Solid-State ^{13}C NMR Study of Oligomeric and Polymeric Azines

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ABSTRACT: The solid-state ^{13}C NMR spectra of a series of oligomeric and polymeric azines based on the 2,3-butanedione dihydrazone monomer have been obtained. The monomer in the series yields single peaks in the methyl region and in the imine region of the NMR spectrum. As the chain length increases, new lines grow in downfield of the monomer resonances while the intensity of the original peaks diminish. This is consistent with the new features being associated with carbons along the interior of the macromolecular chain and the original peaks being associated with carbons at the end of the polymer chain. The downfield shift affiliated with the interior carbons is indicative of a small amount of conjugation of the π system along the chain. The polymer undergoes an irreversible transition in the DSC near 130 °C that has been identified by IR spectra with loss of occluded DMSO from the polymer lattice. Solid-state NMR spectra are consistent with this conclusion.

Introduction

The study of conjugated polymers has been of great interest in recent years,[1-3] due primarily to the discovery that the π systems in these materials can be incompletely oxidized or reduced to give electrically conducting solids. Typical examples of these types of materials include polyacetylene,[4-11] polyaniline,[12-16] and polyazine.[17-21] Polyacetylene is a simple linear chain hydrocarbon, while both polyaniline and polyazine have nitrogen atoms involved in the conjugated pathway. Polyazine, like polyacetylene, has a simple linear chain of atoms while polyaniline has benzene groups as part of the macromolecular arrangement.

The prototype conducting polymer is polyacetylene,[11] which is composed of alternating single and double bonds along a carbon backbone. Although polyacetylene is the simplest conjugated polymer, its properties have not been easily understood,[11] especially the elementary excitations associated with the unique topological properties of the polymer chain, which arise from the degenerate ground state of the π system in the all-trans polymer. In terms of practical uses, polyacetylene also has the undesirable property of being environmentally unstable.

In contrast to polyacetylene, polyaniline is an air-stable conjugated polymer that also can be oxidized or reduced into an electrically conductive state.[16] In the fully reduced (nonconducting) state, polyaniline has benzene rings linked by amine groups at the para positions while in the fully oxidized (also nonconducting) form the bonding through the nitrogens is composed of imine bonds. The introduction of the nitrogen heteroatoms along the macromolecule chain probably contributes to the increased stability of this polymer but also introduces the complication of deciding the incidence and relative importance of amine vs imine linkages in the various stages of oxidation. Polyaniline does not have a degenerate ground state, so direct comparison to the structurally simpler polyacetylene is not straightforward.

This paper is concerned with the structural characterization of oligomeric and polymeric azines via solid-state ^{13}C NMR spectroscopy. Solid-state NMR spectra have been useful for the elucidation of structural characteristics of conducting polymer systems.[22-28] Like polyacetylene and (reduced) polyaniline, polyazine ($H_2N[N{=}C(R)C(R){=}N]_xNH_2$) can be oxidized into an electrically conductive state. But, polyazine has structural properties intermediate to polyacetylene and polyaniline: like polyacetylene, polyazine has a single chain of conjugated atoms that can be put into an all-trans conformation; unlike polyacetylene, it is air stable and has nitrogen heteroatoms along the chain; like polyaniline, because of the heteroatoms, polyazine does not have a degenerate ground state; unlike polyaniline, it has enforced imine linkages and no benzoid or quinoid groups. This gives polyazine a unique position in the hierarchy of conjugated polymers with heteroatoms incorporated in the chain.

Two issues are discussed in this paper. First, the solid-state ^{13}C NMR of a series of oligomeric azines of increasing chain length is compared to the polymer spectrum. The monomer of the series, 2,3-butanedione dihydrazone, has been structurally characterized by X-ray crystallography[21] and is the starting point of our analysis. Because these materials have pendant methyl groups at every carbon along the chain, we are able to probe both on-chain and off-chain effects. The methyl groups also ensure that the polymer obtains the all-trans conformation, as is demonstrated by our results presented both here and previously.[21] Second, we note the effect of thermal treatment on the polymer. Differential scanning calorimetry shows an irreversible phase transition as the polymer is heated, and we show both IR and NMR evidence that indicates that this transition is due to loss of solvent molecules trapped in the lattice.

