

Copolymerization of Ethyl Methacrylate with N-(3- or 4-Halogenphenyl)maleimides: The Monomer Reactivity Ratios

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ABSTRACT: The copolymerization of ethyl methacrylate [I] with N-(3-chlorophenyl)maleimide [II], N-(4-chlorophenyl)maleimide [III], N-(3-bromophenyl)maleimide [IV], and N-(4-bromophenyl)maleimide [V] was carried out in benzene, using α,α' -azobisisobutyronitrile as an initiator at 60°C. The copolymer compositions were estimated by elemental analysis. The monomer reactivity ratios of [I] (r_1) with [II], [III], [IV], and [V] (r_2) were determined by the Fineman–Ross and Kelen–Tüdös methods, and recalculated using the nonlinear minimization algorithm based on Mayo–Lewis's method (RREVM). The Alfrey–Price copolymerization parameters Q and e for N-(3- or 4-halogenphenyl)maleimides were also calculated. The kind of halogen atom (Br- or Cl-) and its position in the phenyl ring of maleimide on the values of reactivity ratios r_1 and r_2 are discussed. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2924–2930, 1999

Key words: copolymerization; ethyl methacrylate; N-(3- or 4-halogenphenyl)maleimides; monomer reactivity ratio

INTRODUCTION

During the past several years many publications appeared describing the chemical modification of various vinyl polymers such as polymers of styrene, alkyl acrylates or methacrylates, vinyl acetate, vinyl chloride, vinylidene chloride, and also butadiene by an addition N-substituted maleimides (N-aryl- or N-alkyl-aryl-), as well as N-(mono-halogenphenyl)maleimides.^{1–9} It is known that such copolymers have better thermal stability than polymers of vinyl monomers or poly(butadiene), and in addition, the copolymers containing N-(monohalogenphenyl)maleimides are also less flammable. In earlier papers we described the reactivity ratios of some alkyl methacrylates with N-(tolyl)maleimide¹⁰ as well as some properties of copolymers of alkyl methacrylates with N-(phenyl)maleimide,⁹ N-(4-chlorophenyl)maleimide,¹¹ or N-(4-bromophenyl)maleimide.¹²

This paper presents further results on the free-radical copolymerization of alkyl methacrylates

with N-(monohalogenphenyl)maleimides. The reactivity ratios of ethyl methacrylate (r_1) and N-(3- or 4-bromophenyl)maleimides and N-(3- or 4-chlorophenyl)maleimides (r_2), respectively, were determined in benzene and calculated by Fineman–Ross (F-R)¹³ and Kelen–Tüdös (K-T)^{14–16} procedures, and next recalculated by nonlinear minimization algorithm (RREVM)¹⁷ based on Mayo–Lewis's method.^{18,19} The aim of this work was the determination of reactivity ratios for the pairs of comonomers as well as evaluation of the Alfrey–Price's²⁰ copolymerization parameters Q_2 and e_2 for N-(3- or 4-halogenphenyl)maleimides. On the other hand, we tried to compare the influence of the kind of halogen atom (Br- or Cl-) and its position in the phenyl ring of maleimide on the values of reactivity ratios r_1 and r_2 .

EXPERIMENTAL

Monomers

Ethyl Methacrylate (EtMA), Pure (Fluka AG, Switzerland)

The monomer was separated from the inhibitor in a standard manner²¹ and dried over anhydrous

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magnesium sulphate, and then distilled under reduced pressure just before use. ($n_D^{20} = 1.4140$; $d_4^{20} = 0.9110 \text{ g/cm}^3$).

N-(3- or 4-Halogenphenyl)maleimide

N-(3- or 4-halogenphenyl)maleimide were prepared in the same manner as for other maleimides,^{8,11,12,22,23} i.e., by the reaction of maleic anhydride with 3- or 4-bromoaniline and 3- or 4-chloroaniline, respectively, followed by cyclodehydration of the resulting maleamic acid. All the reactions were carried out in acetone using acetic anhydride and a small amount of sodium acetate as dehydrating agents, which greatly increased the reaction rate. The monomers were recrystallized from different organic solvents and the structures confirmed by measuring melting point and by elemental, IR, and ¹H-NMR analysis.

