The Carbon-13 Spin Relaxation Parameters of Completely Amorphous and Semicrystalline *cis*-Polyisoprene

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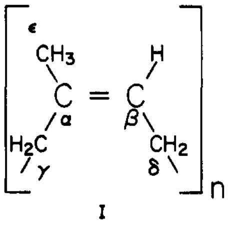
ABSTRACT: By taking advantage of the relatively slow crystallization rate of *cis*-polyisoprene, a comparison has been made for the first time between the carbon-13 spin-relaxation parameters of a completely amorphous (supercooled) polymer and the noncrystalline regions of the corresponding semicrystalline polymer. At 0 °C the spin–lattice relaxation times and nuclear Overhauser enhancement factors are the same for both the amorphous and partially crystalline sample, where the optimum level of crystallinity attained is 31%. However, the spin–spin relaxation times T_2, as determined from the measured line widths, decrease with increasing level of crystallinity. These results for the semicrystalline polymer are similar to those reported in the literature for carbon black filled natural rubber. A qualitatively similar interpretation can be formally given to the data for the crystalline polymer. The high-frequency motions appear to be unaffected by crystallization while the line broadening can reflect incomplete motional narrowing of the segments in the amorphous regions, the reorientational motions of which are associated with the relatively long correlation times. The relaxation parameters for the completely amorphous and semicrystalline polymers can be marginally fitted to the distribution of correlation time function given by Schaefer. We have also found that although both polyisobutylene and *cis*-polyisoprene have the same glass temperature resolvable spectra can be obtained some 20–30 °C lower for the polyisoprene. This result can be attributed to the fact that there are two orders of magnitude difference in the average correlation time between the two polymers at 40 °C.

It has been suggested that the carbon-13 NMR spectra and the associated spin-relaxation parameters (spin–lattice relaxation time T_1, spin–spin relaxation time T_2, and the nuclear Overhauser enhancement factor, NOEF) are sensitive to the structure of the amorphous regions of bulk polymers.[1–3] If so, they could serve as additional and useful parameters to characterize these regions in both completely amorphous as well as semicrystalline polymers. For this latter class of polymers, the important question still remains as to what differences there are, if any, between the structure and properties of the noncrystalline regions of a polymer and the completely liquid (amorphous) state of the same polymer at the same temperature and pressure. To properly answer this question, experiments need to be performed under the same conditions for a given polymer when it is either in the completely amorphous or semicrystalline state. Heretofore, the determination of the NMR relaxation parameters for a semicrystalline polymer has only been reported for *trans*-polyisoprene[1] where a comparison with the completely amorphous polymer was not made.

The stringent conditions set forth above are not easily met for most polymers under convenient operating conditions. One polymer for which these requirements can be achieved is *cis*-polyisoprene (I). This polymer has an equilibrium melting temperature of about 30 °C[4,5] and crystallizes very slowly.[6–8]



I

Thus experiments can be performed on the supercooled, completely amorphous polymer at 0 to −10 °C without crystallization ensuing within the requisite time. On the other hand, in an independent experiment, the polymer can be crystallized at a lower temperature and still be maintained crystalline at 0 to −10 °C. For these reasons *cis*-polyisoprene was chosen for the study of the effect of crystallinity on the ^{13}C spin-relaxation parameters and comparison with the completely amorphous polymer. Well-resolved spectra for the bulk amorphous polymer have already been reported[1,9] as have the spin-relaxation parameters at 40 °C and 22.6 MHz.[1]

Experimental Section

Carbon-13 spectra, under conditions of scalar proton decoupling, were acquired at 67.9 MHz on a Bruker HX-270 Fourier transform NMR spectrometer using a quadrature detection scheme. Generally total spectral widths of 10 or 15.15 kHz were used, with 4096 frequency domain points. Free induction decays were multiplied by a suitable exponential function to enhance sensitivity. The 90° rf pulse used was usually of 47 μs duration.