Experimental Section

2,3-Butanedione dihydrazone ($x = 1$), oligomeric ($x = 2, 3, 5, 7, 11$), and polymeric ($x > 40$) azines were prepared as previously described.[21] Bulk samples for NMR and IR investigation of the thermal effects on the polymer were prepared by heating finely ground powders of the dry polymer in a lightly corked tube immersed in an appropriate boiling solvent for 1.5 h and then cooling slowly to room temperature. DSC were run at Brown University on a Du Pont 9900 instrument. IR spectra were run between 600 and 4000 cm^{-1} as KBr pellets on a Perkin-Elmer 281B spectrometer. Solid-state NMR spectra were obtained at Lehigh University on a General Electric NMR Instruments GN-300 spectrometer operating at 75.4 MHz for carbon-13. The locally designed and constructed probe utilized a Doty Scientific, Inc., 7-mm spinning assembly with sapphire rotors and Kel-F end caps containing a sample volume of up to 0.35 cm^3. Spectra were obtained with cross polarization[29] and magic angle sample spinning (MASS).[30] Spinning speeds were measured between 4.2 and 5.1 kHz. Typical conditions included a single cross-polarization contact time of 1.5 ms and an acquisition time of 40 ms. Signal averaging of 128 to approximately 10000 transients improved the signal-to-noise ratio, with a 4-6-s recycle time. Exponential

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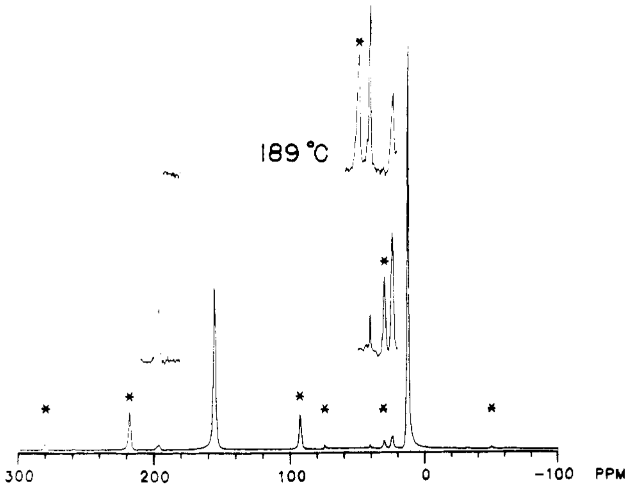

Figure 1. Solid-state ^{13}C NMR spectrum of permethyl polyazine. The strong center bands at 12.5 and 155.2 ppm arise from the methyl and imine carbons, respectively. Stars denote the weaker rotational sidebands. The weak features shown in the expansions (×10) are explained in the text. The 189 °C inset shows the changes of the weak bands upon heating.

line-broadening equivalent to 25 Hz was applied before zero-filling and Fourier transformation. Peak integration included intensities from the rotational sidebands, although rotational sidebands for methyl resonances were very weak. Maximum radio-frequency field strengths were 1.4 and 4.2 mT for protons and carbons, respectively. Chemical shifts are referenced to tetramethylsilane via external adamantane, with an estimated error of ±0.2 ppm.[31]

