

## Measurement of Crystallization in Stretched Rubber by Rapid-Passage NMR

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### Synopsis

Continuous-wave rapid-passage proton NMR (30 MHz) was performed on lightly crosslinked natural *cis*-polyisoprene at elongations up to 720%, at temperatures between  $-100^{\circ}$  and  $100^{\circ}\text{C}$ , and after delays of up to several weeks after stretch. A method of separating the spectra into a narrow and a wide component was developed and applied. The results are interpreted in terms of the effects of a glass transition and strain-induced crystallinity and are in general agreement with results by other methods. The degree of crystallinity is found to increase strongly with strain (from zero for unstretched samples to 31% at elongations of 720% at room temperature), to increase with time, reaching equilibrium most rapidly in the most highly strained samples, and to decrease approximately linearly with temperature above about  $20^{\circ}\text{C}$ .

### INTRODUCTION

Absolute measurements of crystallinity are a matter of considerable interest in the study of polymers and, more particularly, rubbers.<sup>1,2</sup> Nuclear magnetic resonance (NMR), usually of the protons, has for some time been used in the study of polymers, including phase transitions and crystallinity determinations.<sup>3,4,5,6</sup> (Reference 3 contains comprehensive references on this subject to about 1968.)

The utility of NMR for crystallinity determinations depends on the fact that in an immobile structure, the magnetic field contributions from neighboring nuclei are not identical at the locations of all the nuclei whose resonance is under observation; while in a liquid or other mobile structures when molecular degrees of freedom are rapidly and randomly activated, these field contributions average toward zero on the pertinent time scale, the nuclear spin-spin relaxation time  $T_2$  in the rigid lattice (about  $10^{-5}$  sec). Thus, the wide components of the proton NMR in rubber will be due to relatively immobile crystalline and glassy phases, possibly accentuated by crosslinking, while the narrow components will arise from amorphous phases above the glass transition as well as unconstrained methyl groups, and even crystalline phases at temperatures sufficiently high to produce rapid molecular chain motion.<sup>3,4,6</sup> It has been shown<sup>3,5,7,8,9</sup> that in a two-component system, the relative NMR intensity of each (e.g., wide and narrow) line is identical to the relative amount of resonant nuclei in each phase. This proportionality is difficult to exploit conveniently using magnetic field (or frequency) modulation in continuous-wave wide-line slow-passage NMR, both

because of the finite modulation amplitude and the emphasis in the spectral derivative on the narrow features of the spectrum. These effects are most pronounced in the case of separating a narrow from a much wider component, of interest here.

Conversely, observation of the free-induction decay, while rapidly performed, makes substantial demands on the receiver recovery time if the wide-line intensity is to be reliably determined.<sup>10</sup>

One purpose of this paper is to demonstrate a relatively convenient method of measuring the wide-line fraction of such a resonance using a conventional wide-line c.w. NMR spectrometer whose audio phase-sensitive detector is replaced by a digital time averager with an integrating facility and whose audio modulation unit is used to produce a field scan encompassing the entire resonance. This configuration yields a signal-enhanced recording of the customary oscilloscope display of the resonance absorption without the distortion from finite modulation amplitude.<sup>8,11</sup>

The second purpose is to apply this technique to study the crystallinity in stretched rubber as function of strain, time, and temperature. Since the subject has been explored by other techniques<sup>1</sup> but a comprehensive NMR study has not to our knowledge been reported, this application may serve to contribute another viewpoint of strain-induced crystallinity. Hirst and Chen<sup>10</sup> have only recently dispelled earlier impressions<sup>3,12</sup> that in partially crystalline samples of natural rubber, no two-component spectra can be observed. Preliminary accounts of this work have been presented.<sup>13</sup>

## EXPERIMENTAL

### NMR

A Mid-Continent wide-line NMR spectrometer was used with a crossed-coil probe at 30 MHz in the absorption mode. The audio output of the receiver was stored in the memory of a Nicolet 1072 (9 bit ADC) instrument computer as function of a sweep field displacement. The sweep was scanned at 20 Hz with a total excursion of typically near 40 gauss; only the increasing half of the field sweep cycle was acquired. Typical accumulation runs of 1024 cycles were followed by subtractions of an equal number of passes without the sample to eliminate small spurious proton resonances from the probe assembly. The results and their integrals were recorded (see Fig. 1). Spectral integration is performed digitally by the Nicolet 1072 and is invoked after zero adjustment of the background wings.

