

220-MHz NMR Studies of Poly(propylene oxide- α -*d*)

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ABSTRACT: Analysis of the 220-MHz proton NMR spectra of several kinds of poly(propylene oxide- α -*d*) samples prepared with anionic, cationic and coordinate catalysts provided additional and confirming evidence for the previous analysis by 100-MHz proton NMR spectral studies. The spectra are exactly analyzed in terms of dyads for absorptions arising from methylene protons in the main chain of the polymer.

KEY WORDS: NMR / Poly(propylene oxide- α -*d*) / Tacticity /

Since discovery of the stereospecific polymerization of propylene oxide by Price, *et al.*,¹ a great number of papers about the mechanism of polymerization of this monomer have been published. Nevertheless, until recently there were very few investigations concerning the microstructure of poly(propylene oxide). Ramey, *et al.*, reported that the NMR spectra of methylene and methine protons decoupled from methylene protons in the poly(propylene oxide) consisted of two kinds of absorptions.² Recently Schaefer analyzed the C-13 NMR spectra of this polymer on the basis of relative peak intensities and chemical shifts of the fractionated polymer samples to resolve the dyads in the methylene and methine carbons of the polymer.³ Very recently reinvestigation of the C-13 NMR spectra of poly(propylene oxide) by us provided new information about triads in the absorptions of methine carbons in the main chain of the polymer.⁴ This paper describes the analysis of the 220-MHz proton NMR spectra of poly(propylene oxide- α -*d*).

EXPERIMENTAL

Materials

Propylene oxide- α -*d*^{5,6} was prepared by the reduction of monochloroacetone with lithium aluminum deuteride (Merck Co., deuterium content 99%) in dry ether at -78°C for 1/2 hr, followed by the epoxidation of the resulted 2-

deuterated propylene chlorohydrin with concd KOH solution at 70°C . The product was dried over calcium hydride and distilled. Yield, 64% based on lithium aluminum deuteride; bp 34.5°C .

All solvents were purified by ordinary methods, dried over calcium hydride and distilled under a dry-argon atmosphere.

Organometallic compounds (triethylaluminum and diethylzinc) were purified by distillation under reduced pressure.

Polymer samples

Sample I is the acetone-insoluble crystalline fraction of poly(propylene oxide- α -*d*) prepared using toluene as the solvent at 30°C for 24 hr with a $\text{ZnEt}_2\text{-H}_2\text{O}$ (1 : 0.7) freeze-dried catalyst system. Sample II is the amorphous fraction of the polymer obtained by the above procedure. Sample III is the amorphous fraction of the polymer prepared with an $\text{AlEt}_3\text{-H}_2\text{O}$ (1 : 1) catalyst system in toluene at 0°C for 24 hr. Sample IV is the amorphous polymer prepared with a KOH catalyst in bulk at 70°C for 7 days.

Fractionation of the polymer was carried out as follows. The raw polymer was dissolved completely in hot acetone (0.5 g/100 ml), the crystalline fraction was precipitated by cooling the solution to 0°C and filtered off. The soluble amorphous fraction was obtained by evaporating the acetone.

NMR Measurements

The 220-MHz NMR spectra of poly(propylene oxide- α -*d*) were taken at 50°C in deuteriochloroform and deuteriobenzene solution ($W/V=0.03$

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(g/ml) with a Varian HR-220-MHz NMR spectrometer. Tetramethylsilane was used as the internal standard.

RESULTS AND DISCUSSION

Poly(propylene oxide) may contain both head-to-tail and tail-to-tail (head-to-head) linkages between two contiguous monomeric units, due to the two possible modes of attack on the monomer by the active end of the growing polymer, so-called α - and β -opening. In addition to this structural problem, four kinds of triad sequences and two kinds of dyad ones, in principle, should be distinguishable because poly(propylene oxide) contains true asymmetric carbon atoms in each monomeric unit; for example, ddl is not equivalent to ldd.

The deuteration of the methine proton can simplify the spectra of the methylene protons in the polymers. An AB spectrum of the methylene protons is anticipated, because the two methylene protons are in magnetically different environments from each other, *i.e.*, they are "non-equivalent". Actually the 100-MHz NMR spectra of poly(propylene oxide- α - d) showed three kinds of AB quartets, which were assigned to a dyad in a tail-to-tail linkages and to isotactic and syndiotactic dyads of the methylene protons in head-to-tail linkages.^{5,6} Nevertheless, chemical shifts between these quartets are not so large as to analyze the spectra with absolute unambiguity. The 220-MHz NMR study not only unambiguously solves this problem, but also provides more exact information on the microstructure of the polymer.

Since analysis of the X-ray fiber diagram⁷ shows that the crystalline poly(propylene oxide) obtained

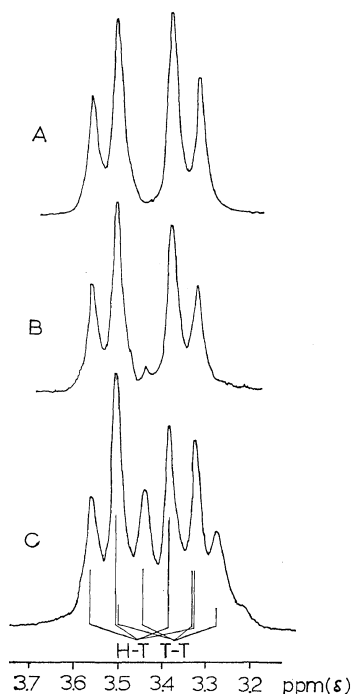


Figure 1. The NMR spectra of poly(propylene oxide- α - d)s at 220-MHz in CDCl_3 solution at 50°C : (A), the crystalline sample I prepared with ZnEt_2 - H_2O (1 : 0.7) freeze-dried catalyst; (B), the amorphous sample II prepared with the same catalyst as used for (A); (C), the amorphous sample III prepared with AlEt_3 - H_2O (1 : 1) catalyst system. The spectrum of the amorphous sample IV prepared with KOH catalyst is quite similar to that of (A).

