Macromolecules **1987**, *20*, 1234–1237

(5) Toniolo, C.; Bonora, G. M.; Palumbo, M.; Peggion, E. *Biopolymers* **1978**, *17*, 1713.
(6) Bonora, G. M.; Maglione A.; Toniolo, C. *Polymer* **1974**, *15*, 767.
(7) Narita, M.; Doi, M.; Sugasawa, H.; Ishikawa, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1473.
(8) Narita, M.; Ishikawa, K.; Sugasawa, H.; Doi, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1731.
(9) Narita, M.; Chen, J. Y.; Sato, H.; Kim, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2494.
(10) Narita, M.; Fukunaga, T.; Wakabayashi, A.; Ishikawa, K.; Nakano, H. *Int. J. Peptide Protein Res.* **1984**, *23*, 306.
(11) Narita, M.; Ishikawa, K.; Chen, J. Y.; Kim, Y. *Int. J. Peptide Protein Res.* **1984**, *24*, 580.
(12) Narita, M.; Ishikawa, K.; Kudo, K.; Endo, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3125.
(13) Asakura, T. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 227.
(14) Pysh E. S.; Toniolo, C. *J. Am. Chem. Soc.* **1977**, *99*, 6211.
(15) Stimson, E. R.; Zimmerman, S. S.; Scheraga, H. A. *Macromolecules* **1977**, *10*, 1049.
(16) Urry, D. W.; Cunningham, W. D.; Ohnishi, T. *Biochemistry* **1974**, *13*, 609.
(17) Iqbal, M.; Balaram, P. *J. Am. Chem. Soc.* **1981**, *103*, 5548.
(18) Zimmerman, S. S.; Scheraga, H. A. *Biopolymers* **1977**, *16*, 811.
(19) Vijayakumar, E. K. S.; Balaram, P. *Biopolymers* **1983**, *22*, 2133.
(20) Vijayakumar, E. K. S.; Balaram, P. *Tetrahedron* **1983**, *39*, 2725.
(21) Nagaraj, R.; Shamala, N.; Balaram, P. *J. Am. Chem. Soc.* **1979**, *101*, 16.
(22) Balaram, H.; Prasad B. V. V.; Balaram, P. *J. Am. Chem. Soc.* **1983**, *105*, 4065.
(23) Toniolo, C.; Bonora, G. M.; Barone, V.; Bavoso, A.; Benedetti, E.; Blasio, B. D.; Grimaldi, P.; Lelj, F.; Pavone, V.; Pedone, C. *Macromolecules* **1985**, *18*, 895.
(24) Raj, P. A.; Balaram, P. *Biopolymers* **1985**, *24*, 1131.
(25) Bystrov, V. F.; Ivanov, V. T.; Portnova, S. L.; Balashova, T. A.; Ovchinnikov, Y. A. *Tetrahedron* **1973**, *29*, 873.
(26) Asakura, T. *Makromol. Chem.* **1981**, *182*, 1135.

Heteronuclear *J*-Resolved Solid-State NMR of Filled Natural Rubber

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ABSTRACT: Heteronuclear *J*-resolved ^{13}C NMR spectra of solids can be obtained by the combined use of magic angle spinning and proton multiple-pulse decoupling. In a cured, carbon black filled, natural rubber, MAS alone appears to be sufficient to reveal scalar ^{13}C–^{1}H couplings, meaning that there must be extensive molecular motions. The nature of these motions are discussed by making a comparison to the motions in the plastic crystal adamantane. It is concluded that susceptibility effects due to the presence of the filler play an important role in the ^{13}C line width.

