe	sol (w/w)[b]	ν_Q for satd sample, kHz[c]
benzene-d_6	0.15	7.0
chloroform-d	0.30	7.1
acetone-d_6	0.02	2.3
p-xylene-d_{10}	0.12	4.7 (CD_{ar}) 9.1 (CD_3)
o-xylene-d_{10}	0.12	3.1 (CD_3) 7.6 (D_{ortho}) 11.3 (D_{meta})
pyridine-d_5	0.02	6.0 (D_γ) 10.9 (D_α, D_β)

[a] Elongation ratio $\lambda = 4.3$. [b] Determined from the appearance of the isotropic liquid signal in the NMR spectrum. [c] Asymptotic value at high probe concentration.

As for the line width (LW in Figure 5), there is a minimum at ≅ 1.7, followed by a linear increase with the parameter λ. A probable major contribution to the line width is macroscopic inhomogeneity of the polymer film. It seems therefore that in the commercial film there is a high degree of mosaicity. The stretching process initially makes the film more uniform, but as λ is increased, the degree of inhomogeneity slowly rises again.

2. Low-Density PE. Other Probes. We have performed similar measurements on a number of other deuterated organic probes. The general behavior of the results was quite similar to that found for benzene, and in Table I we summarize the solubilities (as determined by the appearance of the signal due to isotropic liquid) of these probes and the asymptotic values of ν_Q (for high probe concentrations). In Figure 6 representative spectra are shown and in the following some comments on the various probes are made.

(a) Chloroform-*d*. As for benzene, an increase in ν_Q and the line width was observed with decreasing probe concentration, but even though the solubility in PE is high (Table I) the signal-to-noise ratio is very unfavorable due to the low deuterium content per molecule.

(b) Acetone-d_6. Here sensitivity is not a problem, but solubility is: above 0.02 w/w the splitting and the line width are independent of the amount of acetone added. The limiting value of ν_Q is rather small, probably in view of the various facile modes of motional averaging.

(c) *p*-Xylene-d_{10}. As can be seen in Figure 6 the two types of deuteron lead to two distinct doublets, which can be assigned on the basis of their chemical shifts. Two more samples were run at concentrations down to 0.02 w/w, and while the ν_Q and line width do increase as concentration is lowered, the ratio between the ν_Q values for the two doublets remains constant, indicating that the average orientation of the molecules does not depend on the concentration. The large splitting of the methyl relative to the aryl deuteron signals reflects the fact that the *p*-xylene molecule aligns itself preferentially with the axis containing the C–CD_3 bonds parallel to the stretching direction.

(d) *o*-Xylene-d_{10}. The spectrum of this compound consists of three pairs of lines (Figure 6). The assignment of the CD_3 doublet is straightforward on the basis of its relative intensity and chemical shift, but the distinction between the "ortho" (i.e., ortho to one of the methyls) and the "meta" (meta to one methyl and para to the other) is not obvious. Our assignment in Figure 6 and Table I was based on the assumption that the ν_Q's of the CD_3 and the "meta" deuterons should differ by a factor of 3–4 due to their respective geometrical positions, taking into account the fast rotation of the methyl groups.[12-14]

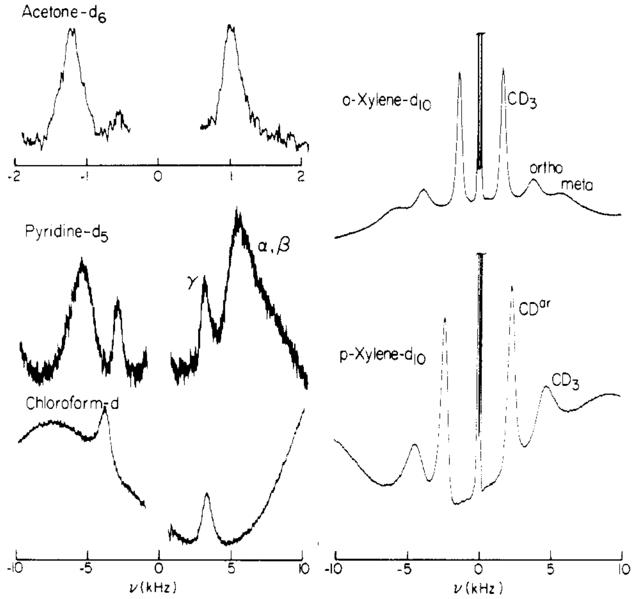

Figure 6. Examples of deuterium NMR spectra of several perdeuterated compounds saturating hand-stretched, low-density PE. Notice that the frequency scale is different for the spectrum of acetone-d_6 relative to the others. The centers of some of the spectra (lines corresponding to the isotropic liquids) have been deleted for the sake of clarity.