### Samples

Two series of samples were prepared from strips (about 7 in. by  $\frac{1}{8}$  in. by  $\frac{1}{32}$  in., weighing ca. 0.5 g) of lightly crosslinked high *cis*-1,4-polyisoprene; infrared spectra showed no extraneous lines in the cured compound. Batch A (12 samples) came from stock ca. four years old and showed slight degradation, while batch B (15 samples) was freshly obtained from a single preparation. Each specimen was extended to the desired elongation using weights; the degree of extension was uniform to within  $\pm 5\%$  along the length of each sample. The elongations given are the end-to-end lengths referred to the values prior to each

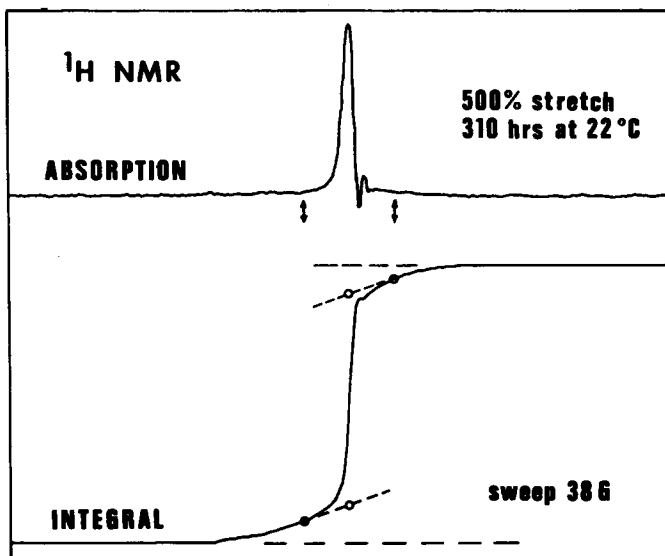


Fig. 1. Rapid-passage proton NMR in stretched rubber at room temperature, accumulated in 50 sec. The wide-line component (fractional intensity  $0.16 \pm 0.03$ ) is more evident in the integral. The total field sweep excursion was 38 gauss. The dashed lines are used in separating the components.

specimen's first significant stretch experience. Each strip was then wound, at room temperature under constant load, on a 7-mm O.D. Pyrex capillary tube, in the form of a layered coil 1 cm in length. This region was later coaxially centered in the NMR receiver coil; the NMR spectrum thus represents a cylindrical average of stretch direction with respect to the static field  $H_0$  and the rf field  $H_1$ .

In the variable-temperature studies, a Varian Model V4540 temperature controller was used. The samples were cooled within a few minutes from  $0^\circ\text{C}$  to  $-100^\circ\text{C}$ . NMR runs were then performed at  $10^\circ\text{C}$  increments up to  $+100^\circ\text{C}$ ; each temperature step was maintained for about 35 min.

### Method

Only the simpler separation of the NMR spectrum into one wide and one narrow component was considered essential; a direct separation of the wide part into crystalline and glassy components at low temperatures was prevented by a lack of discernible features in the spectrum. Figure 1 shows a typical spectrum and its integral.

The method of decomposition is schematized in Figure 2. First, two points equidistant from the center of the narrow line and encompassing most of it are selected; their distance (4.1 gauss) is identically adhered to in all NMR runs, even when only a wide or a narrow component is evident. The separation is most conveniently performed in the spectral integral. Tangents are drawn to the integral at the above markers, and the distance between their intersections with a vertical line drawn through the peak is measured as  $N$ , the total intensity being  $T$ . The fraction of the protons accounting for the wide line, to a first approximation, is now  $X'' = 1 - N/T$ .