Introduction

It is known that *J*-resolved ^{13}C NMR spectra of solids can be obtained by the combined use of magic angle spinning (MAS) and proton multiple-pulse decoupling.[1] The effect of multiple-pulse decoupling is to average the proton homonuclear dipolar interaction $H_{D,II}$[3] and thus render the ^{13}C–^{1}H heteronuclear dipolar interaction $H_{D,IS}$ inhomogeneous so that it can be averaged by magic angle spinning.[4] Then, in contrast with standard heteronuclear decoupling, the isotropic carbon–proton coupling $H_{J,IS}$ remains present. It is scaled however by multiple-pulse decoupling.[3]

Until now most applications of this technique were on spherical organic molecules, like camphor and adamantane,[1a,b,c,2] which, at room temperature, are in a "plastic" crystalline state where the molecules reorient rapidly around their symmetry axes and even diffuse through the lattice. This results in considerable averaging of the dipolar interactions. The remaining part of the homonuclear dipolar interactions can then be averaged by proton multiple-pulse decoupling. It must be noted, however, that Miura et al.[1d] recently succeeded in resolving *J* multiplets in rigid solids using a double-bearing probe with an accurate setting of the rotation axis and a short multiple-pulse cycle (i.e., short 90° pulses).

Early proton NMR studies of rubber samples by Gutowsky et al.[5] show very narrow lines at room-temperature, indicating that dipolar interactions are averaged by CH_3 rotation and segmental motions. Duch and Grant[6] succeeded in getting direct ^{13}C spectra of natural rubber using conventional high-resolution techniques. Thus natural rubber seems a good candidate for *J*-resolved spectroscopy in the solid state. It appears that even for cured, carbon black filled rubber MAS alone is sufficient to obtain heteronuclear *J*-resolved spectra, showing that there are extensive molecular motions present. The nature of these motions are discussed by comparing a series of spectra, obtained with and without MAS and dipolar decoupling, to those of the well-studied plastic crystal adamantane.

Experimental Section

Materials. Adamantane (Gold Label) was obtained from Aldrich Chemical Co. The rubber samples were prepared from Standard Malaysian rubber and contained 50 parts per hundred HAF carbon black. The samples were cured with 2.5 parts per hundred sulfur. The average molecular weight between cross-links is of the order of 10 000.

Measurements. Spectra were recorded on a Bruker CXP 300 (carbon frequency, 75.4 MHz) and on a home-built 180-MHz spectrometer (carbon frequency, 45.3 MHz). On the CXP 300 spectra were obtained in a double-bearing CP-MAS probe operating with 4.5-μs 90° pulses. The MAS experiments were carried out with spinning speeds between 2 and 3 kHz.

Results and Discussion

Figure 1 shows the heteronuclear 2D *J* spectrum of cured, carbon black filled, natural rubber at room temperature obtained with the proton-flip experiment.[7] The

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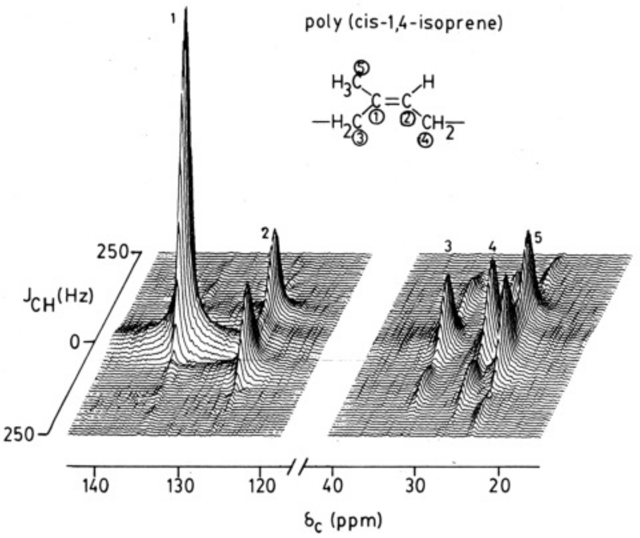