Results and Discussion

The permethyl polyazine is prepared by an acid-catalyzed condensation of 2,3-butanedione, $O{=}C(CH_3)C(CH_3){=}O$, and 2,3-butanedione dihydrazone, $H_2NN{=}C(CH_3)C(CH_3){=}NNH_2$, in dimethyl sulfoxide (DMSO). Previous IR and single-crystal X-ray studies[21] on 2,3-butanedione dihydrazone showed it to have a planar backbone with a small degree of delocalization along the carbon–nitrogen skeleton; the methyl groups were in the trans conformation. IR spectra demonstrated that the methyl groups remain trans in the longer chain materials while the invariance of the position and shape of the C=N stretch as a function of chain length suggested that the local geometry about the double bonds remained planar and conjugated. The end groups in this polymer can be either ketone, $-C(CH_3){=}O$, or hydrazone, $-C(CH_3){=}NNH_2$. Ideally, all of the terminating groups would be hydrazones, but both IR and NMR spectra show peaks attributable to carbonyl moieties. End-group analysis, both by IR spectroscopy and elemental analysis, indicated that the polymer molecular weight exceeded 3800 amu, corresponding to 45 (or more) monomer units. Solid-state NMR can be used for end-group analysis, provided identifiable features are present in the spectrum (vide infra).

The solid-state ^{13}C NMR spectra of the monomeric, oligomeric, and polymeric azines show strong resonances in two ranges: near 10–12 ppm, attributed to the methyl carbons and near 150–165 ppm, due to imine carbons. In addition, some spectra contain other very weak features at 196.3, 24.0, and 40.8 ppm. These lines are readily assigned to unreacted chain end carbonyl groups, terminal methyl groups bonded to the carbonyl moieties, and occluded solvent (dimethyl sulfoxide), respectively. All these lines are present in Figure 1, the solid-state ^{13}C NMR spectrum of the azine polymer. The weak features have been expanded by a factor of 10. The two primary spectral regions of 10–12 and 150–165 ppm will be discussed separately.

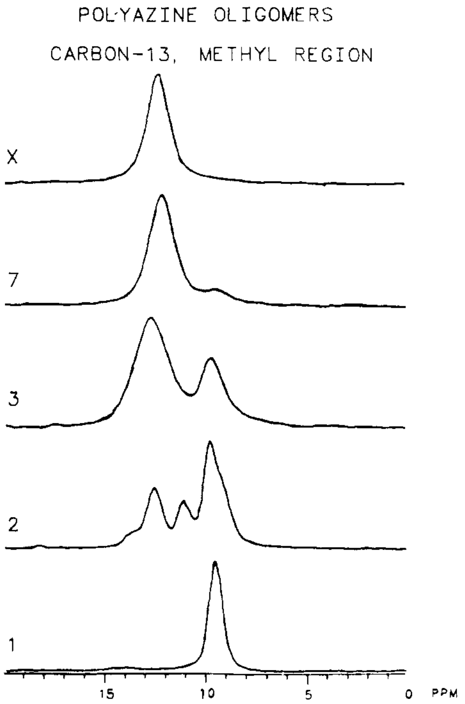

Figure 2. Solid-state ^{13}C NMR spectra of the methyl region for $-[N{=}C(CH_3)C(CH_3){=}N]-_x$ for x = 1–3, 7, and >40. Different degrees of π delocalization and packing effects lead to shifts in resonance positions.

The solid-state ^{13}C NMR spectrum of 2,3-butanedione dihydrazone shows a single peak in the methyl region at 9.5 ppm as demonstrated in Figure 2. This is consistent with the inversion symmetry found from the X-ray crystal structure.[21] The dimer spectrum displays three distinct peaks at 9.7, 11.1, and 12.5 ppm with the intensity of the upfield peak being roughly twice that of each of the other two peaks. The resonance at 9.7 ppm arises from methyl groups at the end of the chain adjacent to the hydrazone moieties, similar to the monomer. The two methyl groups along the interior of the chain give rise to the 11.1 and 12.5 ppm peaks; the existence of these two methyl resonances indicates either that the dimer is not rigorously planar or that the solid-state packing is such that the methyl groups are magnetically nonequivalent. This phenomenon is also seen less dramatically in the terminal methyl resonance, which is slightly split with a shoulder appearing to the upfield side of the peak.