(e) Pyridine-d_5. The solubility of pyridine in PE is low (Table I) and therefore the resulting spectrum, which consists of two unequal doublets (Figure 6), has a poor signal-to-noise ratio. On the basis of geometrical considerations we expect the ν_Q's of the α and β deuterons to be nearly the same, hence the assignment in Figure 6, which is also consistent with the observed relative intensities of approximately 4:1.

3. Benzene-d_6 in Cross-Linked PE. The usefulness of the observation of quadrupolar splittings in the characterization of samples of PE can be exemplified in the data obtained for a biaxially oriented film. During the blow extrusion process, this film is stretched perpendicularly to the roll direction; it is then stretched parallel to it in the rolling process; finally this ordering is "frozen in" through radiation-induced cross-linking of the chains. In the process, this originally low-density, branched-chain type PE becomes more dense, with a more rigid lattice.

The effect of C_6D_6 probe concentration on $\delta\nu$ was examined for two orientations of the PE sample, i.e., with H respectively along the x and y directions of the roll (see Figure 7 for the definition of coordinate axes with respect to the the PE roll). In all orientations a doublet was observed, accompanied by a singlet in the center of the spectrum (corresponding to the isotropic liquid) when the ratio was above 0.20 w/w (vs. a maximum solubility of 0.15 w/w in the previously examined low-density PE). Above the "saturation point" the doublet component of the spectrum remains invariant, while the singlet is intensified. It is likely that the higher rigidity of the (cross-linked) amorphous regions as compared to the low-density PE accounts for the sharp break in the $\delta\nu$ curves in Figure 8 around the 0.20 w/w ratio; above this, all of the added benzene goes into the liquid phase and the composition of the polymer film remains invariant. If the benzene concentration is decreased below the "saturation" point, the splittings increase, reaching a plateau for ratios <0.03 w/w.

In order to determine the relative signs of $\delta\nu_x$ and $\delta\nu_y$, two additional experiments were done: one with H in the xy plane at 45° to each axis ($\theta = \pi/2$, $\phi = \pi/4$) and the

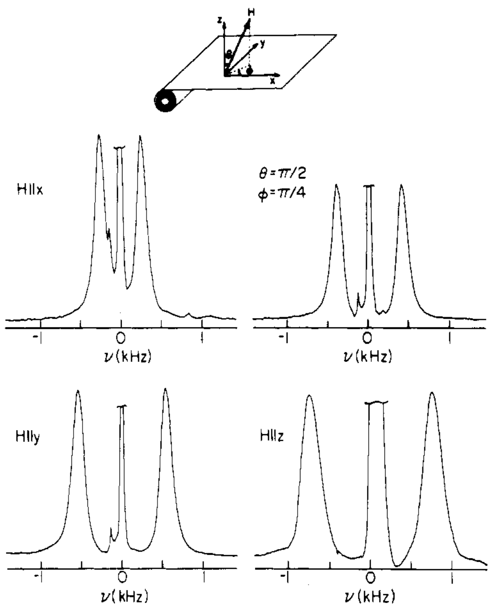

Figure 7. Deuterium NMR spectra of benzene-d_6 dissolved in biaxially oriented, cross-linked PE for different orientations of the film relative to the magnetic field (concentration 0.4 w/w). The inset gives the coordinate system with respect to the original roll.

