Estimation of Reactivity Ratios of *N*-Methacryloyloxyphthalimide Copolymers by ^{1}H NMR

A. F. SHAABAN and A. A. KHALIL, *Chemistry Department, Faculty of Science, Benha University, Benha,* and N. N. MESSIHA, *Laboratory of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt*

Synopsis

Copolymerizations of *N*-methacryloyloxyphthalimide (NMP) with methyl acrylate (MA), methyl methacrylate (MMA), and acrylonitrile (AN) was carried out in dimethylformamide using azobisisobutyronitrile (AIBN) as an initiator at 60°C. The estimation of the copolymer compositions were carried by ^{1}H nuclear magnetic resonance (NMR) spectroscopy. The monomer reactivity ratios for NMP-MA, NMP-MMA, and NMP-AN systems were found to be $r_1 = 1.223$, $r_2 = 0.208$, $r_1 = 1.441$, $r_2 = 0.704$, $r_1 = 1.496$ and $r_2 = 0.228$, respectively, by Kelen-Tüdős method. Also, the Q and e values for NMP monomer was found to be $Q = 0.90$ and $e = 0.01$, respectively.

INTRODUCTION

Interest on multifunctional synthetic polymers or copolymers is steadily increasing, either as macromolecular catalysts,[1-4] or as macromolecular drugs (antiheparin)[5-8] or antimetastatic agents.[9] In our previous work, activated drug-binding matrices were prepared based on *N*-acryloyloxy- and *N*-methacryloyloxyphthalimides.[10] Free radical copolymerization is a method of modifying the properties of polymers. The incorporation of higher proportions of functional monomers and its better distribution within the polymer chain can be achieved through fundamental studies on copolymerization parameters under specified reaction conditions. ^{1}H nuclear magnetic resonance (NMR) spectroscopy offers simple and rapid evaluation of copolymer composition[11-13] compared to other techniques such as radiometry[14] and isotopic labelling.[15] In recent years, the value of ^{1}H NMR spectroscopy in the analysis of copolymers and of sequence distributions has been fully recognized. In the present article, the estimation of copolymer composition from ^{1}H NMR measurements and the determination of monomer reactivity ratios for copolymerizations of *N*-methacryloyloxyphthalimide (NMP) with methyl acrylate (MA), methyl methacrylate (MMA), and acrylonitrile (AN) are reported.

EXPERIMENTAL

NMP was prepared by the reaction of methacryloyl chloride with *N*-hydroxyphthalimide in the presence of triethylamine according to the method previously described.[10] MA, MMA, and AN (E. Merck, Darmstadt, Germany) were freed from inhibitors by distillation under reduced pressure and the

Journal of Applied Polymer Science, Vol. 37, 2051–2058 (1989)
 CCC 0021-8995/89/072051-08$04.00

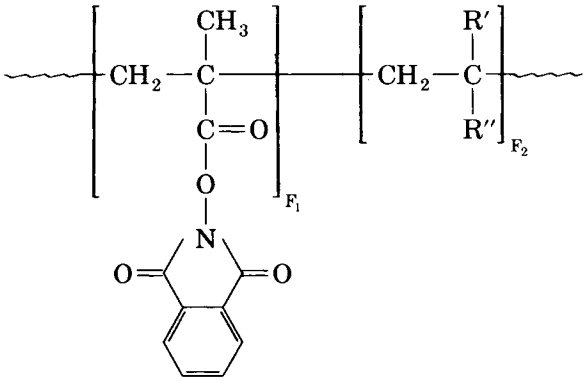
center cuts retained for use. Azobisisobutyronitrile (AIBN) was purified by recrystallization from absolute alcohol (m.p. 102°C).

The copolymers were obtained by solution polymerization. Predetermined amounts of the comonomers were placed in glass tubes, and diluted with dimethylformamide so that the total monomer composition was about 1.5 mol/L. Polymerization was commenced by adding AIBN in a concentration of 1 mol/100 mol monomers. The tubes were flushed with oxygen-free nitrogen for 10 min, capped, and thermostatted at 60°C for 30–60 min depending on the comonomer pairs and composition. The conversions were kept low (7–10%) and all copolymers were purified by reprecipitation from methanol, washed several times, dried, and weighed.