The oligomers with x = 3, 5 (not shown), 7, and 11 (not shown) all exhibit only two peaks in the methyl region, one at 9.6 (±0.3) ppm and one at 12.2 (±0.4) ppm. As with the dimer, the upfield peak is assigned to methyls at the chain termini while the downfield peak is due to methyls along the interior portion of the chain. The downfield peak grows in intensity with increasing chain length at the expense of the upfield peak. The ratio of the integrated intensity of the two peaks matches the ratio of the number of interior methyls to the number of terminal methyls, confirming the assignments of the resonances and consistent with the chain lengths determined by elemental analysis and IR spectroscopy.[21] The dimer and trimer spectra show evidence of sample heterogeneity. The multiple methyl peaks in the dimer spectrum suggest that solid-state packing effects could be quite important. The trimer methyl resonances are much broader than any of the other methyl lines in this series. The methyl line widths are narrow for the monomer and polymer (approximately 1 and 1.2 ppm, respectively), while the trimer methyl line width is over 2 ppm. The imine region of the trimer spectrum helps clarify these observations (vide infra).

The polymer has a single peak in the methyl region located at 12.6 ppm. This is assigned to methyl groups along the interior of the chain, in accord with the results found on the oligomers. There is virtually no trace of a resonance below 10 ppm, indicating a chain length of at least 40 monomer units, consistent with the IR results. The line width is quite small, implying a relatively narrow molecular weight distribution in the polymer (a broad molecular weight distribution would lead to somewhat wider lines than observed because of the small variation in chemical shifts found in the shorter chain materials). The absence of a resonance below 10 ppm also supports the contention that only very small amounts of oligomeric species exist in the sample.

The ~2.5 ppm downfield shift of the interior methyl resonances relative to the terminal methyl lines is compatible with increased π-bond delocalization along the chain backbone. Previous IR and single-crystal X-ray results on 2,3-butanedione dihydrazone both demonstrate that even the monomer has some delocalization,[21] thus the polymer must also have a significant amount of delocalization along the carbon–nitrogen backbone. However, the change in chemical shifts with respect to chain length is not continuous, indicating that in this system the effective conjugation length does not extend the length of the backbone but is limited to three to five double bonds. None the less, the electronic band formed from the π orbitals must have a reasonable width, on the order of 1 eV. This conclusion is in accord with extended Hückel calculations done for this polymer system.[17,19]

The resonances in the imine region of the ^{13}C NMR spectrum follow similar patterns as the methyl resonances, as shown in Figure 3. 2,3-Butanedione dihydrazone has a single, narrow peak at 147.3 ppm, again consistent with the inversion symmetry found from the crystal structure of this compound. The dimer has two major features: a single peak at 165.6 ppm and a broad resonance that is composed of three peaks at 148.6, 149.4, and 151.0 (sh) ppm. This is similar to the observations of the methyl resonances; here, the peak at 165.6 ppm is interpreted as arising from interior imines while the peaks centered around 150 ppm originate from carbons at the end of the chain. Again, the splitting seen in the 150 ppm region must be due to some nonplanarity in the chain or from packing effects in the solid state.

For the $x = 3$ oligomer, three broad features are seen, each arising from a number of peaks. Major absorptions are observed at 149.5, 155.6, and 165.8 ppm, with each peak having an identifiable shoulder near 147.7, 156.5, and 168.4 ppm, respectively. This could be interpreted as a resonance for each imine carbon on the chain or as arising from a nonuniform molecular weight distribution. An alternative explanation is that the trimer chain length is just at the boundary between well-defined electronic states and true delocalization. Packing and crystallization effects could then be sufficient to yield a number of different species. In principle, the neighboring nitrogen-14 can broaden the imine resonances, especially if the ^{14}N quadrupole coupling is large.[32] The similarity of all the solid-state carbon line widths, the high magnetic fields, and the lack of characteristic patterns associated with this interaction suggests it is not the primary source of the observed line widths. The spectra from oligomers with $x = 5$ (not shown), 7, and 11 (not shown) only have two peaks each centered at 155.2 (± 0.2) ppm and at 149.0 (±0.3) ppm. The intensity of the upfield peak decreases with increasing chain length and is associated with imines at the chain ends while the downfield peak stems from imines along the interior of the chain. Integration of the rotational sideband manifolds of these peaks is in agreement with the number of monomer units indicated by the synthetic conditions.