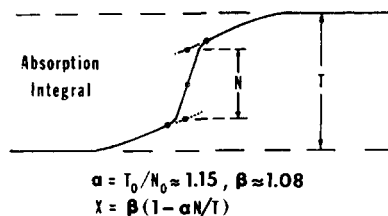


Fig. 2. Schematic representation of an absorption integral of a two-component NMR spectrum, indicating the strategy used in separating the components (see text). The values of  $\alpha$  and  $\beta$  apply to the present experiment only.

This estimate is now improved in two ways. Firstly, the presence of some wing intensity of the narrow line outside the markers causes  $X''$  not to be zero even in the absence of a wide component. Analyzing the room-temperature spectra of unstretched bands (subscript zero), after annealing at 100°C for several hours to remove any trace of crystallinity,<sup>1</sup> yields the correction factor  $\alpha = T_0/N_0$ . However, the value of  $X' = 1 - \alpha N/T$  cannot reach unity even in the presence of only a wide component, since the drawing of the straight tangents implies the unreasonable assumption that the broad component is flat-topped between the markers. This effect is eliminated by multiplying the present best estimate of the wide component,  $X'$ , by a factor causing it to be unity for spectra at the lowest temperatures consisting only of wide components. The best determination of the wide-line fraction is thus

$$X = \beta(1 - \alpha N/T) \quad (1)$$

where, throughout our experiment,  $\alpha = 1.15, \beta = 1.08$ . It is understood that  $\alpha$  and  $\beta$  will depend on the choice of the marker points and will most closely approach unity for cases where the ratio of component widths is largest, deferring the need for reference spectra containing only one component. Irrespective of the marker point locations, however, this method of decomposition is theoretically exact whenever the wide and narrow line shape components each have unvarying fractions of their intensity outside the marker points. This condition is easily satisfied when both components of a composite line shape change only in relative amplitude, but not shape. A more detailed study of the accuracy of this method is the subject of a separate article.<sup>14</sup>

A number of tests were performed to optimize the operation of the method. First, it was found that the results for the wide-line fraction  $X$  were unaffected by field inhomogeneities introduced by displacing the NMR probe a few centimeters from the center of the magnet. At the optimum position, the inhomogeneity of our magnet near 7 KG is somewhat less than 0.3 G over the sample volume; the height reduction of the narrow component due to its field inhomogeneity broadening was actually helpful by reducing the dynamic range in the spectral digitization.

When the rf field  $H_1$  was raised to the spectrometer's maximum, the values of the wide-line fractions increased by some 20% over their measurements at low  $H_1$ , showing that the narrow component saturates at lower  $H_1$  than the wide line.<sup>15</sup> As a precaution against possible temperature or strain dependences of the saturation, the rf current used in the experiment was one twentieth of the value at which  $X$  was first observed to rise with  $H_1$ .

The field sweep frequency chosen, 20 Hz, was well below the value (80 Hz) where the receiver audio output time constant produced line broadening in excess of the effects of field inhomogeneity. The sweep amplitude (30–40 G between extrema) was chosen to establish reliable baselines beyond the wide spectral component.

Finally, the pulsed NMR determination of the crystallinity in a stark rubber specimen<sup>10</sup> ( $40 \pm 4\%$ ) was reproduced by the present method ( $37 \pm 3\%$ ), while in a recently reheated sample of the same material we find  $X \leq 2\%$ .

The experimental accuracy of the method was estimated statistically from repeated identical measurements. Once  $\alpha$  and  $\beta$  were known, the wide-line fraction  $X$  under our conditions, in one 100-sec accumulation, could typically be determined within  $\pm 0.05$  for  $0.15 \leq X \leq 0.8$ ; at lower  $X$ , the precision increases slightly ( $\pm 0.03$ ). The most important limit to the reproducibility of  $X$  was small admixtures of the dispersion phase in the recorded traces. Improvements in efficiency can be obtained if it is possible to increase the rf power or omit the background signal subtraction after accumulation, or by using a sawtooth field sweep to save most retrace time.

## RESULTS AND DISCUSSION

Figure 3 shows the temperature dependence of  $X$ , the wide (rigid lattice) fraction of the proton NMR in four samples of batch B; samples having other values of elongation in all cases yield data intermediate between these and monotonic in extension. Two unstretched samples did not differ greatly from the 50% extended specimen.

