

ESTIMATION OF REACTIVITY RATIOS OF METHYL ACRYLATE WITH N-ARYLMETHACRYL-AMIDE COPOLYMERS BY ^1H NMR METHOD

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ABSTRACT

The copolymerizations of methyl acrylate (MA) with different N-arylmethacrylamide (N-ArMA) were carried out in benzene solution by free radical initiation. The compositions of the copolymers were determined by ^1H NMR method. The monomer reactivity ratios were calculated by the Fineman-Ross (F-R) method. The reactivity ratios and the activity of various N-ArMA with MA were investigated.

INTRODUCTION

Measurement of reactivity ratios in vinyl copolymerizations is still to be a problem. The necessary experiments appear to be straightforward, providing the equation for the relation between monomer feeds and copolymers compositions. The fitting of corresponding feed and copolymer compositions is not without pitfalls, however. Many of the available reactivity ratios in the literature are deficient because of unsuspected problems which were involved in estimation procedures, use of inappropriate mathematical models to link polymer and feed compositions and experimental or analytical difficulties.^[1,2] Many of the analytical difficulties can be avoided by replacing the compositional analysis of copolymers by gas chromatographic measurement of the monomer loss during the course of the copolymerization.^[3,4] In recent years, the value of ^1H NMR spectroscopy in the analysis of copolymers and of sequence distributions has been fully recognized.^[5,6] Many copolymer systems have been studied by means of ^1H NMR spectroscopy including a number of them involving dienes^[7-13].

Comparing to the chemical methods the ^1H NMR method are sensitive and rapid. In fact, ^1H NMR spectroscopic techniques is well established as convenient method for determining the composition ratio of the constituent monomer units in copolymers.^[14,15]

In the present article, a convenient and rapid method for the determination of copolymer composition and the calculation of monomer reactivity ratios, the estimation of copolymers composition from ^1H NMR measurements and the determination of reactivity ratios are reported.

EXPERIMENTAL

Copolymerization

Methyl acrylate (MA) was washed successively with 5% sodium hydroxide solution and distilled water, then dried over anhydrous sodium sulfate, and finally distilled under vacuum, B. P. 81 — 82 °C

N-Arylmethacrylamide monomers were purified by recrystallized from benzene — methanol mixture. Their M.P.s were 102—104°C for N-p-Bromophenylmethacrylamide (N-p-BrPhMA), 90 — 92 °C for N-o-Tolylmethacrylamide (N-o-TMA), 86 — 88 °C for N-p-Tolylmethacrylamide (N-p-TMA), 106 — 107 °C for N-p-Chlorophenylmethacrylamide (N-p-ClPhMA).

2, 2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from chloroform.

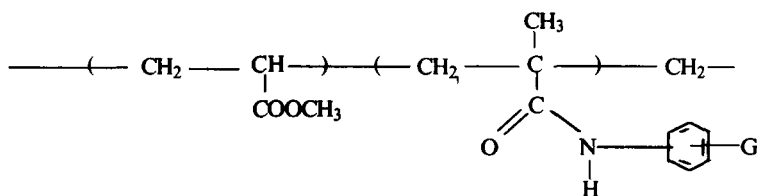
Copolymerization reaction for different monomer feed ratios were carried out in benzene solution at 70 °C with AIBN as the initiator. Since the differential form of the copolymer equation was used to calculate the monomer reactivity ratios, the conversion of monomers was in all cases restricted within 10%.

Measurement of ^1H NMR spectra :

^1H NMR spectra of all the copolymer samples, dissolved in CDCl_3 , were obtained with a Varian FT80A spectrometer, and TMS as an internal reference.

RESULTS AND DISCUSSION

The monomer units of the copolymer, poly (MA-co-N-ArMA), can be written as :



where G represents: $-\text{CH}_3$, $-\text{Br}$, $-\text{Cl}$.

The distribution of protons is an important factor to distinguish the units in the copolymers chain. Figure 1 shows typical spectra for a series of MA-co-N-p-BrPhMA copolymer samples. The signals due to methoxyl protons of MA units and phenyl protons of N-p-BrPhMA units appear distinctly at 3.59 and 7.48ppm. It can easily be seen from the spectra that the composition of the above copolymers is best determined from the respective peak areas of these group. The peak areas of these copolymers are printed out to facilitate the determination of copolymer composition. The alpha methyl protons, methylene and methine protons in MA and N-p-BrPhMA units overlap with each other and consequently are of very little use in the determination of composition.