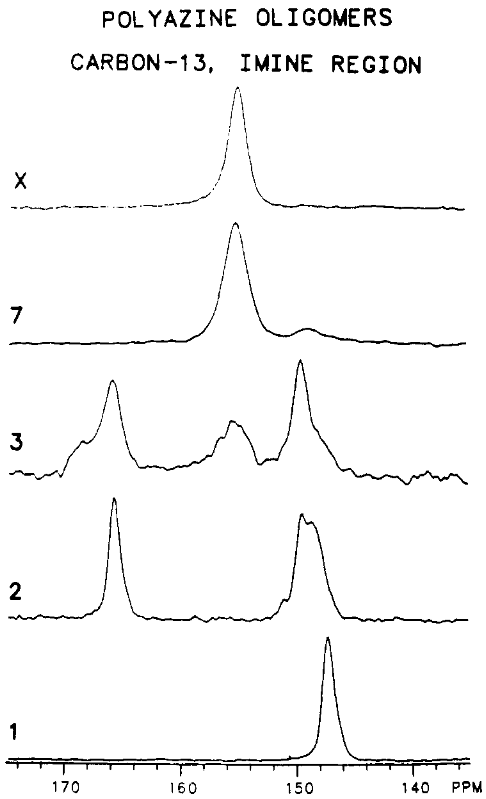

Figure 3. Solid-state ^{13}C NMR spectra in the imine region for $-[N{=}C(CH_3)C(CH_3){=}N]-_x$ for x = 1–3, 7, and >40. The appearance of the line at 155 ppm confirms the increasing delocalization of the π system for chains with $x \geq 3$.

The polymer has a single peak at 155.2 ppm in the imine region of the spectrum. As with the methyl resonances, this indicates a chain of sufficient length that end groups do not yield appreciable intensity in the spectrum. Rough correlations of the integrated intensity again are consistent with a molecular weight in excess of 3500 amu. The imine peak is shifted almost 8 ppm downfield from the peak in the monomer, again signifying the increased delocalization in the bulk of the polymer chain relative to the monomer. Not surprisingly, the imine resonances originating from carbons that are part of the chain are more sensitive to the delocalization than the methyl groups located off the chain.

The solid-state ^{13}C NMR spectra can give an indication of the average polymer chain length through end-group analysis. As discussed above, the absence of terminal methyl and terminal imine resonances only gives a lower limit to the average molecular weight. However, the very weak features at 196.3 and 24.0 ppm are assigned to end-group carbonyls and the methyl groups attached to these carbonyls, respectively (see Figure 1). Comparing integrations between the 24.0 ppm methyl resonance and the main feature at 12.5 ppm yields a ratio of 1:23. Thus, if every chain ended in a carbonyl, the shortest average chain length would be about 12 monomer units (MW ~ 1000). The synthetic conditions for the polymer preparation are about 1:1 of 2,3-butanedione dihydrazone to 2,3-butanedione, statistically suggesting one carbonyl per chain or a chain length of about 23 monomers (MW ~ 1900). However, closer examination of the synthetic procedure is important for two reasons: first, the 2,3-butanedione