Figure 1. Stacked plot of the heteronuclear 2D *J* spectrum of cured, carbon black filled, poly(*cis*-1,4-isoprene) (natural rubber). The proton flip experiment was used with high-power proton decoupling during the detection time. The experiment was performed with the sample spinning at the magic angle.

only difference with this experiment is that during the detection period t_2 high-power proton decoupling is applied. Furthermore the sample was spinning under the magic angle. Thus unlike the "plastic" crystals it is not necessary to apply multiple-pulse decoupling, meaning that dipolar interactions are even averaged to a greater extent in the rubber sample than in, e.g., adamantane. In the F_1 dimension we now find the full unscaled scalar ^{13}C–H couplings, being 150 Hz for the C-2 carbon and 127 Hz for carbons C-3, C-4, and C-5. These values are identical with those found in a chloroform solution of depolymerized natural rubber. The chemical shift values are, within the experimental error of 1 ppm, identical with those found by Duch and Grant.[6]

In order to get more insight in the motional processes causing this averaging of dipolar interactions in rubber we took spectra under various conditions and compared them to adamantane spectra (Figure 2). Adamantane molecules are globular molecules that are cubic close packed (fcc). The barrier to molecular reorientation at a site is low. As a result adamantane rotates fast about its molecular axes in the crystal (τ = 1.7 10^{-11} s at room temperature).[8] Proton second-moment studies[9,10] show that this rotation averages intramolecular dipolar interaction to zero; at room temperature the proton second moment is determined by intermolecular dipolar interactions whose magnitude depends on the distance between the molecular centers (lattice parameter 9.45 Å) and amounts to 9 kHz. Diffusion is not very prominent at room temperature; only at temperatures above 475 K does diffusion influence the proton T_2.

Gutowsky and Meyer[5a] performed proton second-moment studies of poly(*cis*-1,4-isoprene) (natural rubber) as a function of temperature and cure time. With rising temperature the line width shows two regions of change. The lines start to narrow at temperatures of 140–170 K; this is assigned to the onset of CH_3 group rotation. A second larger decrease (per degree kelvin) in line width was observed at ~225 K, assigned to the onset of segmental motion. The lines do not narrow further at temperatures above 263 K. The line width is relatively narrow for a solid, indicating that the chain segments are undergoing a considerable amount of random reorientational motions at frequencies of the order of 50 kHz or faster.[5b] ^{13}C free-induction decays of polyisoprenes have been obtained by Schaefer[11] and also indicate that there is considerable motional narrowing. In a carbon black filled rubber the lines appear to be 5–10 times broader, which is interpreted as inhibition of certain motions of the polymer chains by the filler. This line broadening can be partly removed by MAS.[12] Multiple-pulse narrowing of the proton resonance of both filled polyisoprene and the pure gum has been carried out by Dybowski and Vaughan,[13] showing that in both samples a line broadening is introduced by anisotropic reorientational motions.