Carbon-13 T_1's were measured using the standard inversion recovery pulse sequence.[10] Pulse sequence repetition rates were at least three times T_1 in all cases. Separate sets of partially relaxed spectra, with optimum placement of the rf carrier for reasons of ^{13}C pulse power, were used for the protonated aliphatic, protonated vinyl, and nonprotonated vinyl carbons. Line widths at half-height were measured directly from printed spectra. Nuclear Overhauser enhancements were measured using a gated decoupling technique.[11] The waiting period between the end of data acquisition and the next pulse was at least eight times T_1 except for the nonprotonated vinyl carbon (C^{α}) in which case this delay was about 3.5 times T_1 at 0 °C. At 40 °C, the waiting period was about ten times the nonprotonated carbon T_1. The spin dynamics of the nuclear Overhauser enhancement experiment has recently been analyzed.[12,13] This analysis indicates that waiting periods of about eight to ten times T_1 may be necessary to obtain accurate NOE values in some cases.[12,13]

The rubber-like samples were packed into the NMR tube in the form of small pieces. For the 40 °C experiments the samples were covered with CD_3OD (D_2O for the 22.6 MHz line width measurement) for locking purposes.

The *cis*-polyisoprene sample was obtained from the Goodyear Tire and Rubber Co. (Natsyn-200). Its cis-1,4 content was greater than 99% by NMR measurements. For the study of the crystalline polymer the sample, cut into small pieces, was packed into the NMR tube and placed in a thermostatic bath maintained at −20 °C for a period of about 4 weeks. This period is well in excess of the time needed to reach the final, pseudoequilibrium level of crystallinity.[4,6] The melting temperature of samples crystallized at this temperature was found from DSC measurements to be 8 °C, in agreement with previous reports.[4] These parameters enabled measurements to be made on the semicrystalline polymers at 0 and −10 °C. The maximum level of crystallinity that could be attained was 31%. The lower level of crystallinity, 12%, that was also studied was obtained by reducing the time of crystallization.

The degree of crystallinity, $(1 - \lambda)$, of a given sample was calculated from its measured enthalpy of fusion obtained with a Perkin-Elmer differential scanning calorimeter. Simultaneous with the crystalli-

Table I
Carbon-13 Spin-Relaxation Parameters for *cis*-Polyisoprene at 40 °C

Carbon	22.6 MHz[a] T_1[b]	NOEF[c]	$W_{1/2}$[d]	67.9 MHz[e] T_1[b]	NOEF[c]	$W_{1/2}$[d]
α	700	1.2	7	940	0.4	38
β	95	1.2	14	166 (200)	0.7 (1.0)	41
γ	50	1.2	20	114 (100)	0.9 (1.0)	41
δ	55	1.2	18	119 (110)	0.8 (1.0)	40
ϵ	350	1.2	12	656	0.9	36

[a] From ref 1. [b] In ms. Estimated accuracy ±10%. [c] Estimated accuracy ±0.1. [d] In Hz. Estimated accuracy ±10–15%. [e] Values in parentheses are predicted from data at 22.6 MHz and a distribution of correlation times model (see text).

zation of the sample in the NMR tube, pieces of the polymer were placed in DSC pans and given the same thermal treatment. When the NMR tubes were removed from the crystallization bath the DSC pans were also removed and stored under liquid nitrogen, which retarded further crystallization, until they were placed in the DSC for the enthalpy of fusion measurements. To calculate the degree of crystallinity the enthalpy of fusion of the completely crystalline polymer was taken to be 15.3 cal/g.[4]

Prior to use, the NMR tubes containing the semicrystalline samples were cooled to −80 °C, in a dry ice–isopropanol mixture. The sample was covered with cold CD_3OD for locking purposes. The tube was then placed in the probe and was allowed to warm slowly to the desired preset temperature below the melting temperature.

Results and Discussion

Frequency Dependence of the ^{13}C Spin-Relaxation Parameters at 40 °C. A detailed study of the relaxation parameters for *cis*-polyisoprene in the completely amorphous state (40 °C) and 22.6 MHz has been reported by Schaefer.[1] Since the resonance frequency used in this work is substantially greater than that of the previous work[1] it seemed desirable, before investigating the major question of interest, to examine the frequency dependence of these parameters. The data previously obtained for *cis*-polyisoprene (T_1, T_2, and NOEF) could not be fitted by a single correlation time model.[1] Instead, a self-consistent explanation of these parameters at fixed temperature and frequency was obtained in terms of a distribution of correlation times.[14] Data at a substantially higher frequency can serve as a check of this analysis. The results at 67.9 MHz are presented in Table I and compared with the previous report at 22.6 MHz.[1]