N-(3-bromophenyl)maleimide [*N*-(3-BrPh)MI]

The monomer was recrystallized from CCl₄, mp 133–134°C. Elemental analysis: Calc. (%) C—47.65, H—2.40, N—5.56. Found (%) C—48.25, H—2.35, N—5.49.

N-(4-bromophenyl)maleimide [*N*-(4-BrPh)MI]

The monomer was recrystallized from CH₂Cl₂, mp 110–111°C. Elemental analysis: Calc. (%) C—47.65, H—2.40, N—5.56. Found (%) C—48.06, H—2.49, N—5.72.

N-(3-chlorophenyl)maleimide [*N*-(3-ClPh)MI]

The monomer was recrystallized from CCl₄, mp 92–93°C. Elemental analysis: Calc. (%) C—57.83, H—2.89, N—6.75. Found (%) C—58.76, H—2.88, N—6.81.

N-(4-chlorophenyl)maleimide [*N*-(4-ClPh)MI]

The monomer was recrystallized from ethanol, mp 108–109°C. Elemental analysis: Calc. (%) C—57.83, H—2.89, N—6.75. Found (%) C—59.78, H—2.88, N—6.81.

α, α' -Azobisisobutyronitrile (AIBN), Pure (BDH Chemicals Ltd., England)

Reagent grade AIBN was dissolved in chloroform. The solution was filtered and the solute was precipitated with diethyl ether. The procedure was repeated twice. The mp was 102°C.

Solvents

The solvents—benzene, methylene chloride, ethanol, tetrachloromethane, acetone, or methanol—were all analytical grade reagents. They were purified using standard methods and were distilled just before use.

Copolymerization

The free-radical copolymerization was carried out in benzene in a sealed glass tubes ($10 \pm 2 \text{ mL}$) at $60 \pm 1^\circ\text{C}$ with AIBN as initiator. The appropriate amount of comonomers in various ratios were weighed and placed with solvent and initiator into the tubes. The total monomer concentration was 1.259 mol/L for EtMA/*N*-(3- or 4-BrPh)MI mixtures and 1.034 mol/L for EtMA/*N*-(3- or 4-ClPh)MI mixtures. The time of copolymerization was established experimentally to reach the conversion of monomers of around 10% (about 2–3 h). After that time the tubes were removed from bath and cooled down to room temperature, and the reaction mixture was poured into a large amount of acetone, while vigorous stirring. The copolymer was isolated and purified by two precipitations—dissolving cycles in acetone and methanol. The copolymer was then filtered off and dried in vacuum to constant weight.

Copolymer Analysis

The copolymer compositions were calculated from nitrogen contents determined by elemental analysis of copolymers, which was performed with EA1108 Elemental Analyzer (Carbo Erba, Italy). Each copolymer was analyzed for nitrogen three times. The results were reproducible within 0.2–0.3%. For each of the comonomers, two series of measurements for nine compositions were made.

RESULTS AND DISCUSSION

The copolymerization of EtMA (M_1) and *N*-(3- or 4-halogenphenyl)maleimide (M_2) with AIBN as initiator at 60°C was carried out in benzene. The conversion was limited to about 5–10%. The average results for two series of copolymerization experiments are shown in Tables I–IV.