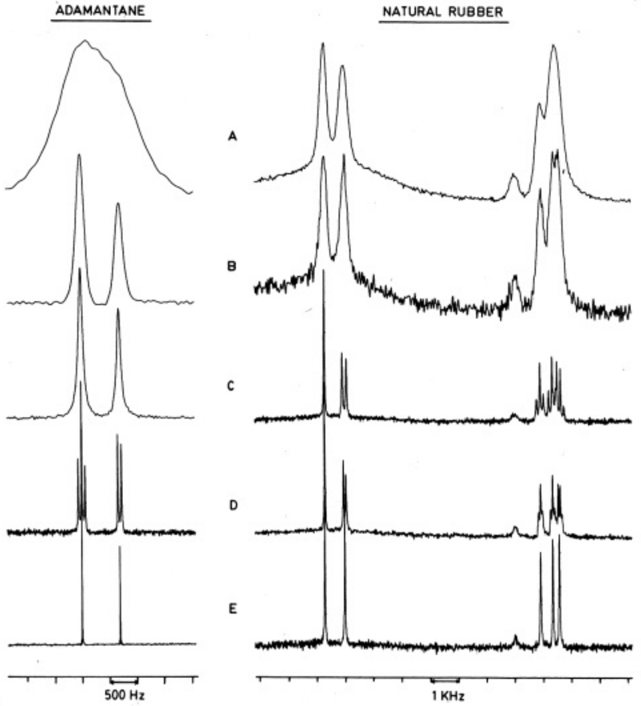

Figure 2. Spectra of adamantane and natural rubber obtained under various conditions. In the rubber spectra there is an extra line present at 43 ppm from an antidegradant which was not a subject of the present study: (A) no decoupling and no magic angle spinning, full width at half height for adamantane (ADA) was 1500 Hz and was 380 Hz for natural rubber (NR); (B) high-power proton decoupling but no magic angle spinning, ADA, 180 Hz, NR, 300 Hz; (C) magic angle spinning but no decoupling, ADA, 90 Hz, NR, 35 Hz; (D) Magic angle spinning combined with multiple-pulse decoupling (semiwindowless MREV-8[21]); ADA, 11 Hz, NR, 35 Hz; (E) Magic angle spinning and high-power proton decoupling, ADA, 3 Hz, NR, 35 Hz.

Such spatial anisotropy of molecular motions has also been found in poly(*cis*-1,4-butadiene) by English and Dybowski.[14] They found that the ^{1}H and ^{13}C NMR lines could be narrowed by coherent averaging techniques, i.e., MAS and multiple-pulse NMR. This anisotropy in the motion, even without the presence of cross-links and filler material, is attributed to the presence of chain entanglements whose lifetime seems to be long on the time scale of an NMR experiment. Extensive theoretical and experimental work on the effect of chain entanglements has been done by Cohen-Addad and co-workers[15] using high-resolution NMR on, among others, molten polybutadiene and poly(dimethylsiloxane).

Figure 2A shows adamantane and filled-rubber spectra obtained without MAS and without high-power proton decoupling. For adamantane we see one broad resonance ~1500 Hz wide, whereas the rubber lines are much narrower (~400 Hz). With high-power proton decoupling, with a static sample (Figure 2B), the rubber lines are narrowed to 300 Hz. For adamantane the change is more drastic; now we can see the two separate carbon resonances, each ~180 Hz wide. In the adamantane spectrum of Figure 2A the line width is determined by intermolecular dipolar interactions; these are removed by the proton decoupling in Figure 2B. The adamantane lines in Figure 2B are inhomogeneously broadened either by chemical shift anisotropy or by susceptibility effects. Broadening by chemical shift anisotropy, however, is very unlikely because the rapid reorientations of the molecule which average intramolecular dipolar interactions will also average the chemical shift anisotropy due to intramolecular interactions. It has been reported that compressing adamantane into a sphere reduces the line widths.[16] It is thought that the compression removes most of the voids in the sample and thus reduces the susceptibility distribution through the sample. The result of the rubber spectra can be explained along the same lines. It has to be noted, however, that the broadening by dipolar interaction of the rubber lines in Figure 2A is 1 order of magnitude smaller than for adamantane (100 vs. 1000 Hz).

The broadening of the rubber spectrum in Figure 2B is quite substantial (300 Hz) and is proportional to the field (a line width of 180 Hz is found on a 180-MHz spectrometer). As the contribution of dipolar interaction to the line width in Figure 2A amounts to only 100 Hz, it is evident that there are fast, nearly isotropic motions present that average the dipolar interaction, and, of course, the chemical shift anisotropy is averaged along with it. Thus the rubber line width found in Figure 2B is probably due to microscopic inhomogeneities generated by the carbon black filler particles. This is in contradiction with the result of Schaefer et al.,[12] who state that the ^{13}C NMR line in a nonspinning, filled, vulcanized sample is purely homogeneous.