At the lowest temperatures, the amorphous portion of the rubber is known to be in a glassy state, while the high-temperature ( $T \geq 10^\circ\text{C}$ ) wide-line fraction is attributed essentially to crystallinity only. Our results indicate that for stretched rubber, there is no well-defined crystalline melting point  $T_m$ ; that the crystalline fraction increases sharply with extension; and that at constant elongation, it decreases nearly linearly with temperature above about  $20^\circ\text{C}$ .

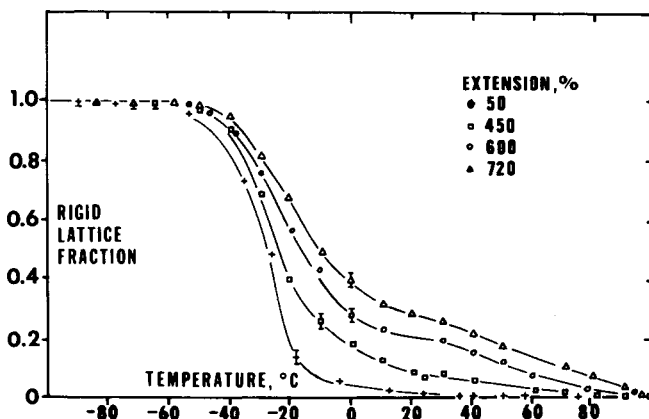


Fig. 3. Temperature dependence of the wide-line fraction ( $X$ , see text) for four stretched rubber specimens. Between  $-50^\circ\text{C}$  and  $0^\circ\text{C}$ , where motional narrowing of the amorphous phase resonance occurs, our definition of rigid lattice fraction has only qualitative significance.

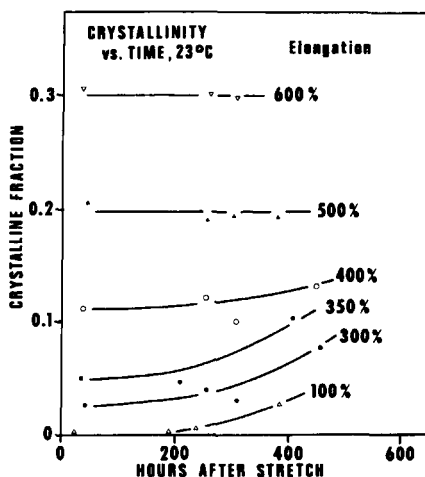


Fig. 4. Crystallization kinetics of six samples of Batch A, showing a large increase with strain in the rate of approach to equilibrium.

These results are in good agreement with reported findings<sup>16</sup> using other methods. Some distributive effect on  $T_m$  may be produced by the hydrostatic pressure on successive layers of the sample coil, reaching several tens of atmospheres on the inner layers of the most highly stretched samples.

Considering the time scale on which the temperature changes were performed (see above) in relation to the kinetics of crystallization,<sup>1</sup> no substantial change in crystallinity will have occurred during cooling from about  $-5^{\circ}\text{C}$  to  $-100^{\circ}\text{C}$  and the subsequent warmup to about  $-40^{\circ}\text{C}$  during the data runs. While it is known<sup>1</sup> that the crystallinity in natural rubber approaches its equilibrium most rapidly (within several hours) near  $-25^{\circ}\text{C}$ , the changes in our wide-line ratios as temperature was increased through this region seem rather to be dominated

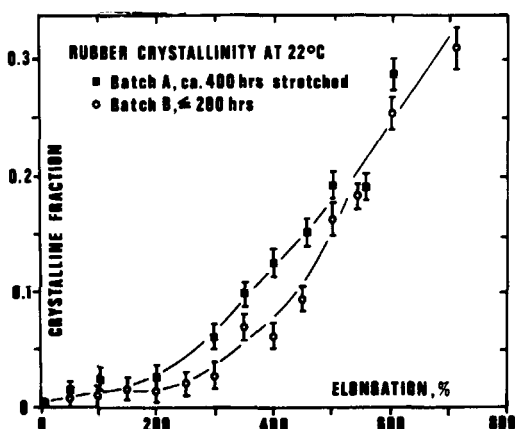


Fig. 5. Room-temperature crystallinity as function of elongation. Equilibrium crystallinity has not been reached for samples of less than 500% elongation. The nonzero values found between 50% and 200% elongation may instead be caused by subtle changes in the shape of the narrow component.

