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Nuclear Magnetic Resonance Spectra of Polyethylene*

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A quantitative study of some structural irregularities of polyethylenes by an improved proton magnetic resonance method is reported. The background noise of a nuclear magnetic resonance spectrometer can be remarkably eliminated with the aid of the Mnemotron Computer of Average Transients. The total numbers of methyl groups in polyethylenes were estimated by this method using 5% solutions of the polymer in tetrachloroethylene. Spectra were obtained at about 110°C in order to suppress the thermal degradation of the polymer. The results agree well with those estimated by an infrared compensating method. Information about the species of branches and, in some cases, the number-average molecular weight of the polymer can be obtained by examining the resonance shape of methyl groups. The chemical shift difference between the triplet due to ethyl branches and that due to the other longer branches was found to be less than 0.05 p.p.m. This method can also be applied to the detection of unsaturations in polyethylene. In this case, however, the signal-to-noise ratio has to be increased to a factor of at least 20. Thus, the purification of the solvent is very important in the experiment.

It is well known that the various solid state properties of polyethylene (PE) are strongly affected by the degree of chain branching. Therefore, many papers1-6) have been published on the determination of the number of methyl groups in PE. Most of them were based on the measurements of the infrared absorption (IR) at 1378 cm^{-1}. Of course, the lengths of the branches as well as

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1) J. J. Fox and A. E. Martin, *Proc. Roy. Soc.*, **A175**, 208 (1940).

2) A. Elliott, E. J. Ambrose and R. B. Temple, *J. Chem. Phys.*, **16**, 877 (1948).

3) L. H. Cross, R. B. Richard and H. A. Willis, *Discussions Faraday Soc.*, No. 9, 235 (1950).

4) F. M. Rugg, J. J. Smith and L. H. Waterman, *J. Polymer Sci.*, **11**, 1 (1953).

5) F. P. Redding and C. M. Lovell, ibid., **21**, 157 (1956).

6) A. H. Willbourn, ibid., **34**, 569 (1959).

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their numbers will be very important in characterizing this polymer.

Recently, an infrared absorption method, a double-beam compensation method,6) has proved to be very effective in the quantitative analysis of chain branching in PE. However, in making an "absolute" measurement of the methyl group content, the IR method appears to present a serious complication because a series of samples containing known different numbers of branches are necessary for the calibration work.

On the contrary, the "absolute" concentration of methyl groups can be directly determined by the nuclear magnetic resonance (NMR) technique. We have already briefly reported that the degree of chain branching in a commercial low-density PE can be estimated by measuring the relative area of the methyl proton signal.7) Though our results are in fairly good agreement with those obtained by the conventional IR method, the accuracy of the ordinary NMR method is not satisfactory because of some difficulties in applying it to commercial PE. Since the methyl proton signal is very weak and appears at 9.1 τ, near the strong methylene peak at 8.7 τ, an overlap occurs between them. Moreover, there is considerable background noise in some cases. Thus, an accurate evaluation of the methyl concentration is difficult. Fortunately, however, if we use a new accessory like the Mnemotron Computer of Average Transients (CAT), we can obtain an improved signal. By repetitively adding the signal under investigation, the signal-to-noise ratio (S/N) can usually be increased by a factor of the square root of the number of scans. With this technique, the exact evaluation of the methyl concentration will be possible by the NMR method.

The work to be described in the present paper was undertaken in an effort to study some structural irregularities of polyethylenes quantitatively. A preliminary experiment of the same kind was first reported by Porter et al.,8) with respect to low-molecular-weight PE.

Experimental

Most of our works were carried out with an NMR spectrometer, Mullard SL44 Mk. II, at 40 Mc./s., together with a variable temperature probe and the CAT 400B. Each spectrum was obtained at about 110°C in order to suppress the thermal degradation of the polymer.

