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β-CYCLODEXTRIN-MEDIATED STEREOREGULARITY IN POLYACRYLONITRILE POLYMERS

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ABSTRACT

Polyacrylonitrile polymers produced in the presence of molar equivalents of β-cyclodextrin (BCD) showed variation in stereoregularity. Thus, an increase in the acrylonitrile:BCD ratio showed an increase in isotacticity in the polymers formed. Inclusion complexation of acrylonitrile by BCD was detected by both ^{1}H-NMR spectroscopy and UV-Vis spectroscopy, which gave a binding constant value of 7242 ± 360 M^{-1} for the 1:1 complex.

Numerous reviews have been dedicated to the subject of inclusion polymerization [1] in which inclusion complex formation is expected between various hosts and different monomer guest molecules depending on the size, shape, and polarity of the latter. Such inclusion formation changes the physical and chemical nature of the included monomers [1], leading to polymers with controlled stereoregularity [2–4].

β-Cyclodextrin (BCD), besides exhibiting the ability to form inclusion complexes with a wide variety of organic molecules, was reported to aid stereoselective organic synthesis as well [5]. Very little work has been done in the field of inclusion polymerization involving BCD [6] for the synthesis of stereoregular polymers.

Stereoregularity in polyacrylonitrile (PAN) synthesis is controlled by such factors as temperature, catalyst, and irradiation [7, 8]. Stereoregularity in PAN polymerization under various conditions resulted in the formation of 25 to 75% isotactic polymers [7–9]. We report here the synthesis of stereoregular PAN polymers in the presence of BCD with varying degrees of isotacticity.

^{1}H-NMR spectra of the PAN polymers prepared are shown in Fig. 1 (C and D). The room temperature spectra obtained at 400 MHz show two huge envelopes centered at 2.09 ppm corresponding to the CH_2 protons, and a CH signal at 3.16 ppm. Although each of these signals shows shoulders with further splittings, the resolution was not satisfactory. For instance, the CH_2 signal at 2.09 ppm showed a sharp signal at 2.04 ppm and a shoulder at 2.12 ppm, probably corresponding to signals from isotactic and syndiotactic components. Similarly, the CH signal at 3.16 ppm was composed of a sharp doublet at 3.17 ppm and a shoulder at 3.14 ppm. In PAN polymer prepared in the presence of BCD, some BCD signals with varying intensities are present even after repeated water washing of the polymer. It is possible that a small amount of BCD adhering to PAN polymer remained as rotoxanes moving through the length of the polymer chain. Similar examples of rotoxane formation have been reported in the literature [10–12]. However, we did not carry out any further work on this subject.

In order to get a better understanding of the stereoregularity distribution in PAN polymers, ^{1}H-NMR spectra were recorded at 100°C on a 270 MHz instrument (Figs. 1 and 2). The CH_2 and CH signals showed splitting and the spectra resemble those reported by Svegliado et al. [13].

An ^{1}H-NMR spectrum of PAN at 100°C is shown in Fig. 1. The quintet at 3.17 ppm corresponds to α-CH, and the multiplet between 2.06 and 2.17 ppm corresponds to β-CH_2 protons present in the polymer irrespective of whether BCD