by the activation of molecular motion in the previously glassy amorphous regions. Our crude definition of the wide-line ratio cannot reflect the line shape changes and is to be regarded over this region only as a qualitative indicator of a glass transition at a much lower temperature. If crystallinity changes between  $-40^{\circ}\text{C}$  and  $0^{\circ}\text{C}$  are for the moment regarded as small over our short time scale, the motional narrowing temperature may be arbitrarily defined as the point at which  $X$  decreases from unity halfway to its value at about  $-5^{\circ}\text{C}$ . For each of the 13 samples and two unstretched samples of batch B, this temperature was found to be in the range of  $-26^{\circ} \pm 3^{\circ}\text{C}$ , so that no effect of extension on the glass transition could be deduced. The difference of about  $50^{\circ}\text{C}$  between this narrowing temperature and the glass transition temperature  $T_g$  is in accord with the theory of Williams, Landel, and Ferry,<sup>17</sup> given the effective measurement frequency of NMR experiments of about  $T_2^{-1}(\text{rigid lattice}) \approx 10^5 \text{ hz}$ .

Figure 4 shows the room-temperature wide-line fraction (i.e., crystallinity) for samples of batch A as function of time after extension. As first observed by Treloar<sup>18</sup> in birefringence studies, crystallization of rubber proceeds on time scales differing greatly with extension: while the 600% specimen had already reached the top of the Avrami curve<sup>19,2</sup> before the first observation, significant crystallinity was just emerging in the 100% sample after ten days at room temperature. The equilibrium crystallinity for samples of small extension is expected to be smaller than that of highly stretched samples.<sup>2,18</sup>

Figure 5 shows the room-temperature crystallinity for both sample batches as function of elongation, demonstrating a crystallinity of about 31% just below the breaking point and an absence of crystallinity in the unstretched samples. A small but probably nonzero wide-line fraction seems to be detected below 200% elongation. Rather than representing crystallinity, this may simply be due to small changes in the shape of the narrow (amorphous) component upon stretching; changes in the amorphous free induction decay and its  $T_2$  have recently been observed at 50% elongation and above by Hirst (unpublished). The two batches seem to follow slightly different strain dependences, but a comparison with Figure 4 suggests that most of the difference in the 150% to 450% region may be related to the different elapsed time since stretching in each batch, although the evident moderate degradation in batch A may have played a role. A similar effect would be expected if the two batches differed significantly in their degree of crosslinking. The general elongation dependence observed corresponds closely to Goppel's results of absolute x-ray measurements in vulcanized rubber.<sup>20</sup>

Our interpretation has omitted reference to the role of entanglements and crosslinks on the magnitude of the wide fraction. From the absence of a wide component above about  $10^{\circ}\text{C}$  in the unstretched samples, and from its disappearance in all samples by  $100^{\circ}\text{C}$ , we conclude that these mechanisms contribute insignificantly. It is also possible that, for some degrees of freedom, molecular motion in the crystalline phase itself may be rapid enough<sup>6,21</sup> to cause motional narrowing and invite attribution of such resonance to the amorphous phase. However, since our approach separates the wide line from a component of full width at a half-height of less than a gauss, any partial narrowing possible in a crystal will be incompletely encompassed within the narrow component. Thus, the complete disappearance of the wide component in all samples by  $100^{\circ}\text{C}$  also suggests that the crystallinity in all samples had vanished at or below  $100^{\circ}\text{C}$ .