The samples examined were commercially-available polyethylenes, manufactured by E. I. du Pont de Nemours & Co. (Alathon 5BNC-10), the Allied Chemical Corporation (AC-617), and the Phillips Chemical Company (Marlex 6009), and some laboratory grades made by the Furukawa Chemical Ind. Co. (Staflen E570L) and the Mitsui Petrochemical Ind. Co. (Hizex E, I and K).

All the samples were reprecipitated from a xylene solution into a large amount of methanol; they were then dried in vacuo at about 60°C. Each sample was put into a specimen tube, together with tetrachloroethylene containing 2% tetramethylsilane (TMS). Then the tube was sealed and heated at 130°C for a few minutes in order to dissolve the PE completely. The concentration of the polymer solution suitable for our experiment was found to be 5% (w/w).

The CAT-averaging technique in the methyl resonance region was accomplished by using the TMS peak itself as a reference point from which a sweep of the decreasing magnetic field started. In the other cases, a sideband technique was employed to place the TMS sideband just before the region of interest in the spectrum, and an increasing magnetic field sweep was adopted. In order to complete each analysis as quickly as possible, a sweep rate of about 1.7 milligauss/sec. was chosen. A little slower sweep rate is needed, however, to avoid the relaxation wiggles which distort the line shape. The averaged spectra were read out in analog form onto an ordinary stripchart recorder. In our experiment, each division of 0.25 c. p. s. or less was stored in each memory address of the CAT.

Results and Discussion

Linearity.—The accuracy of the CAT-averaging technique depends upon the linearity of the modulator incorporated in it. This is shown in Fig. 1.

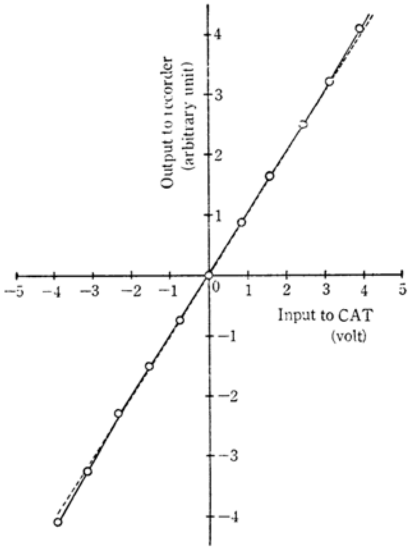

Fig. 1. Modulator linearity.

The linear relationship between the area under the averaged resonance curve and the number of runs is also shown in Fig. 2. If the magnitude of the input signal to the CAT is chosen to be less than ±3 V., and if we take care to avoid the saturation phenomenon, the area under the resultant

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7) Y. Kato and A. Nishioka, Lecture at the Annual Meeting of the Physical Society of Japan, Nagoya, October, 1964.

8) R. S. Porter, S. W. Nicksic and J. F. Johnson, *Anal. Chem.*, **35**, 1948 (1963).

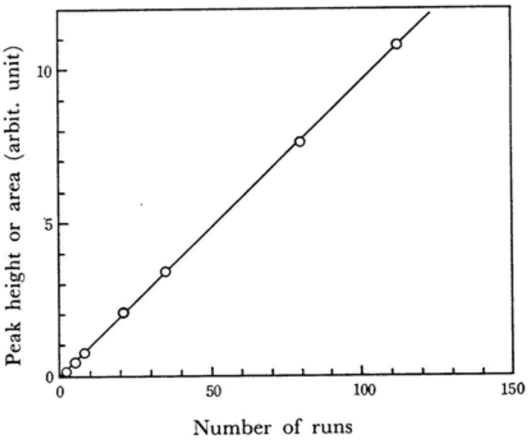

Fig. 2. Linearity check of CAT averaging technique.

peaks can be expected to be closely proportional to the number of protons involved.