The well-known monomer–copolymer composition equation^{18,19} was linearized by Fineman and Ross¹³ as follows:

Table I Experimental Data for the Copolymerization of Ethyl Methacrylate (M_1) with N-(3-Bromophenyl)Maleimide (M_2) at 60°C in the Presence of AIBN (0.5%) in Benzene^a

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt %)	Polymerization Rate (wt %/h)	N Content in Copolymer (wt %)	Fraction of N-(3-BrPh)MI in Copolymer (mol %)	Mean Sequence Length	
M_1	M_2						μ_1	μ_2
90	10	1.82	6.88	3.78	0.22	1.87	294	1.00
80	20	1.87	6.44	2.83	0.49	4.20	128	1.00
70	30	2.10	5.96	2.83	0.80	7.08	74.1	1.00
60	40	2.25	4.80	2.13	1.18	10.77	47.1	1.01
50	50	2.42	6.05	2.50	1.50	14.40	34.1	1.01
40	60	2.56	6.41	2.51	2.00	20.23	23.0	1.01
30	70	2.75	8.67	3.15	2.51	27.16	15.9	1.02
20	80	3.00	12.53	4.18	3.21	38.15	10.0	1.04
10	90	3.05	13.60	4.44	3.95	52.65	3.0	1.06

^a Total monomer concentration: 1.259 mol/L.

$$\frac{F}{f}(f-1) = r_1 \frac{F^2}{f} - r_2 \quad (1) \quad \text{where}$$

where

$$f = \frac{dM_1}{dM_2}; \quad F = \frac{m_1}{m_2}$$

Graphical plotting of Eq. (1) gives r_1 as the slope and r_2 as the intercept.The Kelen-Tüdös equation is also based on copolymerization equation^{18,19} and like other differential methods is obviously suitable for low-conversion data (<10%). The K-T procedure, in brief, is applied as follows¹⁴⁻¹⁶:

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad (2)$$

$$\eta = \frac{G}{\alpha + F}; \quad \xi = \frac{F}{\alpha + F}$$

$$G = \frac{X(\gamma - 1)}{\gamma}; \quad F = \frac{X^2}{\gamma}$$

$$\chi = \frac{M_1}{M_2}; \quad \gamma = \frac{m_1}{m_2};$$

 M_1 and M_2 are the molar concentrations in the monomer feed; m_1 and m_2 are the molar concentrations in the final copolymer for both eqs. (1) and (2).

$$\alpha = \sqrt{F_m \cdot F_M}$$

Table II Experimental Data for the Copolymerization of Ethyl Methacrylate (M_1) with N-(4-Bromophenyl)Maleimide (M_2) at 60°C in the Presence of AIBN (0.5%) in Benzene^a

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt %)	Polymerization Rate (wt %/h)	N Content in Copolymer (wt %)	Fraction of N-(4-BrPh)MI in Copolymer (mol %)	Mean Sequence Length	
M_1	M_2						μ_1	μ_2
90	10	1.08	7.64	7.06	0.24	2.01	268	1.00
80	20	1.29	6.85	5.29	0.51	4.39	120	1.01
70	30	1.35	6.26	4.65	0.83	7.37	68.2	1.01
60	40	1.40	6.41	4.59	1.23	11.40	43.5	1.02
50	50	1.35	7.29	5.39	1.66	16.11	29.5	1.02
40	60	1.54	9.57	6.22	2.19	22.68	19.7	1.04
30	70	1.65	10.65	6.47	2.79	31.26	13.0	1.05
20	80	1.75	11.90	6.80	3.34	40.54	9.03	1.08
10	90	1.82	12.40	6.91	4.18	57.74	5.01	1.16

^a Total monomer concentration: 1.259 mol/L.

