

STUDY ON SEQUENCE STRUCTURE OF ACRYLAMIDE-ACRYLATE COPOLYMERS BY ^{13}C -NMR METHOD

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ABSTRACT

Triad sequence distributions in a series of P(AM/AA) with different AA% were calculated from copolymerization reactivity ratio r_1 and r_2 based on first order Markov statistic model, and the calculated data compared with observed ones from ^{13}C -NMR spectra showed good agreement with each other. The sequence distribution in P(AM/AA) obtained under our experimental conditions fits in with first order Markov statistic model. A significant sequence structure difference was observed between P(AM/AA) and alkaline hydrolyzed polyacrylamide, ABA triad (acrylate unit center), AAA and AAB triads (acrylamide unit center) dominated in hydrolyzed ones.

INTRODUCTION

Sequence structure of acrylamide-acrylate copolymer P(AM/AA) has been received considerable industrial interest, however, a little information is available relating this topic^[1,2,9]. The triad sequences in P(AM/AA) have been determined from the carbonyl carbons' splitting pattern in ^{13}C -NMR spectra as reported^[3]. The statistic model in P(AM/AA) was analysed on the basis of triad distribution for a series of P(AM/AA) copolymers by ^{13}C -NMR method. The sequence structure differences between alkaline hydrolyzed polyacrylamide and acrylamide-acrylate copolymer are also discussed.

EXPERIMENTAL

Preparation of samples

P(AM/AA) copolymers were prepared as follows^[4]: Acrylamide (AM) and acrylic acid (AA) with different ratios dissolved in fresh distilled water were copolymerized at 50°C in the presence of 5% potassium persulfate as initiator. The copolymerization was run under purified nitrogen. The monomer conversion was controlled less than 10%. The copolymer was collected and purified by precipitating with methanol. After drying at 40°C in vacuo, the composition of copolymers was determined by elemental analysis.

Hydrolysis of polyacrylamides

Alkaline hydrolysis was carried in a vessel in which the polyacrylamide was dissolved in 2*N* sodium hydroxide solution at 100°C, after a given time, depending on desired degree of hydrolysis, the product was cooled down and neutralized with HCl, then purified and characterized as above-mentioned method.

Characterization of copolymers

The ^{13}C -NMR experiments were performed in a JEOL FT 100 NMR spectrometer, operating

at 25 MHz. The experimental condition for each sample was as follows: NMR tube 10 mm o.d., solvent H_2O , observed temperature 50°C , interal lock field D_2O , interal reference dioxane, sample concentration 15%, pulse width $14\mu\text{s}$, repetition time 2.0 sec., number of accumulation 4,000. All spectra used as calculation of sequence structure were recorded under condition of broad-band proton decoupling $^{13}\text{C}\{^1\text{H}\}$.

The elemental analysis of copolymers were carried on Carlo Erba Mod. 1102 elemental analyzer.

RESULTS AND DISCUSSION

The resonance absorption signal of carbonyl carbons of P(AM/AA) copolymer usually appears two signal peaks in $^{13}\text{C}\{^1\text{H}\}$ spectrum, but we found that these two peaks could clearly separated into two triplet peaks corresponding to AM center and AA center triads respectively by pH value of the sample solution being 9.2, as shown in Figure 1. The assignments were reported in the previous paper[3]. The triad sequence can be determined from the separated peaks' area.

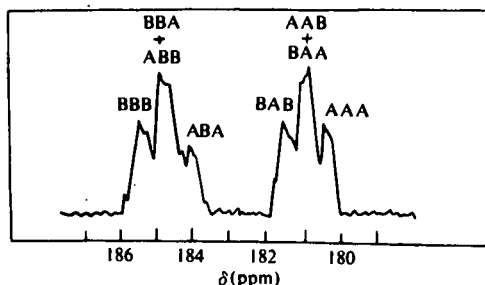


Fig.1 Carbonyl carbon regions of the ^{13}C -NMR spectrum of P(AM/AA) copolymer, recorded at 50°C , pH = 9.2, A = AM, B = AA^[3]

In small molecule quantitative measurements, the nuclear Overhauser effect (NOE) varies from 1 to 3 according to the structure environment as a consequence of proton noise decoupling. However, in polymer analysis, the NOE due to ^1H decoupling has no influence on the estimation of microtacticity from ^{13}C -NMR spectra, as pointed by Inoue [5]. The NOE factor is the same for both carbonyl carbons in AM and AA.