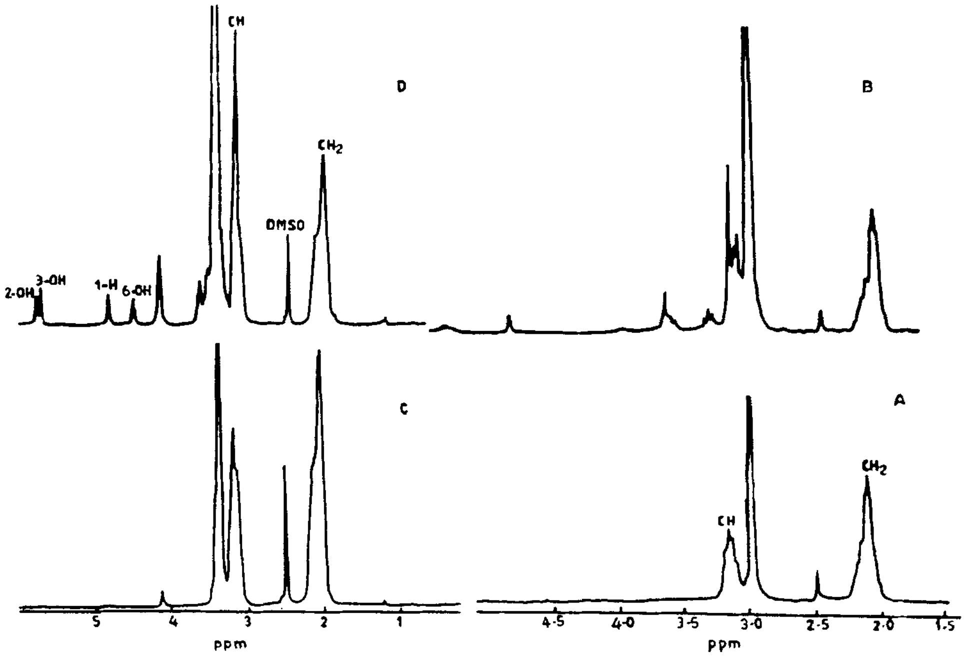


FIG. 1. ^{1}H-NMR spectra of polyacrylonitrile prepared in the presence and in the absence of β-cyclodextrin. (C and D): Spectra recorded on the 400 MHz instrument at room temperature; (A and B): spectra on the 270 MHz instrument at 100°C. (A and C): Without BCD; (B and D): with BCD (AN:BCD = 10:1).

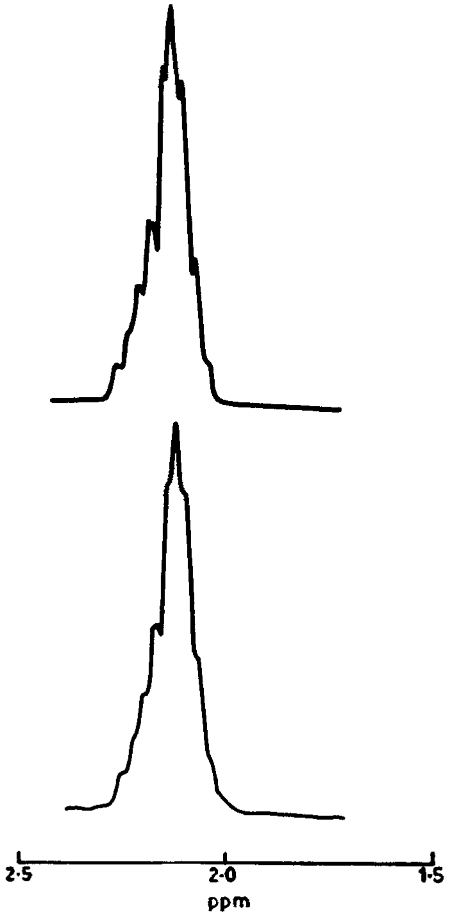


FIG. 2. Expanded region of CH_2 signals from 1.5–2.5 ppm from sample without BCD (lower trace) and 10:1 AN:BCD sample (upper trace).

was employed or not in the polymerization. The multiplet obtained is interpreted as the AB part of an ABX_2 system due to overlapping of the syndiotactic (higher field) and isotactic (lower field) triplets. The tacticity of the polymer prepared was calculated from this NMR spectrum according to the method described by Yamadera and Murano [7] by using the relation

$$D(\tau) = \sum_{i=1}^{6} \frac{b^2 DMi}{b^2 + (\tau - \tau_i)^2}$$

where $D(\tau)$ is the intensity at chemical shift τ, $2b$ is the half-width value, τ_i is the chemical shift of each peak, and DMi is the intensity of the peak at chemical shift τ_i.

The results obtained in this study are given in Table 1. Polymerization carried out in the absence of BCD gave 54% isotactic and 46% syndiotactic polymers. When the molar ratio of acrylonitrile (AN) to BCD was 5:1, the proportion of

TABLE 1. BCD Mediated Stereoregularity in PAN Polymerization[a]

AN:BCD molar ratio	Ratio of isomers, %	
	Isotactic	Syndiotactic
1:0	54	46
5:1	59	41
10:1	64	36
20:1	68	32

[a] Chemical shift values of the six peaks used in the evaluation for calculating the ratio of isomers are 2.06, 2.10, 2.12, 2.16, and 2.19 ppm. Linewidth values for the CH_2 peaks for the four polymers mentioned above are 0.034, 0.347, 0.038, and 0.033 Hz, respectively. The error is +5%. The values are the average of two samples for the same AN:BCD ratio.

isotactic and syndiotactic polymers formed was found to be 59 and 41%, respectively. However, when the molar ratio was increased to 10:1 and 20:1, the isotactic to syndiotactic ratio was found to be 64:36 and 68:32, respectively. Thus a decrease in AN:BCD ratio caused an increase in the percentage of syndiotacticity. In other words, an increase in the AN:BCD ratio caused an increase in the proportion of isotactic polymer formed.