Table III Experimental Data for the Copolymerization of Ethyl Methacrylate (M_1) with N-(3-Chlorophenyl)Maleimide (M_2) at 60°C in the Presence of AIBN (0.5%) in Benzene^a

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt %)	Polymerization Rate (wt %/h)	N Content in Copolymer (wt %)	Fraction of N-(3-ClPh)MI in Copolymer (mol %)	Mean Sequence Length	
M_1	M_2						μ_1	μ_2
90	10	1.83	7.10	3.21	0.38	3.18	88.2	1.00
80	20	1.83	4.60	2.51	0.94	8.17	33.2	1.01
70	30	2.08	6.05	2.91	1.47	13.28	19.7	1.02
60	40	2.16	9.75	2.89	1.89	17.62	14.4	1.03
50	50	2.25	11.00	4.89	2.33	22.48	10.9	1.04
40	60	2.33	6.61	2.84	2.90	29.29	7.91	1.05
30	70	2.45	8.05	3.29	3.36	35.28	6.25	1.07
20	80	2.66	8.60	4.23	4.05	45.21	4.47	1.10
10	90	2.80	9.30	4.43	5.10	62.96	2.68	1.21

^a Total monomer concentration: 1.034 mol/L.

is an appropriately chosen constant to obtain a uniform spread of the data ($\alpha > 0$). F_m and F_M are the lowest and highest values from experimental data. The variable can take only positive values in the interval (0, 1). Thus, by plotting the η values calculated from experimental data against ξ , a straight line is obtained, when extrapolated to $\xi = 0$ and $\xi = 1$, it gives $-r_2/\alpha$, and r_1 (both as intercepts).

Table V summarizes the values of reactivity ratios r_1 for EtMA and r_2 for N-(3- or 4-halogenphenyl)maleimide, determined according to F-R¹³ and K-T¹⁴⁻¹⁶ procedures and next recalculated by microcomputer program¹⁷ based on Mayo-Lewis's method.^{18,19} The program employs the Error-in-Variables-Model (RREVM) method to estimate reactivity ratios. In the calculations, the amounts of monomer 1 and 2 (0.3% accuracy) and

that of units of type 2 in the copolymer (accuracy 3.0%) were introduced as input parameters.

In the K-T methods, two calculation methods were used: the graphical method¹³ (I) and the graphical method with weight conversion taken into account¹⁴⁻¹⁶ (II). Figure 1 shows graphical solution of F-R method for the EtMA/N-(4-Br-Ph)MI system. Figures 2 and 3 show examples of K-T plots for the EtMA/N-(3-ClPh)MI system according to the graphical methods (I), and for EtMA(4-BrPh)MI system according to the graphical methods regarding conversion (II). In each case a good straight line was obtained. A comparison of r_1 and r_2 values resulting from the use of both the F-R and K-T methods shows only small differences between the two methods of calculations (Table V). However, even for the two methods of calculating within the K-T method, slight

Table IV Experimental Data for the Copolymerization of Ethyl Methacrylate (M_1) with N-(4-Chlorophenyl)Maleimide (M_2) at 60°C in the Presence of AIBN (0.5%) in Benzene^a

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt %)	Polymerization Rate (wt %/h)	N Content in Copolymer (wt %)	Fraction of N-(4-ClPh)MI in Copolymer (mol %)	Mean Sequence Length	
M_1	M_2						μ_1	μ_2
90	10	1.16	6.70	5.78	0.43	3.61	94.5	1.03
80	20	1.29	7.65	5.93	0.78	6.70	49.7	1.03
70	30	1.37	10.00	7.27	1.19	10.55	30.7	1.04
60	40	1.45	7.71	5.28	1.55	14.06	22.4	1.06
50	50	1.54	6.23	4.02	2.35	22.71	12.9	1.10
40	60	1.62	8.23	5.06	3.11	31.91	8.47	1.17
30	70	1.70	9.95	5.85	3.80	41.47	5.94	1.25
20	80	1.89	7.31	6.24	4.71	55.94	3.75	1.45
10	90	2.00	9.86	6.24	5.65	73.86	2.24	2.00

^a Total monomer concentration: 1.034 mol/L.

