A Commentary on the Stereoregularity of Poly(α-methylvinyl methyl ether)

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ABSTRACT: We have reexamined the high-resolution nuclear magnetic resonance spectra of poly(α-methylvinyl methyl ether). We find that the spectra show singlets in the methyl, methylene, and methoxyl regions. The spectra are consistent with a syndiotactic structure for the polymer.

In a recent article, Matsuzaki and his coworkers[1] reported their results on the stereoregularities of two poly(α-methylvinyl ethers) studied by nmr spectra with a 60-MHz instrument. According to these authors, the α-methyl protons of the poly(α-methylvinyl ethers) (PMVME) exhibit a triplet signal at τ 8.86, 8.74, and 8.65 corresponding to syndiotactic, heterotactic, an isotactic configurations. They believe that the methylene proton signals occur at τ 7.74 and 8.16–8.22 which they tentatively assigned to the racemic and meso methylenes, respectively. On the basis of their findings, they suggested that the PMVME polymerized with cationic catalysis is atactic in nature which conflicts with earlier results reported from our laboratories.[2a]

In our work we found a singlet in both the α-methyl and methylene proton regions of the PMVME spectra measured in several solvents over a wide range of temperatures.[2] We also found a singlet in the methoxyl region of the nmr spectrum. We suggested that the PMVME polymerized with cationic catalysis is syndiotactic in nature.

The conflicting results reported by Matsuzaki and coworkers are rather surprizing in view of the similarity in their polymerization conditions and instrumentation to those employed by us. The Japanese workers suggest that our polymer may have been degraded; however, a careful examination of their work has revealed that the different nmr spectra observed by these authors are, unfortunately, due to their experimental errors.

As we have discussed in our earlier article, PMVME undergoes degradation readily in solution especially in the presence of residual catalyst in the polymer. The purification procedures employed by us were essential in assuring polymer stability during nmr measurements. In addition we added a stabilizer, phenyl-β-naphthylamine, in order to obtain measurements at very high temperatures. It is not sufficient to follow the procedure of Matsuzaki and his coworkers who isolated their polymers merely by dissolution in benzene and precipitation in methanol. They did not take the necessary step of removing the residual catalyst. Thus the polymers decompose rapidly in chloroform as illustrated in Figure 1a. The degradation resulted in a spectrum remarkably similar to that reported by the Japanese group. We can also produce a spectrum such as Figure 1a from a sample that exhibits only singlets in the methyl, methylene, and methoxyl regions simply by addition of trace amounts of the polymerization catalysts to the polymer in chloroform solution.

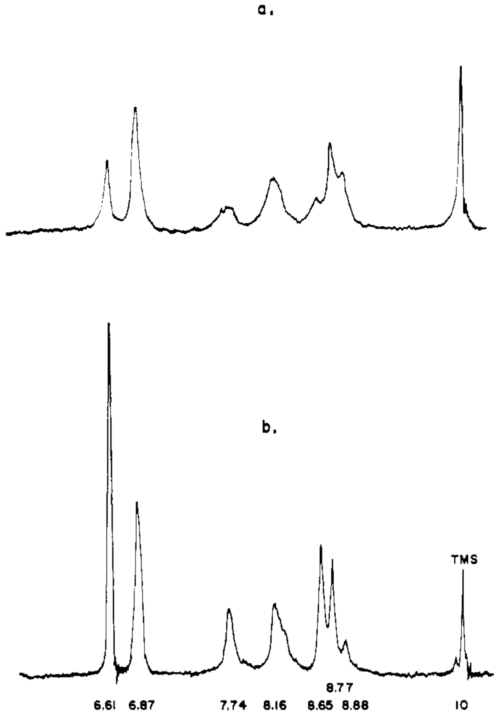

Figure 1. Nmr spectra of PMVME measured in a commercial chloroform solution (10% by weight) at (a) 50° and (b) 107°.

In our Figure 1 (as in the Japanese work), there are marked changes in the α-methyl proton regions and the occurrence of new peaks at τ 7.78 and 6.67. As the degradation proceeds, the signal at τ 7.78 becomes more intense while the α-methyl proton signal diminishes gradually. It is, therefore, not surprising that Matsuzaki found that the ratio of areas under the α-methyl proton envelope to those of the methylene proton signals to be smaller than the calculated values.

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(1) K. Matsuzaki, M. Hamada, and K. Arita, *J. Polym. Sci., Part A-1*, **5**, 1233 (1967).