Total Number of Branches.—A typical NMR spectrum of low-density PE, Alathon 5BNC-10, obtained in an ordinary way is illustrated in Fig. 3. A small signal of methyl protons can be seen near the very strong peak due to methylene protons. We measured the relative areas of these two peaks separately in order to estimate the number of methyl groups in the various states of this PE, which are treated differently. The results are shown in Table I. Since this sample is a low-density PE, it contains as many as 30 methyl branches for every thousand carbon atoms. As has been mentioned above, however, these results are not as accurate as those obtained by a conventional IR method.

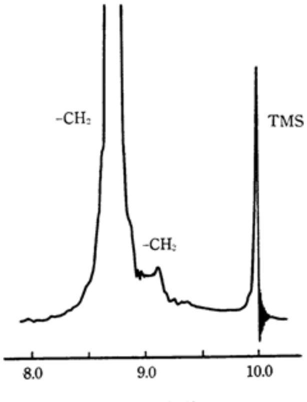

Fig. 3. NMR spectrum of polyethylene (Alathon 5BNC-10, Original pellet).

TABLE I. ESTIMATED NUMBER OF METHYL GROUPS PER 100 CARBON ATOMS IN LOW DENSITY POLYETHYLENE, ALATHON 5BNC-10

Sample	NMR	IR
Original pellet	3.0	—
Reprecipitated sample	2.3	2.8
Lower molecular weight fraction	2.2	—
Higher molecular weight fraction	1.7	—

Figure 4 illustrates the NMR spectrum of PE with CAT. In this case, a slow sweep rate of 25 milligauss per min. was adopted in order to get rid of the relaxation wiggles completely. The lower spectrum b was recorded after 19 runs, while the upper spectrum a was obtained after 30 runs. In practice the a spectrum is equivalent to that recorded after 300 runs except for the S/N, because the magnification of the ordinate is exactly ten times as large as that of the spectrum b.

Two examples of the methyl resonance patterns obtained at 40 Mc./s. are shown in Fig. 5. The methylene peak is not shown in these spectra. The methyl resonance at about 9.1 τ is located in the tail of the methylene peak. With a spectrometer operating at 100 Mc./s., this trouble can be eliminated to a great extent. In this case, however, it should be noticed that a spinning sideband of the TMS signal may appear in this region frequently. Therefore, we have to examine the spectrum very carefully. In the case of a spectrometer operating at 40 Mc./s., we can easily remove the spinning sideband, even to the low field side of the methylene signal, by increasing the rate of spinning. Shoolery[9] obtained the spectra of some *n*-hydrocarbons by a spectrometer operating at 200 Mc./s. with a superconducting electromagnet; they observed a clear-cut separation between the methyl and the methylene resonances.

The total number of runs necessary for the averaging-out of noises depends on the intensity of the signal under investigation. The spectra shown in

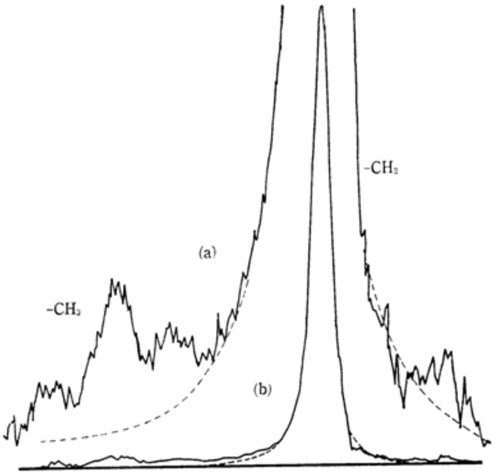

Fig. 4. NMR spectrum of polyethylene with CAT using a slow sweep.

Sample: AC-617, Sweep rate: 25 milligauss/min.

Spectrum	No. of runs	Magnification
(a)	30	×10
(b)	19	× 1

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9) J. N. Shoolery, Paper presented at the International Symposium on NMR, Tokyo, September, 1965.