^{1}H NMR spectra of all the copolymer samples (in DMSO-d6 as a solvent and using TMS as zero reference), were obtained with a Varian EM-390 Spectrometer operating at 90 MHz.

RESULTS AND DISCUSSION

In the present investigation, the copolymerization parameters for NMP-MA, NMP-MMA, and NMP-AN systems were studied. The copolymer composition of each sample was calculated from ^{1}H NMR spectroscopy. The structure of the copolymer systems can be written as:



	R′	R″
NMP-MA	H	$COOCH_3$
NMP-MMA	CH_3	$COOCH_3$
NMP-AN	H	$C\equiv N$

The ^{1}H NMR spectra of NMP-MA copolymer samples showed the following characteristic peaks: (i) one peak at δ7.8 due to the phenyl protons of NMP units.[10] (ii) one peak at δ3.6 due to the methoxy protons of MA unit. (iii) one broad peak in the highest field centered at δ1.5 due to the α-methyl, methyne, and methylene protons of both NMP and MA units. Figure 1 shows typical spectrum for NMP-MA copolymer sample as an example.

The ^{1}H NMR spectra of NMP-MMA copolymer samples have the similar characteristic peaks except that the highest peak due to the α-methyl and methylene protons of both NMP and MMA units was centered at δ1.2. Figure

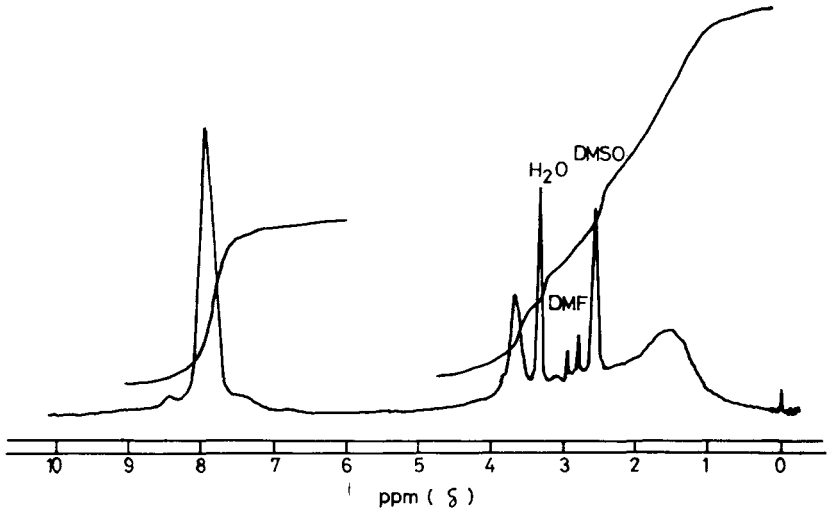


Fig. 1. ^{1}H NMR spectrum of NMP-MA copolymer sample prepared at molar fraction $f_1 = 0.40$.

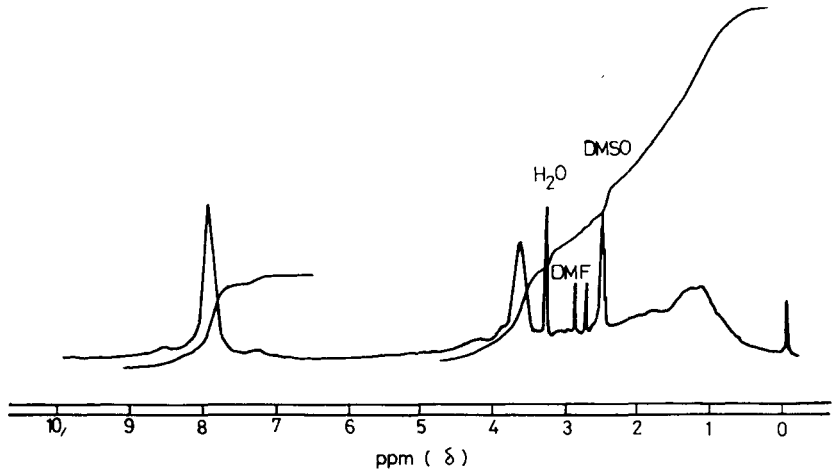


Fig. 2. ^{1}H NMR spectrum of NMP-MMA copolymer sample prepared at molar fraction $f_1 = 0.30$.