All of the parameters, for each of the carbons, are different at the two frequencies. The T_1's for each of the carbons at 67.9 MHz are larger than the corresponding values at the lower frequency. This result would be qualitatively expected even for a single correlation time model when the extreme narrowing condition is not fully satisfied.[15,16] However, these results can be examined more quantitatively with the distribution of correlation times that satisfactorily explained the relaxation parameters at 22.6 MHz. A log χ^2 distribution function was used for this purpose.[14,17] In this formulation a given distribution is characterized by a width parameter p, a mean correlation time $\bar{\tau}$, and a logarithmic time scale of base b. The parameter b was kept constant to allow for a comparison among the different polymers, a procedure which does not alter the interpretation of the results.[14] The larger the value of p, the narrower the width of the distribution. For *cis*-polyisoprene at 40 °C a p value of 14 and a $\bar{\tau}$ of 4×10^{-10} s satisfactorily explains the combined T_1, NOEF, and $W_{1/2}$ data for the backbone methine carbon. With these constants describing the distribution, the relaxation parameters at 67.9 MHz can be calculated. The calculated values for T_1 are given in parentheses in Table I for the β, γ, and δ carbons. The agreement between the observed and calculated values is quite good. No attempt was made to calculate T_1 values for either the methyl or nonprotonated carbons.

At 22.6 MHz the NOEF's of all the carbons, and in particular the backbone carbons, are equal.[1] Similar behavior has been found for other polymers in bulk and in solution.[2,17,18] The NOEF's are reduced at 67.9 MHz and except for the C^α carbon are essentially equal. A reduction in the NOEF's is expected within the framework of a one correlation time model.[15,16] However, a more quantitative comparison can be made utilizing the distribution parameters required to explain the low-frequency data. The calculated NOEF values are also given in parentheses in the appropriate column in Table I. Within the experimental error the agreement between the calculated and observed NOEF's is quite good. Thus as far as the T_1's and NOEF's (except for C^α) are concerned, the detailed distribution function analyis of Schaefer for *cis*-polyisoprene at 22.6 MHz is given an independent experimental verification. It is possible, however, that there are other distribution functions which can also satisfactorily explain the data.[19]

The NOEF of the nonprotonated vinyl carbon (C^α) is substantially reduced from that of the other carbons at 67.9 MHz. On the other hand the NOEF's are the same for all the carbons at 22.6 MHz. In view of the successful explanation, by means of the distribution of correlation times, of the frequency dependence of all the T_1's and the other NOEF's, it would appear unlikely that the lower value for C^α at 67.9 MHz can be due to motional considerations. A reasonable possibility is that another mechanism, chemical shift anisotropy,[20] is contributing to the relaxation of this carbon. If mechanisms other than the ^{13}C–^{1}H dipolar one are involved there will be a reduction in the NOEF. The relaxation rate due to anisotropic chemical shift modulated by segmental mobility depends on the square of the magnetic field strength.[20] Hence it would make a substantially greater contribution at high fields. Chemical shift anisotropy has been shown to contribute to the relaxation behavior of nonprotonated sp^2 carbons in several organic molecules in solution at high field.[21] Hence it is not surprising that this mechanism contributes for a similar carbon in *cis*-polyisoprene.

The distribution function that has been used to explain the relaxation parameters found at 22.6 MHz and has predicted the T_1's and NOEF's at 67.9 MHz quite well leads to the expectation that the line widths would decrease by about 7% at the higher frequency. The data in Table I indicate quite clearly that this expectation is not fulfilled. The resonances are substantially broader at the higher frequency, increasing by a factor of about 2 to 3. On the other hand, their magnitude is much less than for the protonated carbons of polyisobutylene determined at the same field and temperature.[2]

