The NMR Spectra of Molten Polyethylene

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Quantitative analyses of methyl groups and olefinic double bonds (vinyl, vinylidene, and vinylene) are usually performed by the infrared (IR) absorption method, but it can also be done by the high-resolution nuclear-magnetic-resonance (NMR) method.[1,2] The latter method has the advantage of providing an absolute measurement method if the saturation effect can be neglected. However, the analysis of the double-bond content is more difficult than that of the methyl group because of their small quantity of the order 10^{-4}/carbon atoms. To improve the signal-to-noise ratio, a molten sample was used with the NMR accumulation method at 60 MHz by Ferguson,[2] but the details were not presented.

We have obtained better results on molten polyethylene without any accumulation at 180°C by using a 100 MHz NMR spectrometer (JEOL 4H-100) with higher sensitivity than in the early studies.[1,2] The careful preparation of the sample tube is necessary to avoid the formation of voids, which disturb the homogeneity of the magnetic field. At the early stage of our experiment, polyethylene, in either pellet or powdered form, was put into the sample tube and melted on the flame of a Bunsen burner for a relatively short time (about three minutes). Figure 1 shows the NMR spectra of these samples; they consist of very sharp lines similar to those of low-molecular-weight model compounds. The double-bond signals in polyethylene were assigned by comparing them with those of the model compounds: (a) octadecene-1 ($CH_3(CH_2)_{15}CH{=}CH_2$, $\delta=4.72$—4.98 and 5.48—5.92) for the vinyl group, (b) 2-ethyl-butene-1 ($(CH_3$-$CH_2)_2C{=}CH_2$, $\delta=4.56$—4.63) for vinylidene, (c) elaidic acid ($CH_3(CH_2)_7\overset{H}{C}{=}\underset{H}{C}(CH_2)_7COOH$, $\delta=5.22$—5.37) for *trans*-vinylene, and (d) oleic acid ($CH_3(CH_2)_7\overset{H}{C}{=}\overset{H}{C}(CH_2)_7COOH$, $\delta=5.15$—5.36) for *cis*-vinylene.

However, the IR measurement of these samples showed some increase in the double-bond content compared with that of the original pellets; attributable to the dissociation by overheating during the above operation.

We then tried to prepare the sample tube under milder conditions with an oil bath maintained at 180—200°C. Figure 2 shows the spectra of these samples, which give the same kinds of signals as are shown in Fig. 1, but with some broadening and weaker intensities. It was found that the half-height widths of the methylene proton signals of both normal and dissociated samples are not very different from each other, but that the tailing part of the signal is very broad in the normal sample, corresponding to the broad molecular-weight distribution in the original sample.

Thus, the NMR spectra of molten polyethylene is very useful in determining the contents of various types of olefinic double bonds in a relatively short time without any accumulation, that is, in a single scan; moreover, this method provides a broad line width which gives us new information about the molecular motion and the molecular-weight distribution of polyethylene chains.

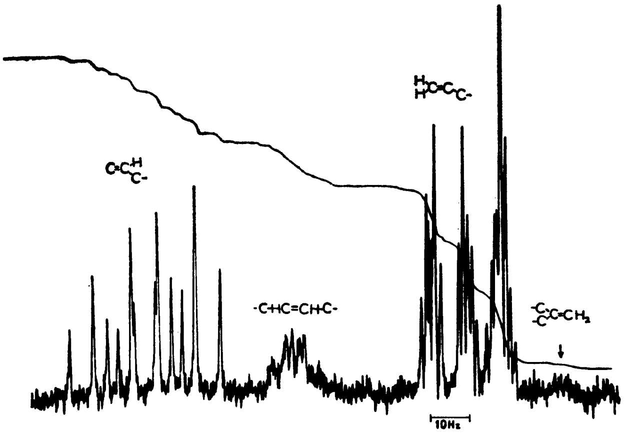

Fig. 1. Expanded spectrum of olefinic double bonds in molten high density polyethylene at 180°C.

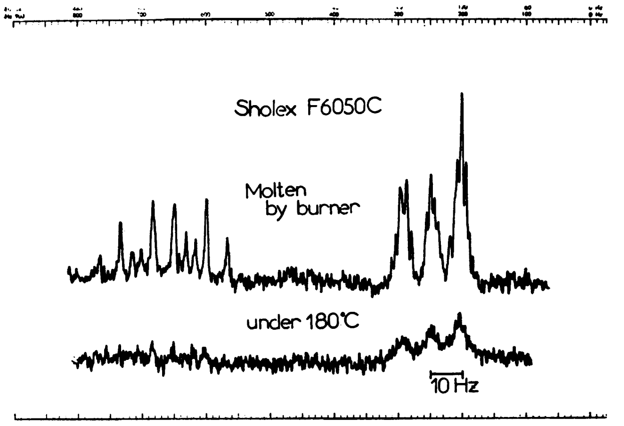

Fig. 2. Double bond spectra of molten high density polyethylene prepared by gas burner (upper) and oil bath (lower).

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[1] Y. Kato and A. Nishioka, This Bulletin, **39**, 1426 (1966).
[2] R. C. Ferguson, *Kautschuk Gummi.*, **18**, 723 (1965).