2 illustrates the ^{1}H NMR spectrum for a copolymer sample of NMP-MMA, as an example.

The ^{1}H NMR spectra of NMP-AN copolymer samples illustrates the following characteristic peaks:

1. One peak at δ7.9 due to the phenyl protons of NMP units.
2. One peak centered at δ3.2 due to methyne proton of AN units.
3. One peak centered at δ2.2 due to methylene protons of both NMP and AN units.
4. One peak at δ1.65 due to α-methyl protons of NMP units. Figure 3 shows typical spectrum for a sample of copolymer NMP-AN as example, as well as a sample of poly(acrylonitrile).

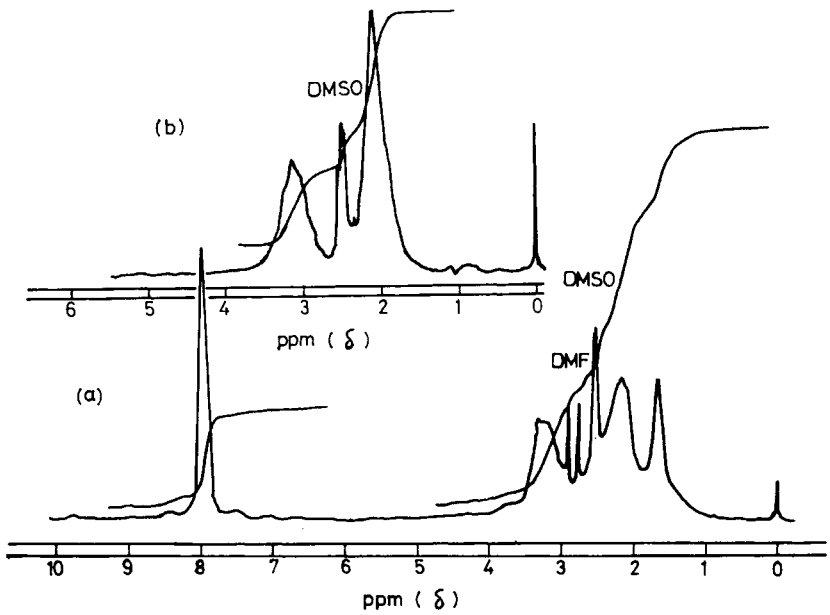


Fig. 3. ^{1}H NMR spectra of (a) NMP-AN copolymer sample prepared at molar fraction $f_1 = 0.10$ and (b) polyacrylonitrile.

The approach of Grassie et al.[16] has been used to estimate the copolymer composition of each sample. From the copolymer structure, the following expressions are derived:

$$I_{C_6H_4} \propto 4(\text{No. NMP units in chain})$$

$$I_{OCH_3} \propto 3(\text{No. MA or MMA units in chain})$$

$$I_{CH} \propto (\text{No. AN units in chain})$$

in which $I_{C_6H_4}$, I_{OCH_3}, and I_{CH} are the integrated tracers of $\diagdown C_6H_4$, $-OCH_3$ and $\diagdown CH-$ protons, respectively. If b is the molar ratio (M_1/M_2) in the copolymer, then:

$$I_{C_6H_4}/I_{OCH_3} = 4/3b \tag{1}$$

for NMP-MA or NMP-MMA copolymers and

$$I_{C_6H_4}/I_{CH} = 4b \tag{2}$$

for NMP-AN copolymer.

Tables I to III give the analytical data for copolymerization reactions of NMP with MA, MMA, and AN. From the values of feed and copolymer compositions, the monomer reactivity ratios were evaluated using the Fineman-Ross[17] and Kelen-Tüdős[18] methods. Figure 4 shows the Kelen-Tüdős

TABLE I
Analytical Data for Copolymerization of NMP with MA

Feed composition (a)	% Conversion	Copolymer composition (b)
2.3333	9.7	3.3750
1.5000	8.4	2.4827
1.0000	7.9	1.9883
0.6667	8.8	1.4353
0.4286	7.1	0.9681
0.2500	7.0	0.7045

[a] a and b are the molar ratios of M_1 and M_2 in the feed and copolymer, respectively.