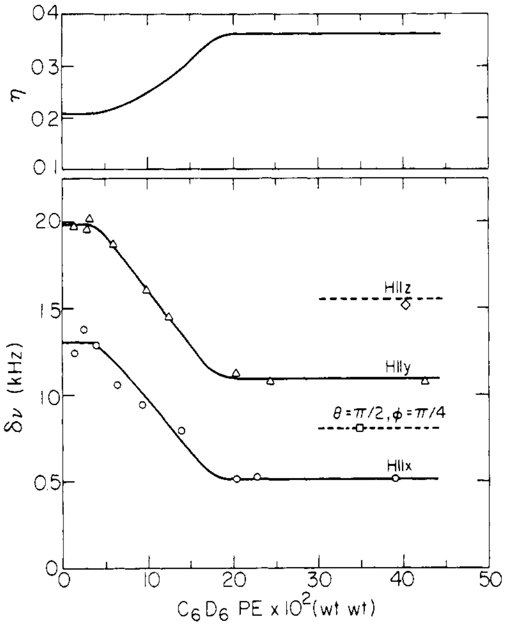

Figure 8. Experimental $|\delta\nu|$ values obtained from spectra like those of Figure 8 as a function of the benzene:PE ratio. The orientations of the films are marked in the graph.

other with $H \| z$. The results are shown in Figure 8, and they indicate that $\delta\nu_x$ and $\delta\nu_y$ must have the same sign, opposite to that of $\delta\nu_z$. This follows from the requirement that the algebraic sum of the $\delta\nu_i$'s along the canonical directions must vanish identically. From this assignment of the signs the asymmetry parameter $\eta = (\delta\nu_x - \delta\nu_y)/\delta\nu_z$ can be determined. This parameter is plotted vs. the probe concentration in the upper part of Figure 8. It is interesting to note that η is not independent of the benzene concentration. Thus at the low end of the concentration range its value is 0.21 while the limiting high-concentration value is 0.36.

Clearly the amorphous region in this sample is on the average biaxial. One possible explanation might be that the first stretching of the PE results in uniaxial amorphous domains that are reoriented by the second perpendicular stretching, resulting in chains forming on the average an angle α with the direction of the first stretch. However, since rotations by α and $-\alpha$ are equally probable and since fast diffusion averages out the interactions in the various domains, the result is a biaxial phase with the principal axes corresponding to the two stretching directions and the perpendicular to them. In this case, however, the value of η would be a function only of the angle α and therefore should be independent of the probe concentration (the cross-links probably preclude any significant benzene-induced reorganization of the PE chains).

Another alternative is to assume that each stretching process unaxially orients a number of independent amorphous domains in the direction of the stretch. Since the two types of domains thus created need not be chemically identical, the partition of benzene between them and/or the ratio of ν_Q values for a particular concentration may be concentration-dependent. As a consequence, η would be a function of the benzene/PE ratio, as found experimentally.

IV. Summary

The deuteron NMR spectra of deuterated probe molecules dissolved in stretched PE exhibit quadrupole splittings that reflect the average interactions over the various domains and sites in the amorphous part of the polymer. There is no simple relation between the magnitude of the splitting and the probe concentration, in view of the variety of sites and the possibility that probe–PE interactions may modify their properties as the concentration of the probe is changed. On the other hand, there appears to be a perfect linear dependence of the quadrupolar splittings exhibited by the probes and the degree of elongation, at least in the range $1 < \lambda < 5$. The magnitude of the splitting is however rather small even for $\lambda = 5$; in fact, the highest order parameters measured in this study are on the order of $S = 0.05$. Since Spiess has shown that the PE chains are in fact quite well ordered even in the amorphous regions of stretched PE,[2] the relatively low overall ordering of the probes is probably due to the efficient averaging by the highly mobile small molecules over various solvation sites and domains. Because of the complexity of the system, a quantitative correlation between the degree of ordering of the solute and that of the lattice remains an open question.

The processing history of PE samples is clearly reflected in the NMR spectra of dissolved probes. Thus a unidirectionally stretched PE exhibits a uniaxial spectrum, with a principal component along the stretching direction and with a magnitude that reflects the degree of elongation in that direction. In contrast, a PE sample, that underwent successive stretchings in two orthogonal directions is biaxial with two of its principal axes coinciding with the stretching directions.

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Registry No. Benzene-d_6, 1076-43-3; chloroform-d, 865-49-6; acetone-d_6, 666-52-4; pyridine-d_5, 7291-22-7; o-xylene-d_{10}, 56004-61-6; p-xylene-d_{10}, 41051-88-1; polyethylene (homopolymer), 9002-88-4.