In this paper, we checked this problem once again, two decoupling programs were used, one was broad-band decoupling $^{13}\text{C}\{^1\text{H}\}$ and another was gate decoupling (NNE), i.e., decoupled spectrum obtained without NOE. The results are listed in Table 1. The triad probabilities are normalized from carbonyl carbon area for acrylamide and acrylate center respectively. There is a small deviation obtained from these two methods within the experimental quantitative error. So the completely proton decoupling was used in our case.

Tab. 1 Comparison of two decoupling methods, broad-band decoupling and gate decoupling

No.	AM:AA	NMR	BBB	BBA + ABB	ABA	BAB	AAB + BAA	AAA
3	7:3	$^{13}\text{C}\{^1\text{H}\}$	0.13	0.47	0.40	0.14	0.50	0.36
		NNE	0.12	0.47	0.41	0.13	0.48	0.39

A traditional method for the determination of microstructure of copolymers is to determine reactivity ratios r_1 and r_2 by means of measuring the monomer ratios in copolymers prepared from varied feed ratios. The composition of a series of low conversion ($< 10\%$) P(AM/AA) samples was

obtained from elemental analysis method. The reactivity ratios r_1 and r_2 for acrylamide (1)-acrylic acid(2) copolymerization were given according to the method of Fineman and Ross[7]. the values are:

$$r_1 = 0.68$$

$$r_2 = 1.45$$

One of the most frequently used statistical methods is the first order Markov model in copolymer analysis[6]. As we know, two conditional probabilities P_{12} and P_{21} are required to test for the first order Markovian behavior. P_{12} means a chain ending in unit 1 will add another unit 2, similar way, P_{21} means a chain ending in unit 2 will add another unit 1. P_{12} and P_{21} can be calculated from the following equations:

$$P_{12} = 1/(1 + r_1 X) \quad (1)$$

$$P_{11} = 1 - P_{12} \quad (2)$$

$$P_{21} = 1/(1 + r_2/X) \quad (3)$$

$$P_{22} = 1 - P_{21} \quad (4)$$

Here X is the feed composition.

Triad distribution equations and number average sequence length equations are given in terms of the conditional probabilities on the basis of first order Markov statistic model ($A = 1$; $B = 2$):

$$P_3\{AAA\} = P_{21} P_{11}^2 / (P_{12} + P_{21}) \quad (5)$$

$$P_3\{AAB\} = P_3\{BAA\} = P_{21} P_{11} P_{12} / (P_{12} + P_{21}) \quad (6)$$

$$P_3\{BAB\} = P_{12}^2 P_{21} / (P_{12} + P_{21}) \quad (7)$$

$$P_3\{ABA\} = P_{21}^2 P_{12} / (P_{12} + P_{21}) \quad (8)$$

$$P_3\{BBA\} = P_3\{ABB\} = P_{12} P_{22} P_{21} / (P_{12} + P_{21}) \quad (9)$$

$$P_3\{BBB\} = P_{12} P_{22}^2 / (P_{12} + P_{21}) \quad (10)$$

$$\bar{I}_A = 1/P_{12} \quad (11)$$

$$\bar{I}_B = 1/P_{21} \quad (12)$$

So, the triad sequence structure can be calculated from equation 5-10, the number average sequence length can be calculated from equation 11 and 12, in terms of P_{12} , P_{11} , P_{21} and P_{22} obtained from equation 1-4.

The triad sequences for $P(\text{AM}/\text{AA})$ can be observed from the separated carbonyl carbon peaks in corresponding ^{13}C -NMR spectrum such as Figure 1.

Table 2 lists the calculated and observed triad sequences data in $P(\text{AM}/\text{AA})$ with different AA contents.