TABLE II
Analytical Data for Copolymerization of NMP with MMA

Feed composition (a)	% Conversion	Copolymer composition (b)
2.3333	7.4	3.4351
1.5000	6.5	2.1464
1.0000	6.3	1.4000
0.6667	8.2	0.9138
0.4282	7.6	0.6389

TABLE III
Analytical Data for Copolymerization of NMP with AN

Feed composition (a)	% Conversion	Copolymer composition (b)
0.4286	8.3	1.0522
0.3333	8.5	0.8616
0.2500	6.8	0.7665
0.1765	7.5	0.5157
0.1111	8.3	0.4227
0.0526	7.1	0.1899

plots for the three systems studied. The values of r_1 and r_2 from the Kelen-Tüdős method are almost identical to those obtained by the Fineman-Ross method. Typical values obtained by the two methods are tabulated in Table IV. The r_1r_2 values for NMP-MA and NMP-AN systems (0.254 and 0.341, respectively) indicate that the copolymers in both cases should have a random distribution of the monomer units with a tendency toward alternation, while for the NMP-MMA system the r_1r_2 value (1.014) illustrates a low tendency of the monomer units to alternate and the copolymer should be composed mainly of small sequences of the same type. Figure 5 illustrates the composition curves and indicates that all systems studied gave no azeotropic copolymers.

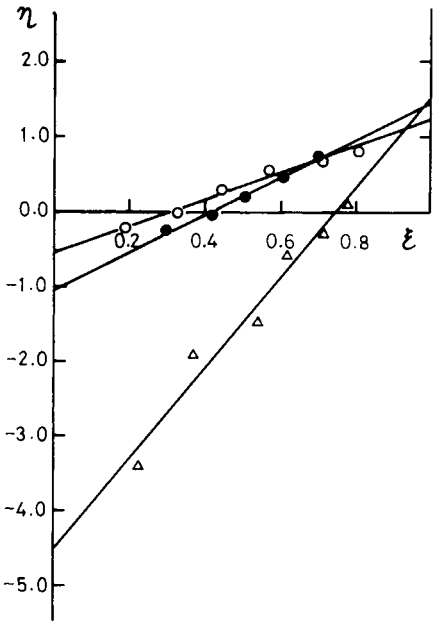


Fig. 4. Kelen-Tüdős plots for copolymerizations of NMP with (○) MA, (●) MMA, and (△) AN.

$$\xi = \frac{a^2}{\alpha b + a^2} \quad \text{and} \quad \eta = \frac{a(b-1)}{\alpha b + a^2}$$

where a and b are the molar ratios (M_1/M_2) of the comonomer in the feed and copolymer, respectively, and

$$\alpha = \frac{a_{\min} \cdot a_{\max}}{(b_{\min} \cdot b_{\max})^{1/2}}$$

TABLE IV
Monomer Reactivity Ratios for Copolymerizations of NMP with MA, MMA, and AN

	Fineman-Ross method		Kelen-Tüdős method		
$M_1 - M_2$	r_1	r_2	r_1	r_2	$r_1 r_2$
NMP-MA	1.147 ± 0.049	0.170 ± 0.039	1.223 ± 0.097	0.208 ± 0.029	0.254
NMP-MMA	1.370 ± 0.254	0.641 ± 0.239	1.441 ± 0.179	0.704 ± 0.110	1.014
NMP-AN	1.400 ± 0.211	0.223 ± 0.021	1.496 ± 0.162	0.228 ± 0.019	0.341

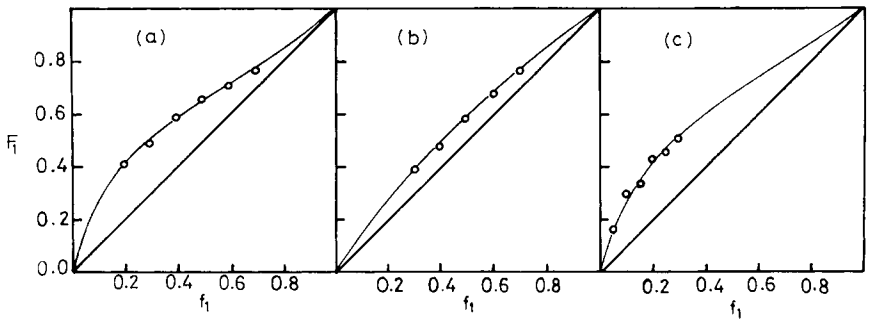


Fig. 5. Composition curves for copolymerizations of NMP with (a) MA, (b) MMA, and (c) AN. Line represents calculated values and (○) represent experimental values. f_1 = molar fraction of M_1 in feed and F_1 = molar fraction of M_1 in copolymer.