If we now turn the proton decoupling off but spin the sample at the magic angle, we observe well-resolved J multiplets in rubber. This means that all interactions except for the isotropic chemical shift and the scalar J_{C-H} coupling are averaged to zero by MAS. In adamantane line widths of 90 Hz are observed, but although the scalar coupling is approximately 130 Hz no sign of a splitting of the lines into J multiplets is observed. Here MAS is not capable of averaging the homonuclear proton dipolar coupling which is of the order of 9 kHz. So there are residual proton dipolar fluctuations that modulate the coupling Hamiltonian $J\vec{I}\cdot\vec{S}$ (I, proton; S, carbon) i.e., make it time dependent. As a result $J\langle I_zS_z\rangle$ is too small to be observed. In adamantane a combination of MAS and multiple-pulse decoupling (Figure 2D) is necessary to observe scalar couplings. However, we believe that MAS alone will be sufficient at spinning speeds above 10 kHz. In the rubber sample the residual dipolar couplings are small enough to be completely averaged by 2 kHz spinning. Here the only effect of multiple-pulse decoupling is to scale the J couplings, which results in a reduction of the resolution (Figure 2D). Figure 2E shows the adamantane and rubber spectra obtained with a combination of MAS and proton decoupling, resulting in 3-Hz-wide lines for adamantane and 30-Hz line width for the rubber. This residual line width in rubber is probably caused by susceptibility effects not averaged by MAS and/or a macroscopic distribution of chemical environments. In conclusion these experiments show us that the heteronuclear carbon-proton as well as the homonuclear proton–proton dipolar interaction is much smaller in cured, filled, natural rubber than in adamantane. This is supported by the fact that it is very difficult to establish cross-polarization for the spinning rubber sample whereas for adamantane polarization transfer is still possible although magic angle spinning already has its effect on the transfer as has been studied by Stejskal et al.[17]

Of course it is not possible to simply translate adamantane results to the natural rubber because the systems are very different. Still we can draw some conclusions. The fact that intrachain dipolar interactions are averaged (which is of the order of tens of kilohertz) shows that there must be fast motions using different degrees of freedom of the chain segments. A simple rotation of the chains for instance would scale the dipolar interaction but cannot make it vanishingly small. However, the motion must still be restricted, i.e., cannot use all the degrees of freedom of a chain segment, otherwise magic angle spinning at the moderate speed of 2 kHz would not be capable of narrowing the lines further as we observed in Figure 2.[18] Several authors have pointed out before that the motions of elastomers above the glass temperature are anisotropic.[11-15] It already exists in uncured rubbers without filler material due to chain entanglements[13,14] and the effects can even be observed by high-resolution NMR.[15] So these entanglements have a lifetime longer than the time scale of the NMR experiment. The only effect of cross-links and filler material is to aggravate the spatial restrictions of the polymer chain.

The fact that (inter-) dipolar interactions between different chain segments are also very small is surprising. As mentioned before intermolecular dipolar interactions in adamantane are rather big (~9 kHz). In the rubber sample discussed here and elsewhere[11-13] the average ^1H–^1H dipolar interaction for protons located on neighboring chains or chain segments is at least 50 times smaller than in adamantane. This in spite of the fact that there are filler particles, cross-links, and entanglements holding different chains together. Apparently, the fact that adamantane is a plastic *crystal* and therefore maintains some degrees of translational symmetry even in its quasi-rotator phase, in contrast to the amorphous rubber structure, makes the difference. It means that in the rubber either the interchain distance is very large or that there is enough diffusion in the natural rubber to average this interaction. With diffusion large-scale lateral movements of chains with respect to each other are meant. It would implicate that large parts of the polymer network have to reorient.