Syndiotactic polymer is more favored at higher BCD concentrations than isotactic polymer because the orientation of the BCD complex in the opposite direction will be more favored from a steric point of view than the presence of two BCD units in adjacent positions which will lead to an isotactic polymer. Steric hindrance between adjacent BCD units is reduced at lower BCD concentrations, thereby favoring more isotactic than syndiotactic polymer. Interestingly, the proportion of isotactic polymer formed at lower BCD concentrations was found to be more than that obtained in the total absence of BCD. The reason for this is not known.

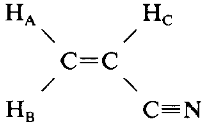
Observed variations in stereoregularity due to complexation of acrylonitrile by BCD were investigated by UV-Vis and ^{1}H-NMR spectroscopy. UV-Vis spectroscopy studies indicated complexation of acrylonitrile by BCD. Acrylonitrile exhibits a strong absorption at 203 nm in water (ϵ = 8342). With the addition of increasing amounts of BCD, the absorption at 203 nm decreased, with an isosbestic point at 210 nm. A titration plot of ΔA (difference in absorbance between acrylonitrile and that at a certain concentration of BCD) versus [BCD]/[AN] exhibited an asymptotic curve with a 1:1 stoichiometry, indicating formation of a 1:1 complex. The binding constant value was determined by the method of Farmoso [14]. A plot of $1/\Delta A$ against 1/[BCD] gave a straight line with a slope equal to $1/(\Delta A_{AB}K)$, where ΔA_{AB} is the difference in absorbance between free acrylonitrile and its BCD complex, and K is the binding constant value for the 1:1 complex. A value of 7242 ± 360 M^{-1} was obtained for the acrylonitrile–BCD complex.

^{1}H-NMR spectra also showed a lot of changes in the acrylonitrile (monomer) multiplets in the 5.72–6.42 ppm region in the presence of BCD (Table 2). Acryloni-

TABLE 2. ^{1}H-NMR Data on Acrylonitrile and BCD-Acrylonitrile[a]

	Chemical shift (ppm)	
Signal	Free	Complex
H_B and H_C	6.42–6.22	6.40–6.20
H_A	5.9–5.72	5.87–5.76

[a]Values from a 1:1 mixture of acrylonitrile and BCD in D_2O:



trile monomer shows two group of signals centered at 5.81 and 6.32 ppm in D_2O. On adding an equivalent amount of BCD, the signals showed slight changes in chemical shift values of the multiplets centered at 5.92 and 6.3 ppm, indicating formation of an inclusion complex.

A typical experimental procedure is as follows. A mixture of acrylonitrile (0.106 mol), BCD (catalyst depending on molar ratio), sodium metabisulfate (36.8 mmols), ammonium persulfate (0.749 mmol), and a drop of H_2SO_4 in water at 35°C was flushed with N_2. It was then treated with hot water (100 mL) and filtered. After washing with hot water and methanol (50 mL), the residue was dried and weighed.

^{1}H-NMR spectra were recorded on Bruker AMX400 and WH 270 MHz NMR instruments, each fitted with a Spectrospin magnet operating at 20°C and an Aspect 2000 computer. About 200 scans were collected for each spectrum, and all the samples were prepared in DMSO-d_6.

UV-Vis spectroscopy was carried out using a Shimadzu UV-240 instrument operating at 20 ± 1°C. Acrylonitrile dissolved in water (1.823×10^{-4} M) was used. A stock solution of BCD (1.815×10^{-3} M) dissolved in the above-mentioned acrylonitrile solution was used for the addition of BCD in increasing amounts. Spectra were recorded at 400–190 nm.

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