The Q and e values were calculated by using the Alfrey-Price equations[19]:

$$e_1 = e_2 \pm (-\ln r_1 r_2)^{1/2} \tag{3}$$

$$Q_1 = (Q_2/r_2)\exp[-e_2(e_2 - e_1)] \tag{4}$$

The Q and e values that represent the extent of resonance stabilization and polarity of the double bond, respectively, in a monomer and its radical are extensively tabulated by Young[20] from earlier copolymerization data. Thus, the Q and e values for NMP were obtained by using the monomer reactivity ratios determined for the copolymer systems NMP-MA, NMP-MMA, and NMP-AN (Table IV) and using the Q and e values for the MA, MMA, and AN.[20] The product $r_1 r_2$ value for NMP-MMA system was found to be > 1 and was thus set equal to 1 so that Eq. (3) could be solved.[21] The average Q and e values for NMP monomer were calculated and were found to be $Q = 0.90$ and $e = 0.01$, respectively, and are in agreement with those reported in the literature[20] for the esters of acrylic acid.

References

1. C. G. Overberger, R. Sitaramaiah, T. St. Pierre, and S. Yaroslwsky, *J. Am. Chem. Soc.*, **87**, 3270 (1965).
2. C. G. Overberger, T. St. Pierre, C. Yaroslawsky, and S. Yaroslawsky, *J. Am. Chem. Soc.*, **88**, 1184 (1966).
3. C. G. Overberger, J. C. Salamone, and S. Yaroslawsky, *J. Am. Chem. Soc.*, **89**, 6321 (1967).
4. C. G. Overberger and H. Maki, *Macromolecules*, **3**, 220 (1970).
5. M. A. Marchisio, C. Sbertoli, G. Farina, and P. Ferruti, *Eur. J. Pharmacol.*, **12**, 236 (1970).
6. M. A. Marchisio, T. Longo, P. Ferruti, and F. Danusso, *Eur. Surg. Res.*, **3**, 240 (1971).
7. M. A. Marchisio, P. Ferruti, and T. Longo, *Eur. Surg. Res.*, **4**, 312 (1972).
8. M. A. Marchisio, T. Longo, and P. Ferruti, *Experientia*, **29**, 93 (1973).
9. P. Ferruti, F. Danusso, G. Franchi, N. Polentarutti, and S. Garattini, *J. Med. Chem.*, **16**, 496 (1973).
10. A. F. Shaaban, M. M. H. Arief, A. A. Khalil, and N. N. Messiha, *Acta Polymerica*, in press.
11. W. M. Ritchy and L. E. Ball, *J. Polym. Sci.*, **B4**, 557 (1966).
12. K. Ito and Y. Yamashita, *J. Polym. Sci.*, **B3**, 625, 631, 637 (1965).
13. S. Pitchumani, C. Rami Reddy, and S. Rajadurai, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 277 (1982).
14. J. C. Bevington and B. W. Malpass, *Eur. Polym. J.*, **1**, 19 (1965).

15. M. Shima and A. Kotera, *J. Polym. Sci.*, **A-1**, 1115 (1963).
16. N. Grassie, B. J. D. Torrence, J. D. Fortune, and J. D. Gemmel, *Polymer*, **6**, 653 (1965).
17. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 258 (1950).
18. T. Kelen and F. Tüdős, *J. Macromol. Sci.-Chem.*, **A9**, 1 (1975).
19. T. Jr. Alfrey and C. J. Price, *J. Polym. Sci.*, **2**, 101 (1947).
20. L. J. Young, *Polymer Handbook*, 2nd ed., J. Brandrup, and E. H. Immergut, Eds., New York, Wiley-Interscience, 1975, pp. II.105–II.404.

Received February 16, 1988
Accepted March 29, 1988