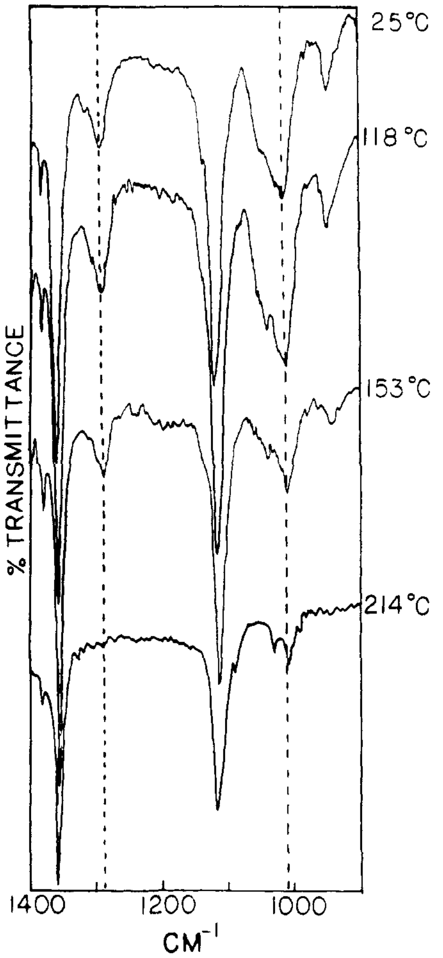

Figure 4. Room-temperature IR spectra of permethyl polyazine as a function of heating temperature. The vertical dashed lines indicate solvent lines that disappear with prolonged heating of the polymer.

dihydrazone is used in a slight molar excess to the 2,3-butanedione; second, the acid used to catalyze the condensation can also promote hydrolysis of the 2,3-butanedione dihydrazone to liberate free hydrazinium in the reacting solution, which can further react with carbonyl end groups to terminate the polymer chain. Both of these attributes of the synthesis will decrease the relative number of carbonyl end groups to less than one per chain. Thus, this end-group analysis also compares reasonably to the previous results. The ketone resonance at 196.3 ppm cannot readily be used in a similar evaluation since it is expected to have a much larger chemical shift anisotropy. Therefore, its intensity is distributed over the center band and rotational sidebands, which are too weak to reliably quantitate.

DSC measurements on the polymer denoted two features of interest. The first is that the polymer decomposes exothermically at 316 °C. Decomposition products have not been determined. The second feature of note is an irreversible endotherm centered at 130 °C, suggestive of a loss of occluded solvent. This latter reaction was further investigated both by IR and NMR spectroscopies.

The IR spectrum of the polymer after various degrees of heat treatment is shown in Figure 4. The major spectral changes are seen between 900 and 1400 cm^{-1}. As the polymer is heated, the intensity of the peaks at 1290, 1015, and 950 cm^{-1} all diminish by about 30% above 130 °C. A plot of the relative intensity of the 1015- and 1290-cm^{-1} peaks is shown in Figure 5. The polymer is synthesized in dimethyl sulfoxide (DMSO) as solvent, and the peaks that lose intensity when the polymer is heated above 130 °C are consistent with the major absorptions found in DMSO. Thus, the conclusion that the 130 °C feature in the DSC is due to a loss of occluded solvent is bolstered by the IR spectra.

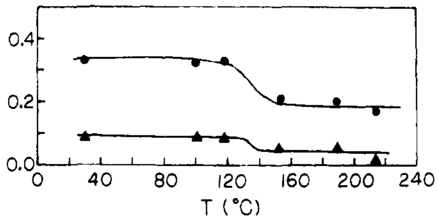

Figure 5. Intensity of the DMSO IR peaks as a function of temperature. Circles denote the 1015-cm^{-1} peak and triangles denote the 1290-cm^{-1} peak. The solid lines are to guide one's eye through the transition at 130 °C.

Room-temperature solid-state ^{13}C NMR spectra of previously heated polymer samples showed very minor effects as a function of heating temperature up to 214 °C. No observable shifts in resonance positions or intensities were noted for the main lines, within experimental error. The only change in the primary features of the NMR spectra was a slight increase in line width for polymers heated to higher temperatures. Again, this is consistent with the loss of occluded DMSO. Since heating (to 214 °C) had no effect on the chains directly, no changes in the chemical shifts of the polymer were expected.