The line widths at 22.6 MHz, given in Table I, are for a sample in the form of a machined plug.[1] Spectra obtained by us at the same frequency with pieces of the sample covered by D_2O gave line widths 3–8 Hz broader. Since the spectra for the two sample configurations were obtained on similar instruments at comparable decoupling rf fields, it is unlikely that differences in decoupling power are the cause of these line width differences at 22.6 MHz. Although the differences in line width are small at the lower frequency they develop into significant differences at the higher one. These differences could be caused by inadequacies in the distribution function or from nonmotional factors such as field inhomogeneity, or macroscopical bulk susceptibility differences in the irregularly configured sample arising from the presence of D_2O or possibly small air bubbles. The contributions of these latter factors depend linearly on field strength and would be three times more pronounced at the higher field.[22,23] Thus the form of the distribution function and the specific parameters which describe the completely amorphous polymer at 40 °C and 22.6

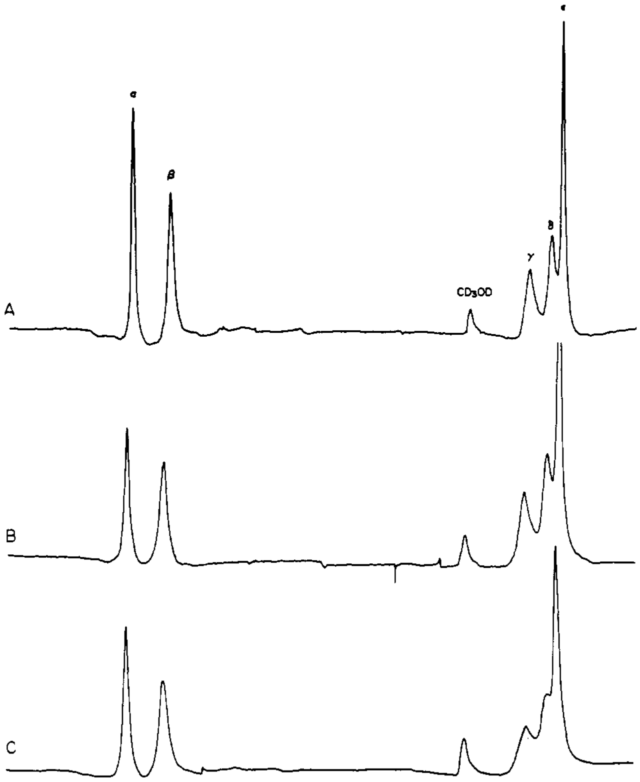


Figure 1. Natural abundance proton decoupled ^{13}C NMR spectra of amorphous and semicrystalline *cis*-polyisoprene at 0 °C. Spectra were accumulated using 15 151 Hz total spectral widths with 4096 (A and C) or 8192 (B) frequency domain points. About 5 Hz broadening due to exponential filtering is present in each case. An 11-kHz region is shown: (A) $1 - \lambda = 0.00$, 50 scans, 9.0 s pulse delay;(B) $1 - \lambda = 0.12$, 256 scans, 5.0 s pulse delay; (C) $1 - \lambda = 0.31$, 250 scans, 9.0 s pulse delay.

Table II
Carbon-13 Spin–Lattice Relaxation Times and Nuclear Overhauser Enhancement Factors for *cis*-Polyisoprene at 0 °C and 67.9 MHz

	Amorphous		Semicrystalline[e]	
Carbon	T_1, ms[a]	NOEF[c]	T_1, ms[a]	NOEF[c]
α	2000	0.1	2400	0.1
β	400	0.3[d]	460	0.3[d]
γ	260[b]	0.3	270[b]	0.4
δ	240[b]	0.3	270[b]	0.4
ε	840[b]	0.8	910[b]	1.2

[a] Estimated accuracy ±10%, except where noted. [b] Estimated accuracy ±15%. [c] Estimated accuracy ±0.2, except where noted. [d] Estimated accuracy ±0.1. [e] Degree of crystallinity equals 0.31.

Table III
Carbon-13 Line Widths[a] (Hz) for *cis*-Polyisoprene at 0 and −10 °C and 67.9 MHz

	Amorphous		Semicrystalline (1) $1 - \lambda = 0.12$	Semicrystalline (2) $1 - \lambda = 0.31$	
Carbon	0 °C	−10 °C	0 °C	0 °C	−10 °C
α	70	90	92	108	290
β	114	205	142	178	500
γ	165[b]		197[b]	248[b]	
δ	124[b]		146[b]	170[b]	
ε	69[c]	85	96[c]	120[c]	250

[a] Estimated accuracy ±4 Hz, except where noted. [b] ±30%, estimated accuracy. [c] ±10%, estimated accuracy.