Figure 2 and 3 shows the probabilities of triad center in acrylamide unit (A) and acrylate unit

Tab. 2 Comparison between the calculated (Calc.) and observed (Obs.) data of sequence distribution in P(AM/AA)

No.		$P_3\{BBB\}$	$P_3\left\{\begin{smallmatrix} BBA \\ ABB \end{smallmatrix}\right\}$	$P_3\{ABA\}$	$P_3\{BAB\}$	$P_3\left\{\begin{smallmatrix} AAB \\ BAA \end{smallmatrix}\right\}$	$P_3\{AAA\}$	I_A	I_B
1	Calc.					0.24	0.76	7.14	
	Obs.					0.24	0.76	7.14	
2	Calc.	0.08	0.38	0.54	0.07	0.39	0.54	3.70	1.37
	Obs.	0.05	0.38	0.58	0.08	0.40	0.52	3.57	1.33
3	Calc.	0.13	0.47	0.40	0.14	0.48	0.38	2.63	1.61
	Obs.	0.12	0.47	0.41	0.13	0.48	0.39	2.70	1.54
4	Calc.	0.34	0.48	0.17	0.36	0.48	0.17	1.69	2.44
	Obs.	0.32	0.53	0.16	0.30	0.51	0.19	1.82	2.44
5	Calc.	0.62	0.38		0.64	0.36		1.30	4.35
	Obs.	0.63	0.37		0.66	0.34		1.25	4.35
6	Calc.	0.76	0.24		0.71	0.29		1.16	7.14
	Obs.	0.73	0.27		0.73	0.27		1.18	6.67

* Blanks in Table are due to that the contents are too low to measure from ¹³C-NMR spectra

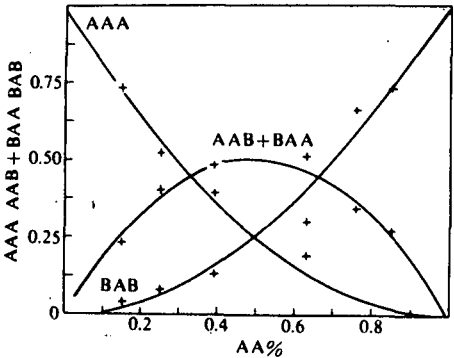


Fig.2 Triad (center in A) sequence probabilities in P(AM/AA) copolymers as a function of AA%
The solid lines were calculated from equation 5-7 and the points were observed from ¹³C-NMR spectra

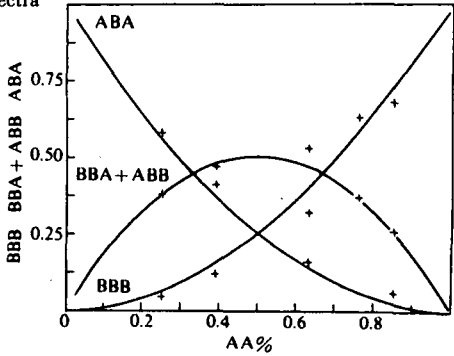


Fig.3 Triad (center in B) sequence probabilities in P(AM/AA) copolymers as a function of AA%
The solid lines were calculated from equation 8-10 and the points were observed from ¹³C-NMR spectra.

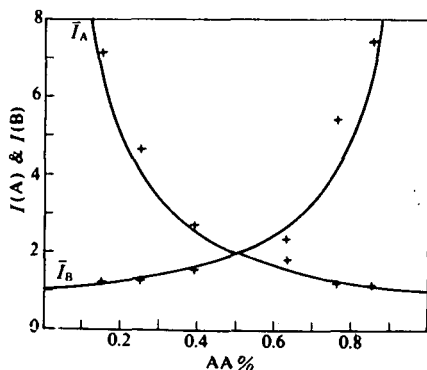


Fig.4 The number average length I_A and I_B as a function of AA%

The solid lines were calculated from equation 11 and 12, the points were observed from ^{13}C -NMR spectra

(B) as a function of B content (AA%) respectively. The solid lines were calculated according to equation 5–10, the points were observed from corresponding ^{13}C -NMR spectra.