To investigate if such a molecular diffusion exists we make use of the fact that rubber ^{13}C lines in the absence of MAS but with proton decoupling are inhomogeneously broadened, presumably by susceptibility effects due to the presence of the filler. We performed a Jeener type 2D exchange experiment[19] with high-power proton decoupling during the detection and evolution period on a nonspinning rubber sample. As T_1 values are of the order of 80 ms (except for the quaternary carbon, which has a much longer T_1), a mixing time of 40 ms was chosen. The result of this experiment is shown in Figure 3. The fact that the lines are extended along the diagonal shows that they are inhomogeneously broadened.[20] From these line shapes it can be concluded that the polymer chains do not diffuse through great volumes in the sample, thereby allowing each ^{13}C spin to sample different values of the inhomogeneous magnetic field on a time scale of 40 ms. If this were so then the lines would broaden in the direction perpendicular to the diagonal because of the carbon spins with a different resonance frequency during the detection and evolution period. A spin that has diffused to another location in the sample, experiencing a different field during the detection period than it did during the evolution period, will not resonate on the diagonal. Thus with this 2D experiment no molecular diffusion can be detected. The negative

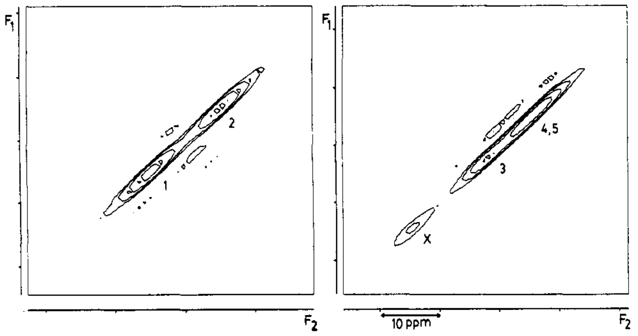

Figure 3. Contour plot of a 2D exchange spectrum (mixing time τ_m = 40 ms) of a nonspinning rubber sample with high-power proton decoupling during the evolution and the detection period. For the assignment of the lines, see Figure 1. The line denoted X is from the antidegradant. The fact that the lines are drawn out along the diagonal shows that they are inhomogeneously broadened.

result may point to the absence of diffusion on a time scale of 40 ms, in which case the relatively small interchain dipolar interactions must be due to a large distance between different segments. An alternative explanation can be, however, that reorientations are limited to small regions, i.e., in voids between filler particles, where the magnetic field is rather constant. This point will be investigated further.

Conclusions

From the above-mentioned experiments it can be concluded that the effect of the carbon black filler particles on the ^{13}C NMR line width of the rubber is twofold. First, the filler particles introduce microscopic inhomogeneities by susceptibility effects. Second, the filler does not allow the chains to move in a random way, so residual dipolar couplings are present. Such anisotropy, however, is also caused by the presence of chain entanglements. Both effects can be averaged to a great extent by MAS, allowing *J* resolved spectra to be recorded in the solid state. By comparison to adamantane the interchain dipolar interaction is surprisingly small. A 2D exchange experiment, however, cannot detect molecular diffusion on a time scale of ~40 ms.

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Registry No. Adamantane, 281-23-2.