MHz[1] adequately explains the T_1's and NOEF's at the higher frequency. However, the line widths cannot be explained unless there is some static contribution. The validity of this contribution will require further independent study.

Comparison of Relaxation Parameters in the Completely Amorphous and Semicrystalline States. As we have indicated previously, because the polymer crystallizes very slowly[5,8] there is a temperature range where it is possible to compare parameters of the completely amorphous and semicrystalline polymer at the same temperature. Convenient temperatures at which to carry out these experiments are at 0 and −10 °C. The spectra, at 67.9 MHz, for the completely amorphous polymer and two crystalline samples with degree of crystallinity, $1 - \lambda$, 0.12 and 0.31, respectively, at 0 °C, are given in Figure 1. The T_1's and NOEF's for the amorphous and highest crystallinity samples are given in Table II and the line widths are presented in Table III. Because of the peak overlap in the aliphatic carbon region, particularly for the semicrystalline sample, the T_1's and NOEF's are not as accurate as at the elevated temperature.

We compare first the parameters at 40 and 0 °C in the completely amorphous state. The T_1's for each of the carbons are longer at 0 °C than the comparable value at 40 °C. These results suggest that the "slow solution" for the correlation time, $\bar{\tau}$, is appropriate at 0 °C.[15] Except for C^{ϵ}, all the NOEF's in the amorphous state are reduced relative to their value at 40 °C. This result is consistent with the expected reduction in the backbone mobility at the lower temperature. The fact that the NOEF of the C^{ϵ} does not decrease with temperature can be attributed to the additional motional freedom of the methyl group. The rapid methyl group rotation very often has a lower activation energy relative to other rotational processes.[24] The NOEF of the C^{α} at 0 °C is still less then that of the other backbone carbons and appears to be reduced in approximately the same proportion.

We have analyzed the relaxation parameters for the completely amorphous polymer at 0 °C in terms of the distribution of correlation times given by Schaefer.[14,17] Considering the average values for the β, γ, and δ carbons, the three relaxation parameters can be fitted by a p value $\simeq 30$ and a $\bar{\tau} = 3.2 \times 10^{-8}$ s. The observed values are $NT_1 = 467$ s, NOEF = 0.3, and line width = 134 Hz. The corresponding calculated values are 467, 0.2, and 125, respectively. Thus, not only does the average segmental mobility decrease by two orders of magnitude in the amorphous state at the lower temperature, but the distribution of correlation times is substantially narrowed in comparison with the results at 40 °C. This result is surprising, if the analysis is taken literally, since one would expect that the increased freedom introduced into the polymer backbone with increasing temperature would result in a narrower distribution of correlation times,[14] as well as a smaller $\bar{\tau}$. With increasing temperature cooperative interactions among successive units would presumably be decreased. However, it would appear that the different types of segmental motion, particularly the extremes, are attenuated at different rates with temperature because of differing activation energies. Hence the shape of the distribution function will be changing with temperature.

The data in Table II allow for a comparison of the T_1's and NOEF's for the completely amorphous sample and the one which is 31% crystalline at 0 °C. Within the experimental error, both parameters are essentially the same in both states for each carbon. Thus, the levels of crystallinity that have been achieved here do not effect the relatively fast motions in the remaining amorphous region that are reflected in the T_1's and