(2) M. Goodman and Y. L. Fan, *J. Amer. Chem. Soc.*, **86**, 4922 (1964). (b) We supplied a sample of poly(α-methylvinyl methyl ether) to Dr. Frank A. Bovey and Mr. John Ryan of the Bell Telephone Laboratories, Murray Hill, N. J., who carried out measurements of the high-resolution nuclear magnetic resonance spectrum at 220 Hz in chlorobenzene at 90°. They found only sharp singlets for methylene, methoxyl, and methyl protons, in complete agreement with our results at 60 and 100 Hz. We wish to thank Dr. Bovey and Mr. Ryan for their efforts.

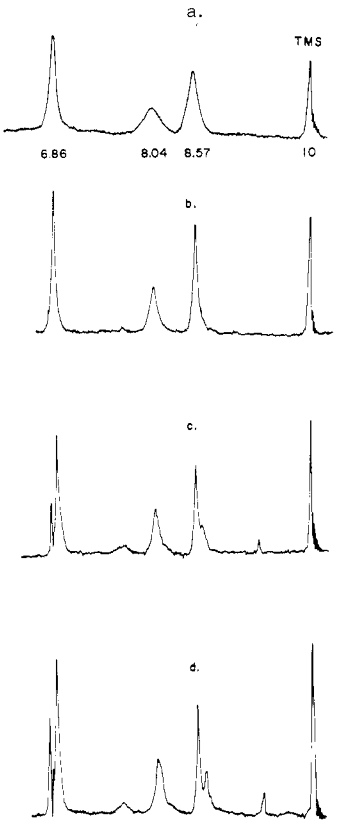

Figure 2. Degradation of PMVME followed by nmr spectra in chlorobenzene solution at (a) 61°, (b) 92°, (c) 120°, and (d) 148°.

In addition, we have been able to produce the fine structure similar to that found in Figure 1 in the α-methyl proton regions solely from thermal degradation of the polymer. This is illustrated in Figure 2 where a PMVME sample was deliberately degraded at elevated temperatures in chlorobenzene solution. The occurrence of polymer degradation is evidenced by the fact that the original spectrum, Figure 2a, cannot be reproduced after heating. These spectral variations during the degradation are similar to those observed in a chloroform solution (Figure 1b). It should be noted that the peak for the methylene protons (τ 8.15) sharpens substantially with increase in temperature (compare Figure 2a with 2b).

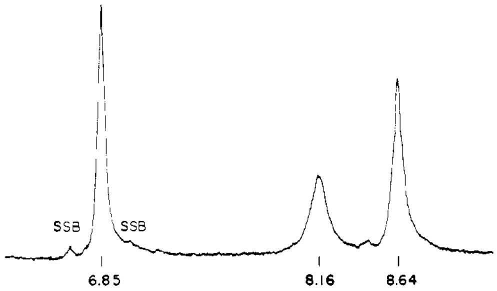

Figure 3. Varian 100-MHz nmr spectrum of PMVME (10% by weight) in ethanol-free $CDCl_3$ at room temperature. The small trace of a peak at approximately τ 8.4 arises from a minor impurity. The SSB noted peaks arise from spinning side bands of the main methoxyl peak.

Finally, we undertook to examine the nmr spectrum of the polymer in ethanol-free deuteriochloroform, using a Varian 100-MHz instrument. The results are shown in Figure 3. They fully support our explanations and conclusions based on a 60-MHz spectra.

It is, therefore, reasonable to attribute the results reported by Matsuzaki and his coworkers to polymer degradation. We have shown that when necessary precautions are taken, a 60-MHz nmr spectrum of PMVME exhibits singlets in the methyl, methylene, and methoxyl regions.

In analogy, their results and interpretations about the stereoregularity of poly(α-methylvinyl isobutyl ether) are suspect. The splitting of the α-methyl proton signal and the racemic methylene signal at τ 7.74 may result from the same errors made by them on PMVME.

In conclusion, our earlier work on the stereoregularity of PMVME remains correct and valid. The syndiotactic nature of this polymer is not only in agreement with its nmr spectrum but also consistent with the optical rotatory dispersion behavior of other members in its family which we will report in a future article.[3]

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(3) Y. L. Fan and M. Goodman, submitted for publication. A brief report on these results has appeared in our review article, M. Goodman, A. Abe, and Y. L. Fan, *Macromol. Rev.*, **1**, 20 (1966).