The largest observable effect heat treatment of the polymer had on the consequent spectra was in the line at 40.8 ppm ascribed to residual DMSO in the polymer matrix. The expansion of Figure 1 indicates the line width of this line is much narrower than any of the polymer lines in an unheated sample. The second expansion (sample heated to 189 °C) indicates an *increase* in *both* the line width and intensity of the DMSO resonance. The line width increases because the residual DMSO left behind after heat treatment is bonded to the matrix more tightly and thus is more constrained and "solidlike". The intensity increases because liquids do not cross polarize under the conditions employed here. The unheated polymer spectrum contains contributions from only a small fraction of the solvent molecules, since in the unheated sample the residual DMSO is more mobile and "liquidlike" while the spectrum from the heated sample has intensity from a larger proportion of the residual solvent molecules because these molecules are more rigid and can cross polarize more efficiently.

In conclusion, this study has used solid-state ^{13}C NMR to probe the properties of a series of oligomeric and polymeric azines. Both the on-chain and off-chain resonances show similar characteristics as a function of chain length: as the molecular weight increases, the amount of conjugation along the chain increases, leading to wider π bands that contribute to the interesting solid-state properties of the polyazines. The imine region of the solid-state ^{13}C NMR spectra suggests that a change in the electronic structure occurs near a chain length of three units. Further, the polymer undergoes an irreversible transition in the DSC at 130 °C suggestive of a solvent loss; IR and solid-state NMR spectra are consistent with this conclusion. Further studies of the solid-state NMR of electrically conductive, iodine-doped polyazines are in progress.

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Registry No. $H_2NN{=}C(CH_3)C(CH_3){=}NNH_2$, 3457-52-1; $(CH_3(CO)_2CH_3)(H_2NN{=}C(CH_3)C(CH_3){=}NNH_2)$ (copolymer), 122408-43-9; $N{=}C(CH_3)C{=}N(CH_3)$ (SRU), 54047-69-7.

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Solid-State Carbon-13 NMR Study of the Structure and Mobility of the 1,4-*trans*-Polybutadiene–Perhydrotriphenylene Matrix System and of the Extracted Polymer

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ABSTRACT: 1,4-*trans*-Polybutadiene has been studied by high-resolution solid-state carbon-13 NMR spectroscopy as its crystalline inclusion compound with perhydrotriphenylene (PHTP). The polymer was formed by ^{60}Co γ-irradiation of the inclusion compound with monomer butadiene. The chemical shifts and spin-lattice relaxation times (ca. 10 s) of the polymer are consistent with a high degree of chain mobility and a substantial content (about 25%) of the cis (versus skew) conformation at the $-CH_2-CH=$ single bonds. The NMR characteristics are very similar to those of the crystalline polymer in its high-temperature modification (form II). The unusual environment of the PHTP canals prevents interchain interactions while interaction with the matrix is nonspecific and permits mobility of the polymer down to very low temperature. The spin-lattice relaxation times of the carbons of the pure matrix (200–350 s) are reduced by half when polymer is present because of increased mobility in the inclusion compound. The splitting of the PHTP carbon resonances of the inclusion compound is diagnostic of altered crystal packing in the presence of polymer.

Introduction

1,4-*trans*-Polybutadiene can be produced by different methods. Ziegler–Natta catalysts based on VCl_3–$Al(Et)_3$ complexes lead to a polymer containing greater than 99.7% trans monomer units, as observed by ^{13}C NMR.[1,2] Inclusion polymerization has been widely employed as an alternative method of synthesis, leading to high molecular weight, highly ordered products. Many authors regard polybutadiene obtained in urea and in perhydrotriphenylene (PHTP) inclusion complexes as reference compounds for characterization methods.[2,3] This process involves an initiation step, brought about by γ-irradiation of the inclusion compound formed by butadiene and the matrix, and a propagation step in which the monomer molecules residing in the canals of the inclusion compound are linked together, leading to a new inclusion compound with the polymer.[4]

The crystal structure of PHTP is not destroyed during the polymerization process, but a solid–solid crystal transformation occurs, which can be followed by X-ray