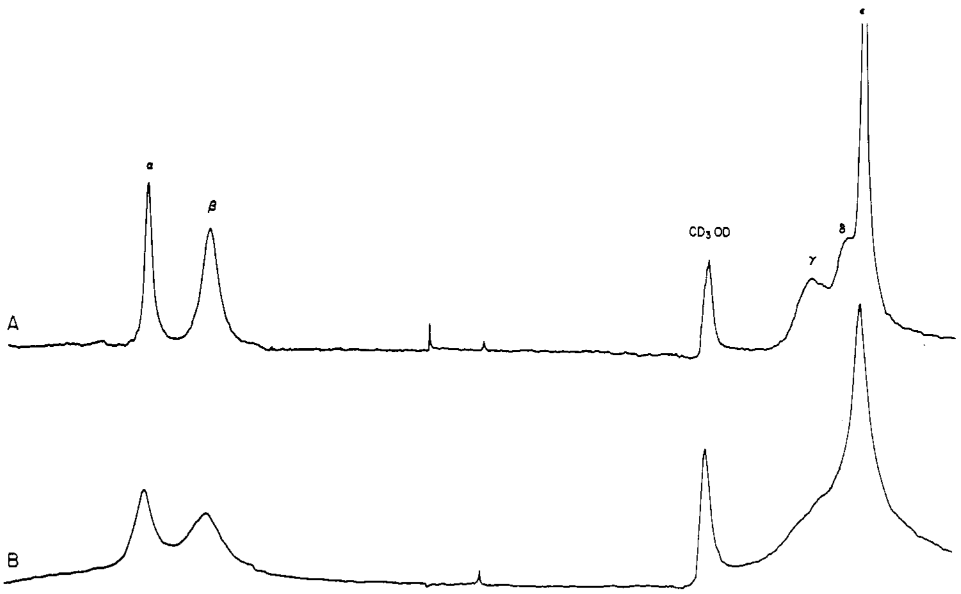


Figure 2. ^{13}C-NMR spectra of amorphous and semicrystalline *cis*-polyisoprene at −10 °C. Total spectral widths of 10 kHz (4096 frequency domain points) were used. Pulse delay = 2.5 s. About 5 Hz broadening is present due to exponential filtering: (A) $1 - \lambda = 0.00$, 512 scans; (B) $1 - \lambda = 0.31$, 2048 scans.

NOEF's. We reemphasize that for *cis*-polyisoprene the comparison is made between the completely amorphous and semicrystalline polymer. It has been found[25] for linear polyethylene at 45 °C, where $1 - \lambda$ has been varied from 51 to 94%, that T_1 was also constant with level of crystallinity. However, for this polymer the NOEF's varied. For $1 - \lambda = 0.51$, the full NOEF of 2 was observed, while, at the very high levels of crystallinity, reduced values were found. If we consider the results for both polymers, whose level of crystallinity has been varied, the generalization can be made that the T_1's are invariant over the complete crystallization range. However, this generalization does not appear to hold for the NOEF's. The NOEF's observed for the backbone carbons of *cis*-polyisoprene at 0 °C in the completely amorphous state are near the theoretical lower limit. Thus, they would only be affected slightly by any changes in the width of the distribution of correlation time function[14] that might be caused by crystallinity and hence would be insensitive to changes in level of crystallinity. On the other hand, the maximum NOEF is observed for polyethylene at the lowest level of crystallinity that has been studied with this polymer. NOEF's in this range are more sensitive to changes in the width of the distribution function and thus indirectly to the level of crystallinity.

In contrast to the T_1's and NOEF's, the line widths of the polyisoprene change with the level of crystallinity. We note first the 2–4-fold increase in line width (depending on the carbon) in the amorphous state at 0 °C relative to the comparable state at 40 °C. There is further increase in the line width for the supercooled amorphous polymer at −10 °C. The spectra obtained for the amorphous polymer and one with $1 - \lambda = 0.31$ at −10 °C are given in Figure 2. As the level of crystallinity increases at either of these temperatures, there is a significant monotonic increase in line width which can be observed even at the lowest level of crystallinity at 0 °C. Line broadening of about the same order of magnitude has been reported for carbon black filled *cis*-polyisoprene relative to the unfilled polymer.[1] The addition of carbon black filler to *cis*-polyisoprene has little effet on T_1 or the NOEF but shortens the methine carbon T_2 by a factor of about 5–10. The same form of the distribution function was used to quantitatively describe these parameters. The value of $\bar{\tau}$ was the same as for the unfilled polymer but the value of p was lowered from 14 to 10.[14]

