

High Resolution NMR Spectra of Poly N,N-Dimethylacrylamide in CDCl_3 Solution

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NMR has been used by Bovey and others to quantitatively determine the stereochemistry of polymethylmethacrylate (PMMA) (BOVEY et al., 1960). Since this pioneering work, investigations have been systematically or briefly reported on other polymers (HATADA et al., 1979). However, synthesis of poly N,N-dimethylacrylamide (PDMA) has only been examined briefly by BUTLER, et al., (1960) by anionic homopolymerization in polar and non-polar media with ethyllithium. It was suggested that these polymers must be highly isotactic compared to those obtained via radical polymerization, since the solubility, rate of hydrolysis, and physical properties (X-ray, thermal analysis) behaved differently (BUTLER et al., 1960, CHAPMAN, 1960). Analogously, poly N,N-dibutylacrylamide synthesized under similar conditions (Li^+ /Hexane) has been reported by BADAMI (1960) to be highly isotactic.

NMR of free radically prepared PDMA in D_2O was briefly investigated by MORAWETZ (1969) in order to study the energy of the rotation around the C-N bond. Since the study on the tacticity has not been reported in the literature, we wish to report in this note some original results on the high resolution NMR spectra of PDMA indicate the type of tacticity obtained via anionic polymerization. Monomer and solvents were vacuum distilled from calcium hydride and syringe techniques under an Argon atmosphere were utilized for the polymerization. Table I summarizes the conditions of polymerization.

The proton NMR spectra of these samples were obtained at 34°C with a Varian EM 390-, at 90 MHz in CDCl_3 using tetramethyl silane (TMS; $\delta = 0$ ppm) as the internal standard. The relative area under the peak (Figure 2) could be obtained by integration or by computer (deconvolution technique). The error is estimated to be 2% to 5%. All of these spectra are shown in Figure 1; Figure 2 gives an enlargement of the region of the dimethyl group (3.3 to 2.8 ppm).

TABLE I

Polymerization Conditions for the
Synthesis of Poly(N,N-Dimethyl Acrylamide)

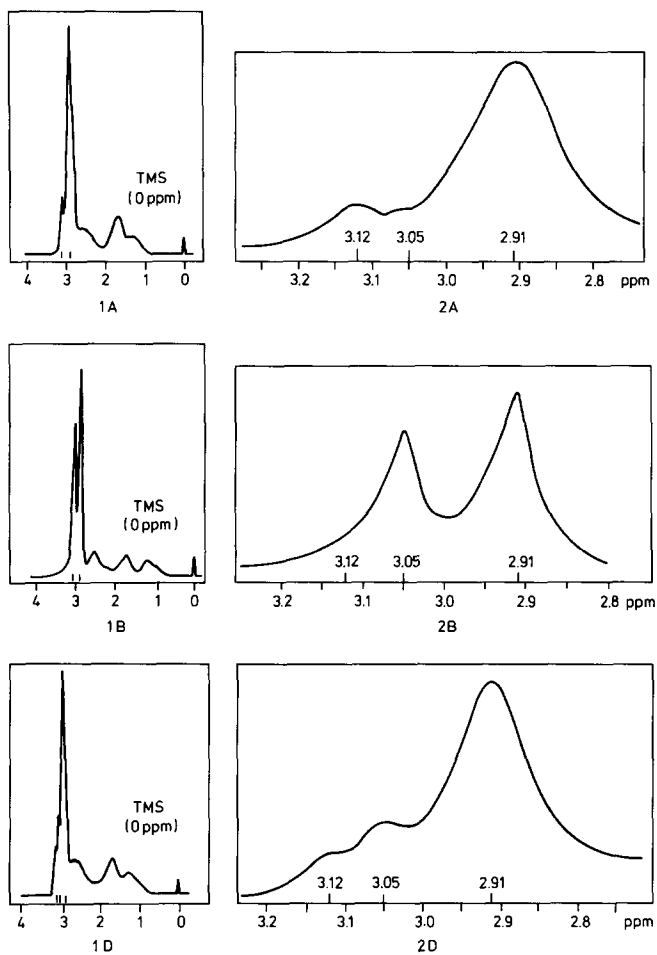
Sample A	Catalyst	Solvent	Temperature	Suggested Configuration of the Polymer
A	AIBN	Benzene	60°C	Syndiotactic
B	sec Butylli	Benzene	60°C	Isotactic
C	sec Butylli	THF	-60°C	Isotactic
D	sec Butylli	n-Hexane	-60°C	Isotactic

As shown in Figure 1 (A, B, D referred to sample A, B, D), these spectra are completely different from each other, as expected, depending on the mechanism of polymerization (Table I). However, the spectra can be divided in three regions: 3.3 to 2.9 ppm due to the dimethyl group, 2.7 to 2.5 ppm due to the -CH-backbone and 1.75 to 1.2 ppm due to the -CH₂-backbone. In Figure 2, one can see more detail of the resolution for the different types of dimethyl (N-(CH₃)₂) peaks. One can easily detect three types of protons: at 2.91 ppm (peak #1), 3.05 ppm (peak #2) and 3.12 ppm (peak #3). The radical polymerization will product mostly atactic polymer (spectra 1A, 2A) and the peak #1 is most predominate. Highly isotactic polymer was obtained via alkyl lithium initiation in benzene. It may be noted that the peak #2 increased slightly while peak #1 decreased (spectra 1B, 2B). It is too uncertain at this moment to attribute these peaks to the tacticity (iso, syndio, hetero) in terms of triad sequence, even though we suspect this is the case. However, one can calculate the relative area of these different peaks (in percent), as shown in Table II.

TABLE II

¹H NMR Relative Areas of Methyl Peaks
for Poly(N,N-Dimethyl Acrylamide)

Sample B	Peak 3	Peak 2	Peak 1
A	10	5	85
B	5	41	54
C	6	30	64
D	8	18	74



Figs 1 and 2: ^1H NMR spectrum of poly(N,N-Dimethylacrylamide) at 90 MHz

Moreover, the shape and the position of the -CH₂- group can be noted to also change with the type of polymerization (Figure 1A, B, D).

In conclusion, these results suggest that one can study quantitatively the tacticity (assuming these peaks are iso, syndio, and heterotactic) of the PDMA. Further detailed results on the effect of the counterion, NMR solvent and temperature of NMR measurement will be published (McGRATH, et al. 1980).

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