Table V Reactivity Ratios of Ethyl Methacrylate (r_1) with N-(3- or 4-Halogenophenyl) Maleimide (r_2) in Benzene and Q_2 and e_2 Values for N-(3- or 4-Halogenophenyl)Maleimide

Monomers	r_1, r_2	F-R	K-T (I)	K-T (II)	RREVM	Q_2^a	e_2^a
EtMA + N-(3-BrPh)MI	r_1	5.68	5.62	5.57	5.440	0.17	1.30
	r_2	0.10	0.08	0.07	0.051		
	$r_1 \times r_2$	0.57	0.49	0.40	0.280		
EtMA + N-(4-BrPh)MI	r_1	5.30	5.30	5.50	5.499	0.15	0.61
	r_2	0.18	0.16	0.16	0.149		
	$r_1 \times r_2$	0.95	0.84	0.88	0.824		
EtMA + N-(3-ClPh)MI	r_1	3.51	3.10	2.87	2.999	0.31	1.27
	r_2	0.21	0.13	0.12	0.100		
	$r_1 \times r_2$	0.73	0.43	0.35	0.300		
EtMA + N-(4-ClPh)MI	r_1	3.32	3.31	3.35	3.009	0.28	0.85
	r_2	0.31	0.32	0.32	0.208		
	$r_1 \times r_2$	1.03	1.07	1.08	0.626		

^a To calculate Q_2 and e_2 values, r_1 and r_2 due to the RREVM method are used. $Q_1 = 0.76$, $e_1 = 0.17$ for EtMA are used.²⁴

differences in r_2 values and somewhat higher in r_1 values are observed. The values of r_1 and r_2 obtained by using the RREVM program differs slightly more from those determined by F-R and K-T methods. By comparing r_1 and r_2 values (from Table V), one can confirm that the kind of halogen atom (Br- or Cl-) as well as their position in the phenyl ring of maleimide exert certain influence on the reactivity ratios. The higher values for r_1 for the EtMA/N-(3- or 4-BrPh)MI than for EtMA/N-(3- or 4-ClPh)MI systems were obtained. And vice versa, the r_2 values for EtMA/N-(3- or 4-ClPh)MI are higher than those for EtMA/N-(3- or 4-BrPh)MI. In general, the values of reactivity ratios r_1 change in the order N-(4-BrPh)MI > N-(3-BrPh)MI > N-(4-ClPh)MI > N-(3-ClPh)MI, while for r_2 the order is N-(4-ClPh)MI > N-(4-

BrPh)MI > N-(3-ClPh)MI > N-(3-BrPh)MI (as calculated by RREVM). No significant effect of the position of halogen atoms in phenyl ring on the value of r_1 was found. More sensitive to halogen position seem to be the values of r_2 .

For all investigated systems of EtMA/N-(3- or 4-halogenophenyl)MI in benzene, the values of r_1 are higher than 1, and r_2 smaller than 1, similar to the reactivities of methacrylates in copolymerization with N-(tolyl)maleimide.^{9,24} It means that both macroradicals in the system prefer the methacrylate monomer, and the resulting copolymers are initially enriched in methacrylate units. Also, the product of the reactivity ratios indicates that the two monomers have the tendency to alternate. An additional measure of the alternating tendency can be the monomer sequence length μ_1

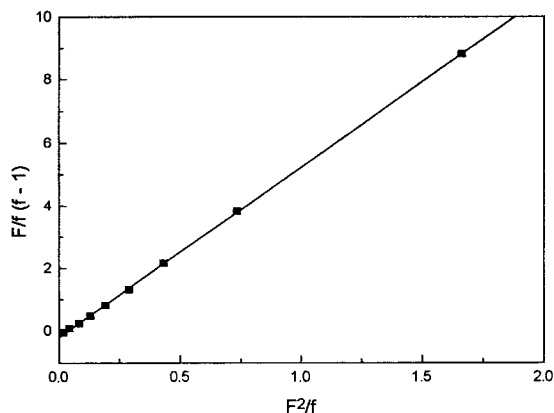


Figure 1 Plot of $F/f(f-1)$ vs F^2/f for the system EtMA/N-(4-BrPh)MI. $r_1 = 5.68$, $r_2 = 0.10$ (Fineman-Ross graphical method). Correlation coefficient $R = 0.999$.