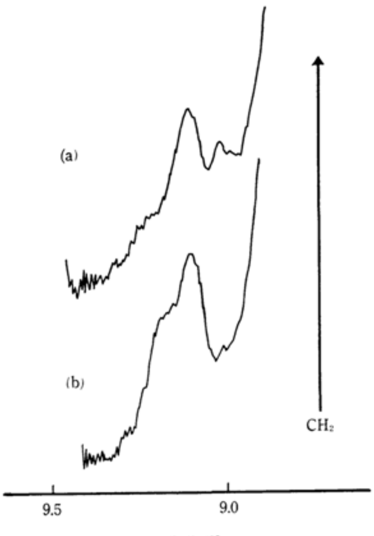

Fig. 5. CH_3 NMR patterns with CAT for polyethylenes.
(a) AC-617 (30 runs), (b) Hizex K (180 runs)

TABLE. II. TOTAL NUMBERS OF BRANCHES IN POLYETHYLENES

Polyethylene	Total numbers of branches per 1000 C atoms			No. of runs	Observed resonance pattern
	IR method	NMR$^{a)}$ method	NMR-CAT method		
AC-617	49	$(4\pm1)\times10$	40 ± 1	70	t
Alathon 5BNC-10	28	$(2\pm1)\times10$	22 ± 1	180	t
Staflen E570L	—	—	14 ± 1	200	d
Hizex-I	4.0	—	3 ± 1	120	d+t (?)
Hizex-E	4.5	—	5 ± 1	60	d
Hizex-K	24	—	20 ± 1	40	d
Marlex 6009	—	—	$<2^{b)}$	400	t

a) NMR Spectrometer in its ordinary operation.
b) The upper limit was determined with the fractionated sample ($M_n=2.0\times10^4$).
t: triplet, d: doublet

Fig. 5 were obtained after 30 and 180 runs. For a linear PE, such as Marlex 6009, it was necessary to scan more than four hundred times; this corresponds to an increase in the S/N by a factor of more than 20. Since exactly the same resonance pattern as that shown in Fig. 5 can easily be obtained by the normal NMR method without CAT when the sample of AC-617 is melted at 130°C, we are confident that this new method can be safely used in estimating the minute concentrations of several types of double bonds, such as terminal vinyl, internal vinylene and vinylidene, in PE.

On the basis of the above-mentioned linearity, we compared the intensities of the two signals including the methyl resonance in a spectrum by taking account of the number of runs. All the results are summarized in Table II. The determination of the total number of branches, i. e. CH_3/1000C, by the double-beam infrared compensating method was carried out by Mr. Kobayashi of our laboratory.

Although the results shown in the second and the fourth columns of Table II agree with each other fairly well, a small discrepancy can still be found between them, mainly in low-density PE. This is perhaps due to a distribution of methyl groups among different species of branches; that is, an ethyl branch may have quite a different absorption coefficient from that of a butyl branch. From this point of view, we would suggest that the total number of branches evaluated by the NMR-CAT method might be the most reliable one at present.

Resonance Patterns of the Methyl Groups.—The methyl proton resonance would be expected to show either a doublet or a triplet, because methyl groups in PE can form either methyl branches, or ends of the main chain and of such branches as ethyl, propyl, butyl and other long-chain branches. This consideration can be easily substantiated by an examination of some model compounds and polymers containing methyl groups such as is shown in