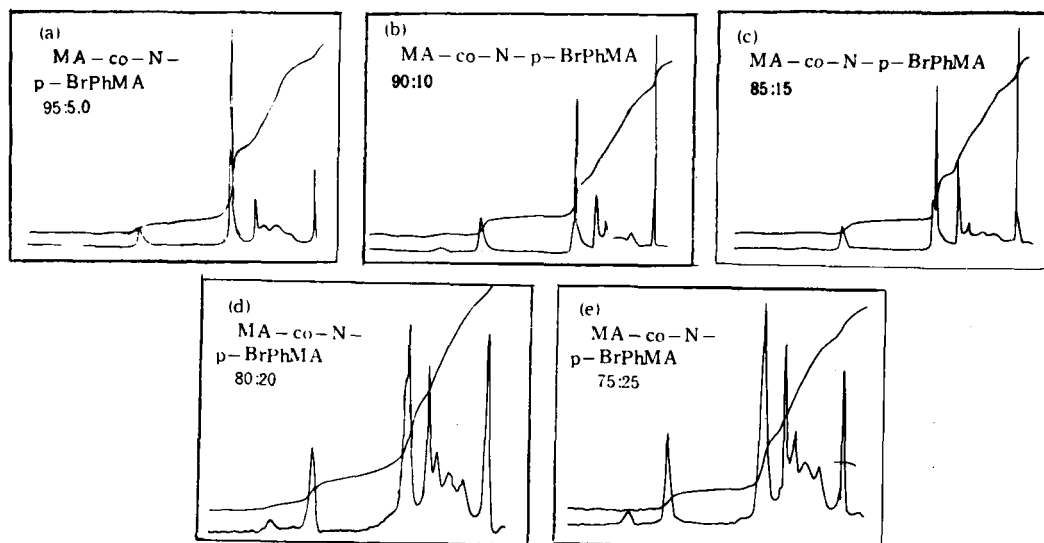


Fig. 1 Typical ^1H NMR spectrum of MA-co-N-p-BrPhMA copolymer, the composition ratio of the copolymers were: (a) 95:5 (b) 90:10 (c) 85:15 (d) 80:20 (e) 75:25.

From the copolymer structure, the following expressions are derived:

$$I_{\text{OCH}_3} \propto 3 \text{ (No. of MMA units in the chain)}$$

$$I_{\text{Ph}} \propto 4 \text{ (No. of N-ArMA units in the chain)}$$

In which I_{OCH_3} , I_{Ph} are the integral peak areas of $-\text{OCH}_3$ and phenyl group protons, respectively.

If X is the molar ratio N-p-BrPhMA/MA in the copolymer, then

$$I_{\text{Ph}} / I_{\text{OCH}_3} = 4/3 X \dots\dots\dots (1)$$

Hence, by measuring the intensities of the $-\text{OCH}_3$ and $-\text{C}_6\text{H}_4-$ protons peaks, the molar ratios of the two monomer units can be obtained.

The intensities of various peaks were obtained from the print out of the spectra; on applying the above expressions, the molar ratios of the two monomer units as well as the molar compositions of the individual monomer units were evaluated. The compositions determined using eq. (1) are given in Table 1

Table 1 Copolymerization of MA (M_1) and N-p-BrPhMA (M_2)

No.	1	2	3	4	5
f_1	0.172	0.252	0.335	0.705	0.722
f_2	0.111	0.167	0.222	0.348	0.372

From the values of feed compositions and molar ratios of monomer units, the reactivity were evaluated by using the Fineman-Ross method. The equation for F-R method can thus be written as :

$$(F/f)(f-1) = r_1(F^2/f) - r_2 \dots\dots\dots (2)$$

The typical values obtained by the F-R method are tabulated (Table 2).

Table 2 Evaluation of reactivity ratios for MA-co-N-p-BrPhMA

No.	1	2	3	4	5
f	0.172	0.252	0.335	0.705	0.722
F	0.111	0.167	0.222	0.348	0.372
F^2/f	0.072	0.110	0.148	0.172	0.192
$(F/f)(f-1)$	-0.536	-0.496	-0.442	-0.418	-0.385

Figure 2 show the plot of F-R method for the determination of reactivity ratios using the compositions obtained from eq. 2 and Table 2.