The relaxation parameters at 40 °C and 22.6 MHz of the partially crystalline (40%) *trans*-polyisoprene have also been reported.[1] Each of the parameters was found to be greater than the corresponding value for the completely amorphous *cis*-polyisoprene. Unfortunately comparison could not easily be made with the completely amorphous *trans*-polyisoprene. Thus, one could not decide what proportion of the increased line width is due to crystallinity and what to the different chemical repeating unit. We have attempted to fit data for the crystalline *trans*-polyisoprene to the form of the distribution function given by Schaefer. We have not, however, been able to fit all of the relaxation parameters. The best fit could be obtained with $p = 20$ and $\bar{\tau} = 1.4 \times 10^{-10}$ s. This $\bar{\tau}$ value is very similar to that for amorphous *cis*-polyisoprene under the same conditions. Using these two parameters, there is very good agreement between the observed and calculated NT_1's and NOEF's. However, the observed line width is 20 times greater than that for the calculated value.

The changes in the parameters upon crystallization for *cis*-polyisoprene reported here are very similar to those observed on adding filler to the amorphous polymer.[1,14] The T_1's and NOEF's are essentially unchanged but the line widths broaden with increasing level of crystallinity. A formal analysis, similar to that given to the filled polymer,[1,14] can also be made. It is not possible to simultaneously explain the T_1, NOEF, and T_2 of the semicrystalline polymer by increasing $\bar{\tau}$, with p remaining constant. For the semicrystalline polymer, the average NT_1 increases from 467 to 513 ms, which is within the experimental error, while the NOEF remains essentially constant. If the distribution is broadened, with p being reduced from 30 to 20, and $\bar{\tau}$ is kept constant, the calculated line width is 245 Hz as compared with the value of 198 Hz. Obviously, changes in the parameters in the log χ^2 distribution function can only serve as a guide to what occurs to the segmental motion at the molecular level. This function should only be applicable when the long correlation times in the tail of the distribution are not in the rigid lattice region. Therefore, it has been successfully applied to completely amorphous polymers well above T_g and to polymers in relatively concentrated solutions.[17] The above conditions would not, however, be necessarily fulfilled for semicrystalline or highly filled systems.

The results for the semicrystalline *cis*-polyisoprene can be interpreted in a manner similar to that given by Schaefer for filled natural rubber.[14] In the present case crystallinity retards complete segmental motional narrowing. The residual dipolar interactions are associated with the longer correlation times. Thus the larger correlation time tail of the distribution function would be effected by crystallization, increasing $\bar{\tau}$ and the breadth of the distribution. Crystallinity has little effect on both the T_1's and the NOEF's of *cis*-polyisoprene, thus indicating that the high-frequency motions are not changed. However, for this polymer, the NOEF's are at or very close to their minimal theoretical value. Hence they are very insensitive to changes in p and to small changes in $\bar{\tau}$.

Temperature Dependence of Amorphous Line Widths. We have also studied the temperature dependence of ^{13}C spectra of the supercooled totally amorphous *cis*-polyisoprene. The main purpose was to determine the lowest temperature at which a useable spectrum could be obtained and to compare it with the glass temperature and with other polymer systems. The glass temperature of *cis*-polyisoprene is −70 °C. No "high-resolution" spectra could be obtained at temperatures less than about 40 °C above this temperature. However, to resolve all the resonances a further increase of about 20 °C is required. For polyisobutylene which has the same glass temperature as *cis*-polyisoprene, the temperature has to be increased an additional 20–30 °C to obtain comparably resolved spectra.[2] The temperature differences that are required may seem surprising since the glass temperatures are the same for the two polymers. However, at 40 °C there are two orders of magnitude difference in the backbone segmental mobility between the two polymers.[1,2] Further investigations are in order to relate the segmental mobility, its temperature dependence, and the glass temperature of different polymers. There is apparently no simple relation between different systems except for the general statement that the glass temperature serves as a lower limit for resolvable spectra.

In summary, we have shown that the frequency dependence of the ^{13}C spin-relaxation parameters of completely amorphous *cis*-polyisoprene at 40 °C confirms the previous analysis in terms of a distribution of correlation times for T_1 and NOEF.[14] The T_1's and NOEF's of each of the carbons are the same in both the amorphous and partially crystalline state. However, with increasing crystallinity at a fixed temperature the line widths increase significantly. Segmental motions associated with the longer correlation times are enhanced and the distribution function describing the amorphous polymer must be modified.

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