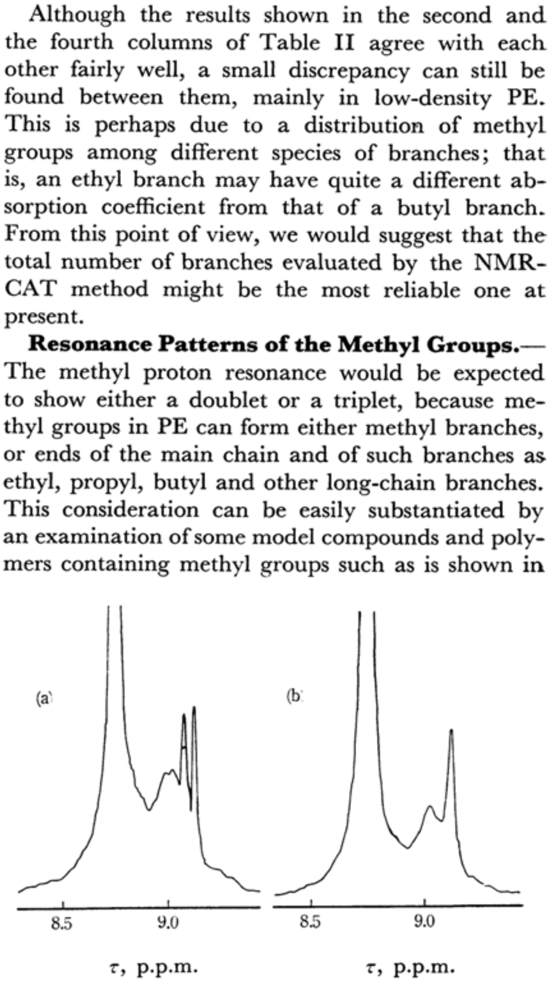

Fig. 6. NMR spectra of (a) 5, 8-diethyl-*n*-dodecane and (b) *n*-hexadecane.

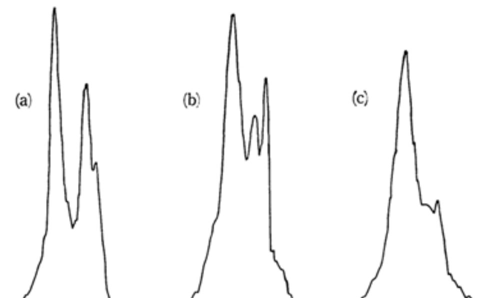

Fig. 7. NMR spectra of (a) ethylene-propylene copolymer, (b) polybutene-1 and (c) polyhexene-1.

Fig. 6. The chemical shifts of methyl protons in these compounds are summarized in Table III. The chemical shift difference between the triplets due to the ethyl branch and those due to other, longer branches is found to be less than 2 c. p. s. at 40 Mc./s. Some kinds of polymers with methyl, ethyl and butyl branches were also examined (see Fig. 7). These results concerning the chemical shifts of the triplets in ethyl, butyl and other longer branches are in accordance with the suggestion that the shape of the triplet seems to be almost independent of the length of chain branches, except for a slight shift.[10] Therefore, it is difficult to discriminate between ethyl and butyl branches by examining the resonance shapes.

TABLE III. CHEMICAL SHIFT (τ) OF METHYL PROTONS IN SOME MODEL COMPOUNDS AND POLYMERS

Compounds and polymers	Types of branches			
	Methyl	Ethyl	Butyl	Longer chain
5, 8-Diethyl-*n*-dodecane	—	9.09	9.13	—
n-Hexadecane	—	—	—	9.12
Ethylene-propylene copolymer	d {9.07 9.17	—	—	—
Poly-butene-1	—	t {9.00 9.12 9.24?	—	—
Poly-hexene-1	—	—	9.11	—

The methyl signal of the AC-617 sample can be recognized as a distorted triplet. However, the intensity ratios of the three peaks are remarkably different from those of a typical triplet, i. e., 1 : 2 : 1. A simple illustration of the theoretical spectrum for the A_3 part of the A_3B_2 spin system is given in Fig. 8, where J and δ represent, respectively, the spin coupling constant and the chemical shift difference between the A and B nuclei. The characteristic feature is that the two outer peaks are much broader than the central one. By assuming a Lorentzian line shape with the half-height line-width of 2 c. p. s., the discrete spectrum can be synthesized into a continuous spectrum, as is shown in the middle pattern. However, the observed spectrum cannot be fully explained by the A_3B_2 spin system. For instance, the downfield peak of the theoretical spectrum seems a little higher than that of the one observed for AC-617. A part of this discrepancy can probably be removed by analyzing a more complicated spin system. The observed patterns of the methyl resonance of various kinds of polyethylenes were identified as being given in the 6th column of Table II.