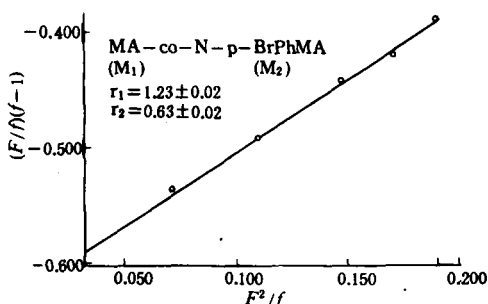


Fig.2 Plot of $(F/f)(f-1)$ vs. F^2/f for MA (M_1) with N-p-BrPhMA (M_2)

The reactivity ratio was found to be $r_1 = 1.23 \pm 0.02$, $r_2 = 0.63 \pm 0.02$.

Similarly, the composition of the MA-co-N-p-ClPhMA, MA-co-N-p-TMA, MA-co-N-o-TMA copolymers estimated by ^1H NMR method are summarized in Table 3.

Table 3 Composition of the MA-co-N-p-ClPhMA, MA-co-N-p-TMA, MA-co-N-o-TMA

No.	MA-co-N-p-ClPhMA		MA-co-N-p-TMA		MA-co-N-o-TMA	
	f_1	F_1	f_1	F_1	f_1	F_1
1	0.121	0.057	0.152	0.053	0.137	0.053
2	0.257	0.111	0.233	0.111	0.386	0.111
3	0.397	0.177	0.306	0.177	0.875	0.177
4	0.504	0.250	0.351	0.250	1.335	0.250

Fig. 3 showed the typical ^1H NMR spectrum of copolymers of the (a) MA-co-N-p-TMA 13.2 : 86.8, (b) MA-co-N-o-TMA 12.0 : 88.0, (c) MA-co-N-p-ClPhMA 20.0 : 80.0.

In ^1H NMR spectra, features to be noted are : (1) the peaks due to the methyl group of the N-ArMA units overlap at 1.19 to 1.75ppm relative to TMS; (2) the peaks due to the backbone methylene group and methine protons overlap at 2.26 to 2.29ppm; (3) the peaks due to the methoxy protons of the MA unit at 3.64 to 3.66ppm; (4) the peaks due to the phenyl group and -NH- group at 7.00 to 7.50ppm

The values of the copolymers obtained by the F-R method are summarized in

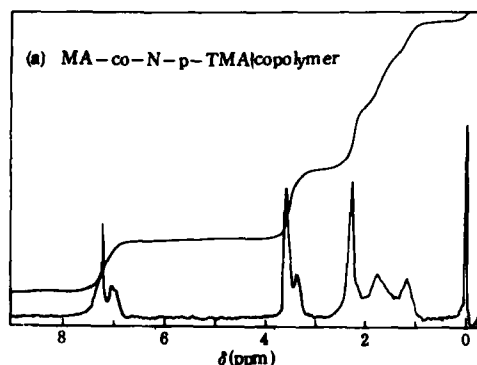


Fig.3 (a) Typical ^1H NMR spectrum of MA-co-N-p-TMA copolymer

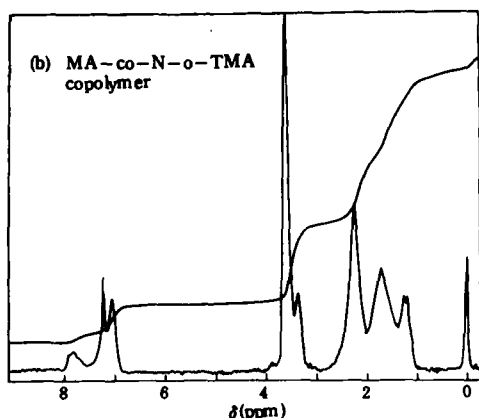


Fig.3 (b) Typical ^1H NMR spectrum of MA-co-N-o-TMA copolymer

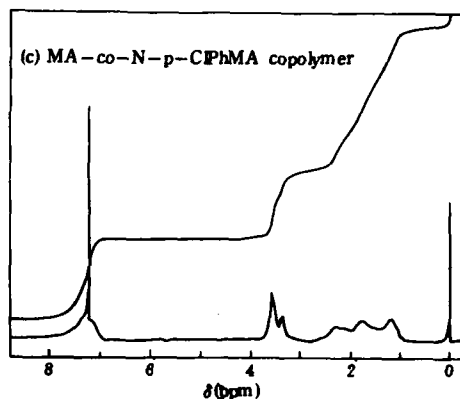


Fig.3 (c) Typical ^1H NMR spectrum of MA-co-N-p-ClPhMA copolymer

Table 4.