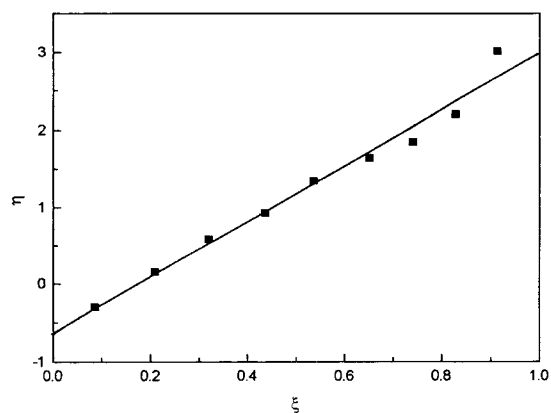


Figure 2 Plot of η vs ξ for the system EtMA/N-(3-ClPh)MI. Kelen-Tüdös method (I); $r_1 = \xi(1)$; $-r_2/\alpha = \xi(0)$, $\alpha = 0.1454$. Correlation coefficient $R = 0.989$.

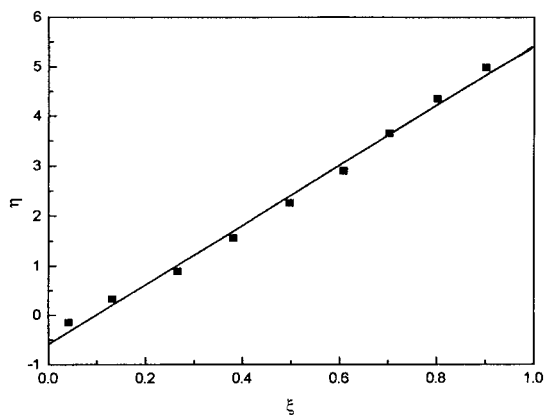


Figure 3 Plot of η vs ξ for the system EtMA/N-(4-BrPh)MI. Kelen–Tüdös method (II); $r_1 = \xi$ (1); $-r_2/\alpha = \xi$ (1), $\alpha = 0.1675$. Correlation coefficient $R = 0.997$.

for EtMA and μ_2 for N-(3- or 4-halogenphenyl)maleimide, calculated from the formula²⁵

$$\mu_1 = 1 + r_1[m_1]/[m_2] \quad (3)$$

$$\mu_2 = 1 + r_2[m_2]/[m_1] \quad (4)$$

where $[m_1]$ and $[m_2]$ are the monomer concentrations in the copolymer. The values of μ_1 and μ_2 are presented in Tables I–IV. The mean sequence lengths μ_1 and μ_2 change with the amount of EtMA and N-(3- or 4-halogenphenyl)maleimide in the feed. For the systems EtMA/N-(3-BrPh)MI, EtMA/N-(4-BrPh)MI, EtMA/N-(3-ClPh)MI, and EtMA/N-(4-ClPh)MI, the value of μ_1 varied from 3.01 to 294, from 5.01 to 268, from 2.26 to 88.2, and from 2.24 to 94.5, respectively, in order of increasing EtMA feed concentration. The mean sequence lengths of N-(3- or 4-halogenphenyl)maleimide, μ_2 , varied from 1.00 to about 1.20 with increasing the N-(3- or 4-halogenphenyl)maleimide feed concentration. This relatively low mean sequence length correlates with the low values of r_2 and confirms the alternating tendency of the EtMA/N-(3- or 4-halogenphenyl)maleimide copolymers.

Figures 4 and 5 show the copolymer composition curves with experimental points for all system studied. We can state that, for the system of EtMA with all halogen-substituted maleimides, the copolymer curves are similar. As can be seen by examining the copolymerization curves, the copolymers of EtMA with N-(3- or 4-halogenphenyl)maleimide formed in benzene are random.