References and Notes

(1) (a) Terao, T.; Miura, H.; Saika, A. *J. Chem. Phys.* **1981**, *75*, 1573. (b) Terao, T.; Miura, H.; Saika, A. *J. Magn. Reson.* **1982**, *49*, 365. (c) Terao, T.; Miura, H.; Saika, A *J. Am. Chem. Soc.* **1982**, *104*, 5228. (d) Miura, H.; Terao, T.; Saika, A. *J. Magn. Reson.* **1986**, *68*, 593.
(2) (a) Zilm, K. W.; Grant, D. M. *J. Magn. Reson.* **1982**, *48*, 524. (b) Mayne, C. L.; Pugmire, R. J.; Grant, D. M. *J. Magn. Reson.* **1984**, *56*, 151.
(3) Haeberlen, U. *Adv. Magn. Reson.* **1976**, Supplement I.
(4) Maricq, M. M.; Waugh, J. S. *J. Chem. Phys.* **1979**, *70*, 3300.
(5) (a) Gutowsky, H. S.; Meyer, L. H. *J. Chem. Phys.* **1953**, *21*, 2122. (b) Gutowsky, H. S.; Saika, A.; Takeda, M.; Woessner, D. E. *J. Chem. Phys.* **1957**, *27*, 534.
(6) Duch, M. W.; Grant, D. M. *Macromolecules* **1970**, *3*, 165.
(7) Bax, A. *Two-Dimensional Nuclear Magnetic Resonance in Liquids*: D. Reidel: Dordrecht, 1982.
(8) Resing, H. A. *Mol. Cryst. Liq. Cryst.* **1969**, *9*, 101.
(9) McCall, D. W.; Douglass, D. C. *J. Chem. Phys.* **1960**, *33*, 777.
(10) Smith, G. W. *J. Chem. Phys.* **1961**, 35, 1134.
(11) Schaefer, J. *Macromolecules* **1972**, *5*, 427.
(12) Schaefer, J.; Chin, S. H.; Weissman, S. I. *Macromolecules* **1972**, *5*, 798.
(13) Dybowski, C. R.; Vaughan, R. W. *Macromolecules* **1975**, *8*, 50.
(14) (a) English, A. D.; Dybowski, C. R. *Macromolecules* **1984**, *17*, 446. (b) English, A. D. *Macromolecules* **1985**, *18*, 178.
(15) (a) Cohen-Addad, J. P. *J. Chem. Phys.* **1974**, *60*, 2440. (b) Cohen-Addad, J. P.; Faure, J. P. *J. Chem. Phys.* **1974**, *61*, 1571. (c) Cohen-Addad, J. P. *J. Phys. (Les Ulis, Fr.)* **1982**, *43*, 1509. (d) Cohen-Addad, J. P.; Dupeyre, R. *Macromolecules* **1985**, *18*, 1612.
(16) Garroway, A. N.; VanderHart, D. L.; Earl, W. L. *Philos. Trans. R. Soc. London, A* **1981**, *299*, 609.
(17) Stejskal, E. O.; Schaefer, J.; Waugh, J. S. *J. Magn. Reson.* **1977**, *28*, 105.
(18) Andrew, E. R. *Philos. Trans. R. Soc. London A* **1981**, *299*, 505.
(19) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.
(20) Szeverenyi, N. M.; Sullivan, M. J.; Maciel, G. E. *J. Magn. Reson.* **1982**, *47*, 462.
(21) Burum, D. P.; Linder, M.; Ernst, R. R. *J. Magn. Reson.* **1981**, *44*, 173.

Interpretation of ^{13}C NMR Sequence Distribution for Ethylene–Propylene Copolymers Made with Heterogeneous Catalysts

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ABSTRACT: The utility of ^{13}C NMR diad and triad distribution data for characterizing heterogeneous Ziegler catalysts used to make ethylene–propylene copolymers is examined. Appropriate statistical criteria are established for determining whether single- or multiple-site models best fit measured sequence distributions. Least-squares data correlations for copolymers made with a variety of heterogeneous titanium catalysts indicate the copolymers are typified by broad compositional distributions and multiple catalyst species. However, a simple two-site model is adequate in some cases. The r_1r_2 of the individual sites is estimated to lie in the range 0.5 to 3.0. The average $\overline{r_1r_2}$ for heterogeneous titanium catalysts determined from polymer composition/monomer concentration data and the copolymerization equation is much lower than the value calculated from the diad distribution. Consequently this former $\overline{r_1r_2}$ does not correctly indicate copolymer sequence distribution.

Introduction

^{13}C NMR analysis for the diad and triad distribution in ethylene–propylene copolymers (EPM) is a well-established technique.[1-4] A number of authors[5-7] have attempted to obtain information on the nature of titanium-based Ziegler catalysts used for EPM synthesis by com-

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