Table 4 Evaluation of reactivity ratios for MA-co-N-ArMA

MA-co-N-ArMA	No.	1	2	3	4
MA-co-N-p-TMA	f	0.152	0.233	0.306	0.351
	F	0.053	0.111	0.177	0.250
	$(F/f)(f-1)$	-0.294	-0.366	-0.401	-0.461
	F^2/f	0.018	0.053	0.102	0.178
MA-co-N-o-TMA	f	0.138	0.386	0.875	1.335
	F	0.053	0.111	0.177	0.250
	$(F/f)(f-1)$	-0.330	-0.177	-0.025	0.063
	F^2/f	0.020	0.032	0.036	0.047
MA-co-N-p-ClPhMA	f	0.121	0.257	0.397	0.504
	F	0.053	0.111	0.177	0.250
	$(F/f)(f-1)$	-0.384	-0.321	-0.268	-0.246
	F^2/f	0.023	0.048	0.079	0.124

Fig. 4 showed the plots of F-R method for the determination of reactivity ratios using the compositions obtained from Eq. 2 and Table 4.

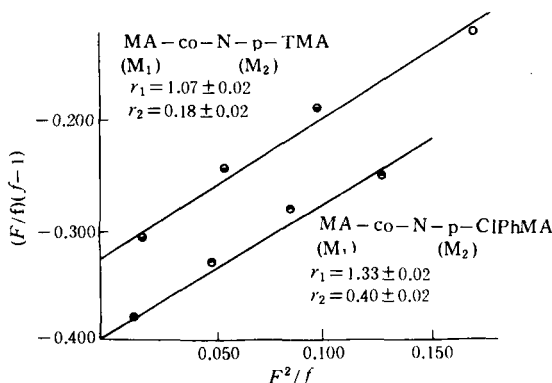


Fig. 4 Fineman – Ross method for the determination of reactivity ratios of the MA-co-N-ArMA copolymers

The activities of various N-ArMA in contrast to MA by $1/r$ are summarized in Table 5.

Table 5 Reactivity ratios for MA with N-ArMA copolymerization

MA-co-N-ArMA	r_1 (MA)	r_2 (N-ArMA)	$r_1 r_2$	$1/r_1$
MA-co-N-p-BrPhMA	1.23 ± 0.02	0.63 ± 0.02	0.77	0.81
MA-co-N-p-CIPhMA	1.33 ± 0.02	0.40 ± 0.02	0.53	0.75
MA-co-N-p-TMA	1.07 ± 0.02	0.18 ± 0.02	0.19	0.93
MA-co-N-o-TMA	2.15 ± 0.02	0.39 ± 0.02	0.84	0.47

It can be seen the activities of N-ArMA with MA are in the following order :

N-p-TMA ($1/r = 0.93$) > N-p-BrPhMA ($1/r = 0.81$) > N-p-CIPhMA ($1/r = 0.75$)

Due to the ease of activity of N-ArMA monomer from above sequence, hence, the ease of formation of free radicals must follow the same sequence :

N-p-TMA $\cdot$ > N-p-BrPhMA $\cdot$ > n-p-CIPhMA $\cdot$

At the same time the stability of free radicals are of the same order :

N-p-TMA $\cdot$ > N-p-BrPhMA $\cdot$ > N-p-CIPhMA $\cdot$

The more stable the free radical, the easier it is formed.

The activity of N-ArMA depends on the structure of N-ArMA. It is well known, any factor that stabilizes the free radical more than it stabilizes the monomer should increase the activity of monomer; any factor that makes the free radical less stable should decrease activity of monomer. The chloro atom in the N-p-CIPhMA monomer which is a strongly electron-withdrawing substituent apparently act-through the benzene ring—to make the carbon-carbon double bond more “positive”, and thus increase stability of N-p-CIPhMA monomer and decrease its activity. The methyl group is a good electron-releasing substituents and thus decrease the stability of N-p-TMA monomer and increase its activity.

Keywords :

Reactivity Ratios; Copolymerization; Methyl Acrylate ; N-Arylmethacrylamide; ^1H -NMR Method.

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