## SUMMARY AND CONCLUSIONS

We have described a convenient wide-line NMR method of measuring the fraction of protons (or other nuclei) in rubbery polymers which do not undergo molecular motion on a time scale more rapid than about  $10^{-5}$  sec. The decomposition of the spectrum typically yields these fractions  $X$  within  $\Delta X \simeq 0.05$  (rather less below  $X \simeq 0.15$ ) using an accumulation time of 100 sec after a background subtraction of equal duration. As with NMR generally, these determinations are absolute; in addition, the method is nearly self-calibrating in that reference samples are used solely to provide the correction factors aiding in the intensity assignment. Once these factors are determined, a single crystallinity measurement, including all interpretation, can be completed in about 8 min. As applied to rubber under stress, the method gives results in agreement with, and extending, results obtained from dilatometric,<sup>2,18</sup> birefringence,<sup>18</sup> and x-ray<sup>16,20</sup> measurements.

The application of pulsed NMR to studies of this kind<sup>10</sup> requires a rapid ( $\leq 3$   $\mu$ s) receiver recovery time in order to observe the free induction decay of the wide component; our presently somewhat greater dead time permits only marginal identification of it. In addition to working toward a reduction of the receiver dead time, we are presently exploring several pulse programs in an effort to undertake complementary pulse measurements. Considerable interest attaches to the crystallization kinetics of rubber under strain. For natural rubber, the temperature of maximum crystallization rate ( $\sim -25^\circ\text{C}$ ) coincides with the glassy motional narrowing temperature in NMR experiments. Even if the amorphous narrowing and the crystalline component cannot be directly separated, any time-dependent changes of the crudely defined wide-line fraction can be attributed to crystallization kinetics. Such a study is presently being undertaken.

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## References

1. L. R. G. Treloar, *The Physics of Rubber Elasticity*, 2nd ed., Oxford University Press, London, 1958, 1967, Chap. 11; L. Mandelkern, *Crystallization of Polymers*, McGraw-Hill, New York, 1964.
2. A. N. Gent, *Trans. Faraday Soc.*, **50**, 321 (1954); *Trans. Inst. Rubber Ind.*, **30**, 139 and 144 (1954).
3. I. Ya. Slonim and A. N. Liubimov, *The NMR of Polymers* (English translation), Plenum Press, New York, 1970, mainly Chap. III.
4. V. J. McBrierty, *Polymer*, **15**, 503 (1974).
5. C. W. Wilson and G. E. Pake, *J. Polym. Sci.*, **10**, 503 (1953); *Phys. Rev.*, **89**, 896 (1953).
6. W. P. Slichter and D. W. McCall, *J. Polym. Sci.*, **25**, 230 (1957).
7. C. W. Wilson and G. E. Pake, *J. Chem. Phys.*, **27**, 115 (1957).
8. A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University Press, London, 1961.
9. R. A. Pittman and V. W. Tripp, *J. Polym. Sci.*, **8**, 969 (1970).



10. R. C. Hirst and H. Y. Chen, *Rubber Chem. Technol.*, **46**, 22 (1973).
11. E. R. Andrew, *Nuclear Magnetic Resonance*, Cambridge University Press, Cambridge, 1955.
12. K. Oshima and H. Kusumoto, *J. Chem. Phys.*, **24**, 913 (1956).
13. E. von Meerwall, et al., *Bull. Amer. Phys. Soc. II*, **20/7**, 888 (1975); E. diCato et al., *Bull. Amer. Phys. Soc. II*, **21/2**, 150 (1976).
14. R. B. Creel, E. diCato, and E. von Meerwall, *J. Mag. Res.*, **23**, 321 (1976).
15. I. Ya. Slonim and A. N. Liubimov, *The NMR of Polymers* (English translation), Plenum Press, New York, 1970, p. 169.
16. J. E. Field, *J. Appl. Phys.*, **12**, 23 (1941).
17. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701 (1955).
18. L. R. G. Treloar, *Trans. Faraday Soc.*, **36**, 538 (1940).
19. M. Avrami, *J. Chem. Phys.*, **7**, 1103 (1939); *ibid.*, **8**, 212 (1940); *ibid.*, **9**, 117 (1941).
20. J. M. Goppel, *Appl. Sci. Res.*, **A1**, 3 and 18 (1949).
21. N. Fuschillo et al., *J. Polym. Sci.*, **25**, 381 (1957).

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