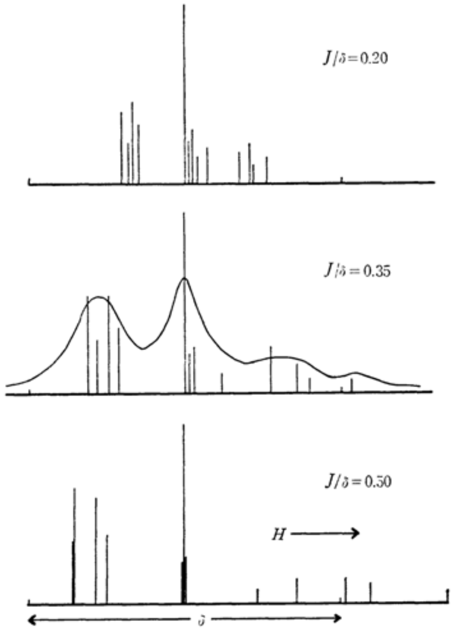

Fig. 8. Theoretical spectra for A_3 part of A_3B_2 spin system.

Figure 9 shows an example of the analysis. The methyl resonance pattern obtained by the NMR-CAT method will give us fruitful information as to the structure of PE. For instance, the spectral pattern of the methyl groups in Staflen E570L, which is a ethylene-propylene copolymer containing a small amount of propylene, appears to be a doublet mixed with a small triplet. This finding is in good accordance with the suggested molecular structure of this copolymer. From the simple graphical treatment illustrated at the bottom right, we find that their areas are in the ratio of about ten to one, where it is assumed that the methyl NMR patterns of AC-617 and Hizex K give a typical triplet and a doublet respectively. If only the terminal methyl groups give rise to the triplet, the number-average molecular weight (M_n) of this polymer is

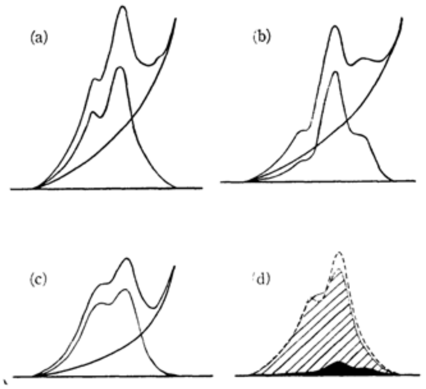

Fig. 9. Line shapes of CH_3 resonance signals of polyethylenes.
(a) Staflen E570L
(b) AC-617, Alathon 5BNC-10
(c) Hizex K and
(d) (Staflen E570L)

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[10] K. W. Bartz and N. F. Chamberlain, *Anal. Chem.*, **36**, 2151 (1964).

about 22000. On the other hand, an osmotic measurement of the M_n for the polymer gave a higher value of 36000. The difference may be explained by the permeation of low-molecular-weight polymers through the osmotic membrane, because it is estimated that the limit of permeation of the membrane is about 11000.

The Determination of Unsaturation.—The problem of determining the degree of bond unsaturation in PE has also been discussed mainly in the field of IR.[3,11-14] We have now also applied the NMR-CAT method to this problem. There are three types of unsaturations in PE, i. e., vinyl, vinylidene, and vinylene. Typical NMR spectra of these groups are shown in Fig. 10, using three kinds of model compounds, that is, hexadecene-1, 2-ethyl-hexene-1 and methyl linolenate, which correspond respectively to the above unsaturation groups.