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End-Group Effect of Styrene Oligomers on the ^{13}C NMR Chemical Shift

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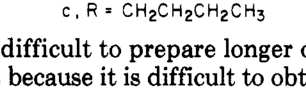
ABSTRACT: Styrene oligomers from dimer to pentamer and having propyl (Ib) and pentyl end groups (Ic) were prepared and separated into each diastereomer. The ^{13}C NMR chemical shifts of methylene and phenyl C(1) carbons of these oligomers were compared to those of oligomers with methyl end groups (Ia) as reported by Jasse et al. Oligomers of Ib and Ic have almost identical chemical shifts for these carbons, while Ia shows slightly different chemical shifts. The resonating order of the carbons in diastereomers of Ib and Ic is almost the same as that of the configurational sequences in polystyrene. It is proved that Ib and Ic oligomers are good models for the analysis of the ^{13}C NMR spectrum of polystyrene.

Introduction

Many oligomers possessing known chemical and stereochemical structures have been prepared for the elucidation of the structure of vinyl polymers. Usually oligomers having methyl end groups have been prepared through a long synthetic route. In the case of polystyrene, oligomers with methyl end groups (Ia) have been prepared up to tetramer and separated into diastereomers. These oligomers are synthesized by Grignard reactions or other condensation reactions.[1-4]



$R{-}(CH_2{-}\underset{\displaystyle Ph}{\underset{|}{C}H})_n{-}CH_2{-}R$

Ia, R = H
b, R = CH_2CH_3
c, R = $CH_2CH_2CH_2CH_3$

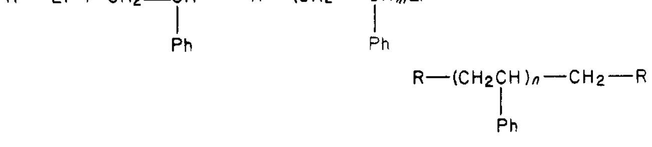
However, it is difficult to prepare longer oligomers using these reactions because it is difficult to obtain the starting materials.

The ^1H or ^{13}C NMR spectra of the oligomers with methyl end groups were measured in order to analyze the spectra of polystyrene.[1-4] However, these oligomers have failed to provide useful information for the analysis of NMR spectra of polystyrene, because the ^1H and ^{13}C spectra from these types of oligomers differed somewhat from those of the polymer.

Styrene oligomers with any desired average degree of polymerization can be obtained through oligomerization of styrene after initiating with alkyllithium. We have prepared symmetric oligomers having propyl end groups (Ib) by the oligomerization of styrene after initiating with ethyllithium and terminating with 1-bromopropane. The oligomer mixture was separated into pure *n*-mers up to 12-mers, and 2–5-mers were fractionated into diastereomers.[5] In our previous paper we have demonstrated that the styrene oligomers with propyl end groups exhibited the same splitting pattern for the methine proton as polystyrene[6] and have found that the resonating order of methylene and phenyl C(1) carbon of polystyrene was almost equal to those of the corresponding carbons in the pentamer of Ib.[7,8] In this report ^{13}C NMR signals of the styrene oligomers having propyl and pentyl end groups (Ib and Ic) were analyzed and their chemical shifts were compared with those of Ia. The effect of end groups of the styrene oligomers on the ^{13}C NMR chemical shift is discussed.

Experimental Section

Oligomers of Ib and Ic. Styrene oligomers with propyl and pentyl end groups were prepared by anionic oligomerization of styrene after initiating with alkyllithium and terminating with 1-bromoalkane:



$R{-}Li + CH_2{=}\underset{\displaystyle Ph}{\underset{|}{C}H} \rightarrow R{-}(CH_2{-}\underset{\displaystyle Ph}{\underset{|}{C}H})_nLi \xrightarrow{R-CH_2Br} R{-}(CH_2\underset{\displaystyle Ph}{\underset{|}{C}H})_n{-}CH_2{-}R$

Ib, R = CH_2CH_3
c, R = $CH_2CH_2CH_2CH_3$

The mixture of the oligomers having different degrees of polymerization was separated into pure *n*-mers by gel permeation chromatography. The dimer to the pentamer of Ib and the dimer to the tetramer of Ic were separated into diastereomers by liquid

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