Polymer Bulletin 9, 241–244 (1983)

Polymer Bulletin

Determination of Tacticity of Polymethacrylamide by C-13 NMR Spectroscopy

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Summary

The tacticity of polymethacrylamide was studied by ^{1}H and ^{13}C NMR spectroscopy. It was found that the fractions of tactic triads could be determined from the resonances of α-methyl and quaternary carbons and those of tactic pentad from the carbonyl carbon resonance. The polymer obtained with radical initiator was syndiotactic and the tacticity is consistent with the Bernoullian statistics.

Introduction

Many papers have been published on the polymerization and copolymerization of methacrylamide and its derivatives, however, no report could be found on the tacticity of polymethacrylamide.

Recently we prepared N-triphenylmethyl methacrylamide and polymerized it with various initiators. All the polymers obtained were not soluble in usual organic solvents but dissolved in concentrated sulfuric acid to give the polymethacrylamides. The tacticity of the original poly(N-triphenylmethyl methacrylamide) was estimated by comparing the spectrum of the derived polymethacrylamide with that of the polymethacrylamide prepared with radical initiator (HATADA et al., 1981).

In this paper a quantitative determination of tacticity of polymethacrylamide by ^{13}C NMR spectrum will be reported briefly.

Experimental

Polymethacrylamide was prepared in water at 60°C with $K_2S_2O_8$ as initiator. ^{1}H and ^{13}C NMR spectra were taken on JNM-FX100(100MHz) and JNM-FX200(50MHz) Fourier transform NMR spectrometers, respectively, in ethylene glycol-d_6 (10 w/v%) at 100°C. The chemical shifts were referred to the solvent signal and converted into TMS scale ($DOCD_2CD_2OD$ - TMS = 61.69 ppm).

Results and Discussion

Figure 1 shows the ^{1}H NMR spectrum of polymethacrylamide. The assignment of each resonance is indicated in the Figure. The backbone methylene protons showed broad singlet similarly to those of syndiotactic polymethacrylates, indicating that the polymer was predominantly syndiotactic. It is well known that most of the polymers of 1,1-disubstituted ethylenes prepared with radical initiator are syndiotactic.

Small splittings appeared in the methyl proton resonance may be due to the triad tacticity as indicated in the Figure. However, a quantitative determination of tacticity from these splittings was not possible.

^{13}C NMR spectra of the polymethacrylamide are shown in Figure 2. The resonances were assigned on the basis of their chemical shifts as shown in the Figure. The resonances of α-methyl and quaternary carbons split into three peaks, respectively, which could be assigned to isotactic, heterotactic and syndiotactic triads with increasing magnetic field. The triad tacticities obtained from these two resonances are in agreement as given in Table 1. These values also agreed well with the tacticity calculated assuming the Bernoullian statistics (Pr=0.83). It is very reasonable that the tacticity of the polymer formed in the radical polymerization is consistent with Bernoullian statistics.

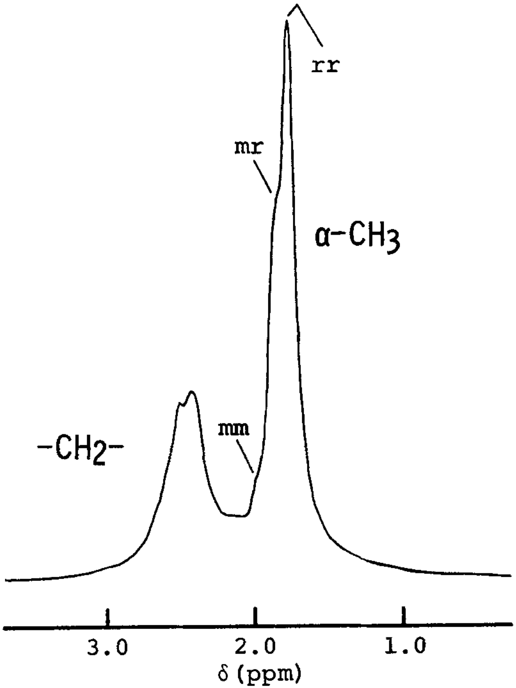

Figure 1 ^{1}H NMR spectrum of polymethacrylamide in ethylene glycol-d_6 at 100°C and 100 MHz

The carbonyl carbon resonance split into several peaks which appeared to correspond to the sequences of configurational pentads. The peaks due to the pentads centered by mm sequence was hardly observable probably owing to the low content of these pentads. The peak assignment was done by comparison of the observed peak intensities with those calculated by assuming Bernoullian statistics, and shown in the Figure. The agreement between the observed and calculated tactic values are fairly well (Table 1).

The resonance of backbone methylene carbon split into two peaks which seem to correspond to racemo and meso dyad with increasing magnetic field. But this peak assignment was not the correct one because the fraction of dyad tacticity calculated according to the assignment (Pr=0.71) did not agree with the values calculated from the triad tacticity obtained from the α-methyl or quaternary carbon resonance. In this resonance the chemical shift difference between the racemo and meso dyads may be of the comparable magnitude with those for the tetrads, which complicates the interpretation of the splittings.