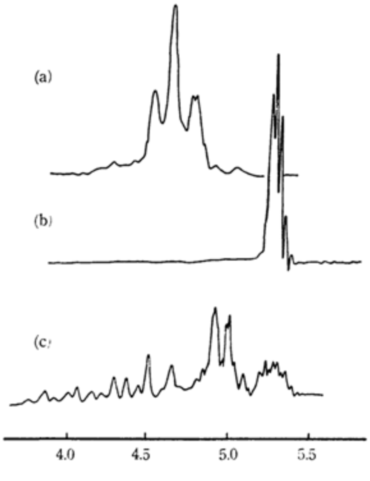

Fig. 10. NMR patterns of unsaturations in (a) methyl linolenate, (b) 2 ethyl-hexene-1 and (c) hexadecene-1.

In Fig. 11 several results obtained by the NMR-CAT method are shown. These three spectra were recorded after 420 runs. The characteristic signals appear between 4.5 and 5.2 in the τ-scale. For instance, the NMR resonance due to vinylene unsaturation can be found at about 4.7 τ; this seems quite reasonable when compared with the chemical shift of vinylene protons in the model compounds. In these experiments the S/N has to be increased to a factor of at least 20. Having done so, the spectrum must be examined vey carefully because a small quantity of impurities in the solvent, or even in TMS, may disturb it. Thus most of the peaks at about 6.5 τ are perhaps due to the impurity in the solvent itself.

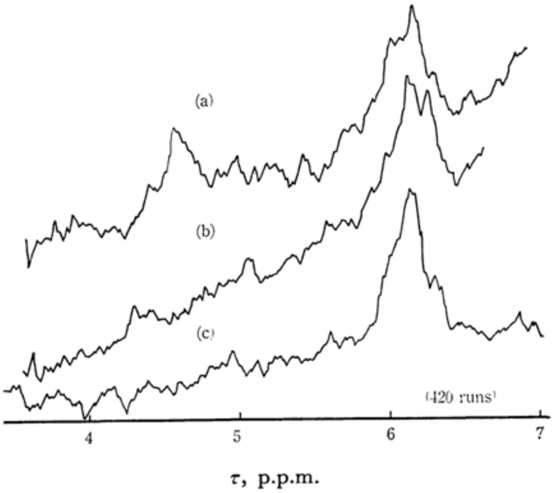

Fig. 11. NMR spectra due to unsaturations in polyethylene.
(a) Staflen E570L, (b) AC-617, (c) Solvent

Summary

In the past decade the number and the length of branches in PE have been estimated mainly by IR methods. We have realized that, with the aid of the CAT, the NMR method is also very useful in studying them. In order to suppress the thermal degradation of the polymer, we obtained the NMR spectrum of PE in solution at about 110°C. In spite of a little uncertainty in our case in separating the NMR signal of methyl protons from that of methylene protons, the total numbers of methyl groups obtained by our NMR-CAT method agree well with those estimated by an infrared compensating method. The small discrepancy between them may be attributed to the IR method's ambiguous treatment of the absorption coefficient for the branch of each length.

From the resonance shape we can obtain information about the species of branches and, in some cases, the molecular weight of PE. With the NMR spectrometer operating at 40 Mc./s., however, the chemical shift difference between the triplet due to ethyl branches and that due to the other longer branches is so small that we cannot discriminate between them.

We have also applied the NMR-CAT method to the detection of the unsaturations in PE.

The authors are indebted to Mr. Kamiya of the Furukawa Chemical Industrial Co., Ltd., for his courtesy in supplying us with the sample of Staflen, to Mr. Kobayashi of our laboratory for his kind permission to quote his results using the IR method, and to Mr. Sekikawa for the osmometry.

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11) J. N. Lomonte, ibid., **34**, 129 (1962).
12) E. C. Cemia, C. Mancini and G. Montando, *Polymer Letters*, **1**, 371 (1963).
13) J. C. Woodbrey and P. Ehrlich, *J. Am. Chem. Soc.*, **85**, 1580 (1963).
14) R. J. de Kock and P. A. H. M. Hol, *Polymer Letters*, **2**, 339 (1964).