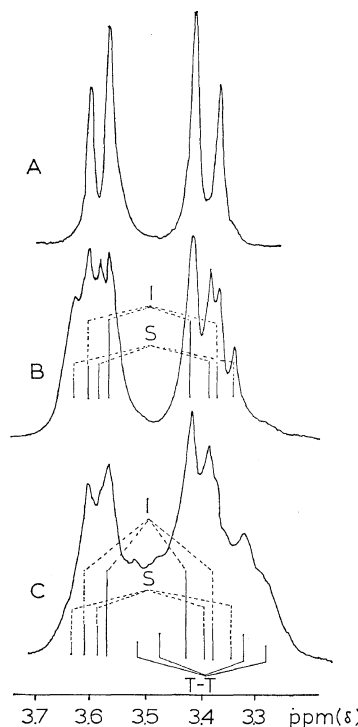


Figure 2. The NMR spectra of poly(propylene oxide- α - d)s at 220 MHz in C_6D_6 solution at 50°C . The samples used in measurement of the spectra, (A), (B), and (C) are equal to those used in Figure 1, respectively.

with a $\text{ZnEt}_2\text{--H}_2\text{O}$ catalyst has an isotactic configuration, the NMR spectrum of the methylene protons of the crystalline polymer, sample I, in CDCl_3 or C_6D_6 solution (see Figures 1A and 2A) shows a typical AB quartet arising from an isotactic dyad. The NMR parameters of this AB quartet can be calculated using the positions of the four lines observed in the spectrum;⁸ parameters in CDCl_3 , $\nu_A=3.52$ ppm(δ), $\nu_B=3.38$ ppm(δ), and $J_{AB}=10$ Hz; in C_6D_6 , $\nu_A=3.58$ ppm(δ), $\nu_B=3.40$ ppm(δ), and $J_{AB}=9$ Hz.

Nevertheless, the absorption in CDCl_3 solution of the methylene protons of sample II, and the absorption of the completely atactic polymer sample IV do not show any splitting, which is anticipated from the difference between isotactic and syndiotactic dyads, but the absorption spectra are almost the same as the spectrum of the isotactic crystalline polymer (see Figures 1A and 1B). Price, *et al.*,⁹ found by ozonolysis that the latter amorphous polymer contains no tail-to-tail and head-to-head linkages in the structure. Therefore, the above AB quartet of the methylene protons in CDCl_3 solution can be assigned to arise from the methylene protons in head-to-tail linkages.

The spectrum of sample III shows an additional quartet in the up-field region of the absorption assigned to the methylene protons of head-to-tail linkages (see Figure 1C). This new absorption can be assigned tentatively to the methylene protons of tail-to-tail linkages. In the 100-MHz NMR spectrum, this absorption appears as shoulders on the quartet of the head-to-tail linkages.⁵ The parameters are as follows; $\nu_A=3.47$ ppm(δ), $\nu_B=3.29$ ppm(δ), and $J_{AB}=10$ Hz.

Although the AB quartet in the NMR spectrum of sample II in CDCl_3 solution is simple, its absorption in C_6D_6 solution consists of two kinds of AB type quartets (see Figure 2B). This splitting of the absorption is assignable to the configurational differences between isotactic and syndiotactic dyads, since the spectrum in C_6D_6 solution of the completely atactic polymer sample IV containing no tail-to-tail linkages shows an equal intensity for these two kinds of absorptions. In relation to the NMR parameters of the crystalline isotactic sample I in C_6D_6 solution, the

absorption of the syndiotactic dyad is assigned to consist of $\nu_A=3.59$ ppm(δ), $\nu_B=3.36$ ppm(δ), and $J_{AB}=9$ Hz.

The NMR spectrum of the amorphous sample III is complicated due to the existence of a large amount of tail-to-tail linkages (see Figure 2C). Following the analysis of the NMR spectrum with a Du Pont-310 Curve Resolver, the parameters of the absorption arising from the methylene protons in tail-to-tail linkages are $\nu_A=3.50$ ppm(δ), $\nu_B=3.29$ ppm(δ), and $J_{AB}=10$ Hz.

The relative intensities of these three kinds of dyads on the four polymer samples were measured using a Du Pont-310 Curve Resolver and are summarized in Table I. The content of the syndiotactic dyad does not exceed 50% in any

Table I. Relative intensities of three kinds of dyads in four kinds of poly(propylene oxide- α -d) samples.^a

Sample no.	Isotactic dyad, % ^b	Syndiotactic dyad, % ^b	Content of tail-to-tail linkages, % ^c
I	98	2	0
II	57	43	7
III	73	27	38
IV	50	50	3

^a Values may contain an error of $\pm 2\%$.

^b Isotactic and syndiotactic dyads were measured on the spectra in C_6D_6 solution.

^c Content of tail-to-tail linkages was measured on the spectra in CDCl_3 solution.

polymer sample examined. This result is similar to that found in the structural study of polyacetaldehyde,¹⁰ and the clarification of its origin must wait for more detailed studies.

Thus the 220-MHz NMR spectra of poly(propylene oxide- α -d) provided exact information on the dyads in two contiguous monomeric units.

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