Further investigation is now under way by using the spectrometer operating at higher magnetic field. The results will be published in near future.

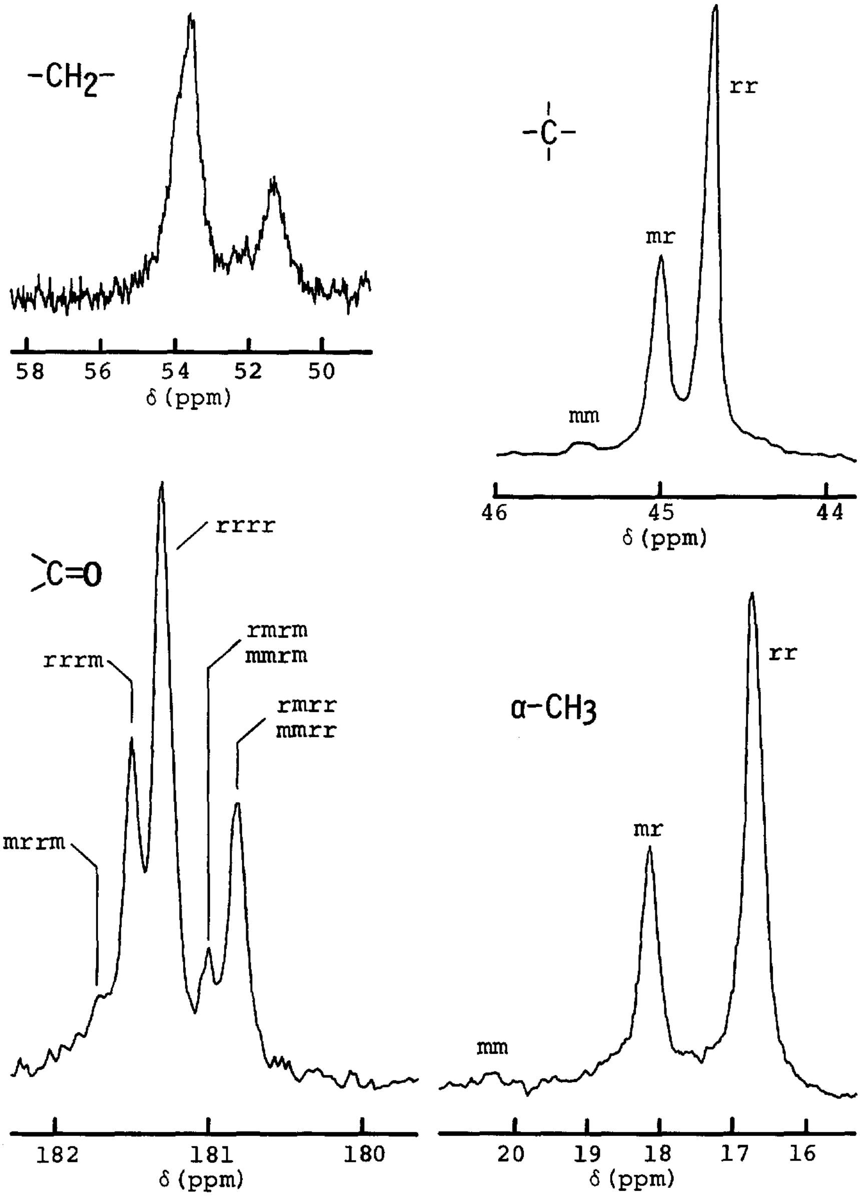

Figure 2 ^{13}C NMR spectra of polymethacrylamide prepared with $K_2S_2O_8$ observed in ethylene glycol-d_6 at 100°C and 50 MHz

Table 1
Triad and Pentad Tacticities of Polymethacrylamide Prepared by Radical Initiator

Carbon	Chemical shift (ppm)	Assignment	Fractions (%)	
			Found	Calcd.[a]
α-CH_3	16.77	rr	64	69
	18.17	mr	34	28
	20.3	mm	2	3
$-\overset{\vert}{\underset{\vert}{C}}-$	44.86	rr	68	69
	45.20	mr	29	28
	45.69	mm	3	3
$>C=O$	180.78	rmrr mmrr	22	23
	181.00	rmrm mmrm	5	5
	181.27	rrrr	48	47
	181.51	rrrm	20	19
	181.75	mrrm	2	2

[a] Calculated by assuming Bernoullian statistics (Pr = 0.83).

Acknowledgement

The authors are grateful to Dr. Y. Kobayashi of Institute for Protein Research, Osaka University, and Dr. H. Sato of Faculty of Technology, Tokyo University of Agriculture and Technology, for the measurements of 50 MHz NMR spectra and also to Mrs. F. Yano for her clerical assistance in preparing this manuscript.

Reference

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Received and accepted December 9, 1982