Figure 4 shows the number average sequence length I_A and I_B as a function of AA%. The solid lines were calculated according to equation 11 and 12, the points were observed from ^{13}C -NMR spectra.

All of data can be evaluated that there is a good agreement between observed and calculated. The results appeared to be that the first order Markov statistic model fits in with P(AM/AA) copolymerization process.

The alkaline hydrolysis of polyacrylamide(PAM) is another important method to produce P(AM/AA) copolymer. The sequence structure difference between the products from preparation methods, one is from copolymerization and another is from hydrolysis, was analysed by comparing number average length data, as given in Table 3, Figure 5 and 6.

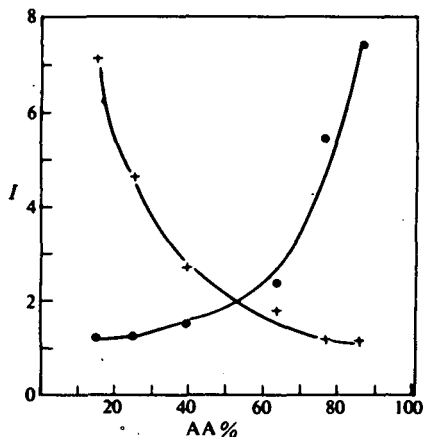


Fig.5 Number average sequence length I_A and I_B as function of AA% in P(AM/AA) copolymers
▲ acrylamide, + acrylate

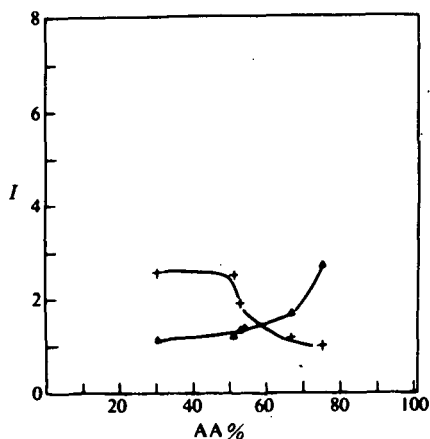


Fig.6 Number average sequence length I_A and I_B as function of AA% in hydrolyzed PAM
▲ acrylamide, + acrylate

The average sequence lengths of hydrolyzed PAM are much shorter than copolymerized ones with similar AA%. For example, 6# hydrolyzed sample (AA% = 74.2%), I_B equals 2.70, but, 5# copolymerized sample (AA% = 76.3%), I_B equals 5.41, the I_B value is double that of hydrolyzed one. Another typical example, 2# hydrolyzed sample (AA% = 50.4%) and $I_B = 1.20$, and 3# copolymerized sample with similar $I_B = 1.22$, but the AA content is only 14.6%, much lower than hydrolyzed one.

Tab. 3 Comparison of number average sequence length I_A and I_B in P(AM/AA) prepared from copolymerization (Co.) and hydrolysis (Hy.)

Co.	1	2	3	4	5	6
AA%	14.6	24.9	39.1	62.5	76.3	85.5
I_A	7.41	4.65	2.70	1.80	1.20	1.16
I_B	1.22	1.25	1.54	2.35	5.41	7.41
Hy.	1	2	3	4	5	6
AA%	30.0	50.4	52.3	53.2	65.8	74.2
I_A	2.56	2.50	1.89	1.89	1.16	1.00
I_B	1.16	1.20	1.34	1.37	1.68	2.70

A sudden change of slope at ~50% AA concentration was found below this value the average length I_B approaching one as shown in Figure 6. It implies ABA triad (centered acrylate unit), AAA and AAB triad (centered acrylamide unit) dominated in the mild hydrolyzed polyacrylamide. Smet^[9] reported that the alkaline hydrolysis of PAM involved two steps, the decrease of the hydrolysis velocity was rapid at about 40–50% conversion, resulted from the accumulation of electrostatic charge on the main chain. Our results can be reasonably explained by his idea.

Keywords:

Acrylamide-acrylate, Copolymer; Microstructure; ^{13}C -NMR.

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* After this paper submitted, we found similar topic was published by Truong.