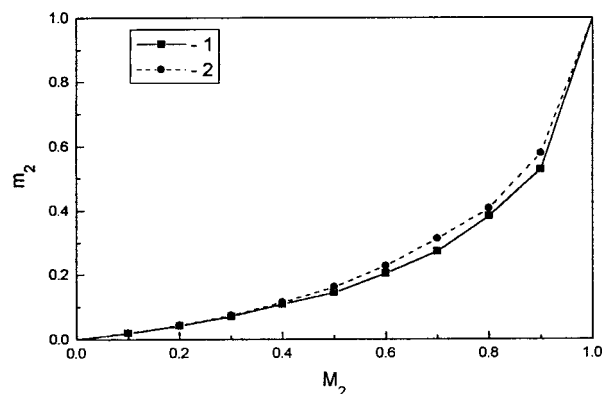


Figure 4 Relationship between the mol fraction of N-(3- or 4-bromophenyl)maleimide in the feed (M_2) and mol fraction in the copolymer (m_2) for the systems: I, EtMA/N-(3-BrPh)MI; II, EtMA/N-(4-BrPh)MI.

From the experimentally determined reactivity ratios of the monomers, the Q and e values for N-(3- or 4-halogenphenyl)maleimide monomers were calculated using the Alfrey–Price Q – e scheme.²⁰ The equations are as follows:

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)] \quad (5)$$

$$r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)] \quad (6)$$

Table V contains the Alfrey–Price copolymerization parameters Q_2 and e_2 for N-(3- or 4-halogenphenyl)maleimide monomers. The values were calculated from the reactivity ratios r_1 and r_2 obtained by RREVM method, by taking the liter-

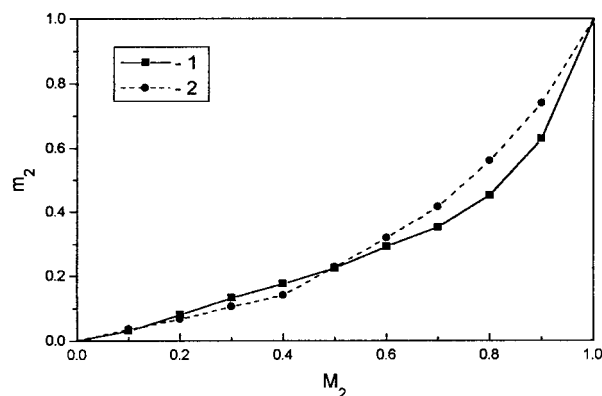


Figure 5 Relationship between the mol fraction of N-(3- or 4-chlorophenyl)maleimide in the feed (M_2) and mol fraction in the copolymer (m_2) for the systems: I, EtMA/N-(3-ClPh)MI; II, EtMA/N-(4-ClPh)MI.

ature data of Q_1 and e_1 for EtMA ($Q_1 = 0.76$, $e_1 = 0.17$).²⁴ The calculated values do not differ significantly among investigated N-(3- or 4-halogenphenyl)maleimides. It is well known that the reactivity of comonomers results from the resonance effects in the molecules of both monomers in the copolymerization reaction and these effects influence the structure copolymers. This structure is formed by the transfer of an electron of ethyl methacrylate double bond to the N-(3- or 4-halogenphenyl)maleimide radical, which gives rise to the pronounced alternation in the copolymerization. The values of e_2 for N-(3- or 4-halogenphenyl)maleimides are large and similar for both N-(3-BrPh)MI and N-(3-ClPh)MI. Bigger differences in e_2 for N-(4-BrPh)MI and N-(4-ClPh)MI are observed. The values of e_2 for N-(3- or 4-halogenphenyl)maleimides are strongly influenced by the type of comonomer and the polymerization medium, and this explains the difference our e_2 and Q_2 values for N-(4-ClPh)MI compared to those reported in literature.²⁴

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