

A Study of the Relative Reactivity of Maleic Anhydride and Some Maleimides in Free Radical Copolymerization and Terpolymerization

ZBIGNIEW FLORJAŃCZYK,* WŁODZIMIERZ KRAWIEC, and
KATARZYNA SUCH, *Institute of Polymer Technology, Technical
University (Politechnika), ul. Noakowskiego 3,
02-664 Warsaw, Poland*

Synopsis

Composition data for the free radical copolymerization of maleic anhydride with *N*-phenylmaleimide in toluene at 60°C have been obtained. Relative reactivity ratios in terminal and penultimate models using nonlinear least-squares optimization routine have been determined. The standard error was found to be somewhat smaller in the penultimate model, but is still larger than the uncertainty estimated for the copolymer composition. Terpolymers of maleic anhydride and styrene with maleimide, *N*-butylmaleimide, *N*-phenylmaleimide, and *N*-carbamylmaleimide were obtained. On the basis of analysis of the product composition at various monomer feeds the relative reactivity of maleic anhydride and maleimides in these reactions is compared and the influence of the structure of these monomers on the rate of some chain growth reactions is discussed.

INTRODUCTION

Synthetic polymers incorporating maleic anhydride (A) and maleimide or *N*-substituted maleimide monomeric units have many potential uses as water soluble materials.¹ Some of them have been reported to possess a wide spectrum of biological activities.² Materials of this type are most often obtained via the reaction of A copolymers or adducts with corresponding amines.^{3,4} The copolymerization of A with maleimides or terpolymerization of these compounds with other monomers are alternative methods, permitting the obtaining of products of a remarkably greater purity. Reactions of this type were not systematically studied until now; however, some copolymers of A with maleimide or its *N*-substituted derivatives have been obtained.⁵⁻⁸

The purpose of this work was the comparison of the relative reactivity of A and *N*-phenylmaleimide (M) in free radical copolymerization and the reactivity of different maleimides in the terpolymerization with A and styrene (S).

EXPERIMENTAL

The polymerizations and all operations connected with the purification and transport of materials used were carried out in nitrogen atmosphere.

A and toluene were purified by distillation. S was distilled under reduced pressure prior to use.

M, *N*-butylmaleimide, *N*-carbamylmaleimide, and maleimide were obtained according to procedures described in References 9, 10, 11, and 11, respectively.

Benzoyl peroxide (BPO) was purified by precipitation from a chloroform solution with methanol.

The polymerizations were carried out and polymer compositions were determined according to the procedures described earlier.¹²

RESULTS AND DISCUSSION

Copolymerization of A and M

A was copolymerized with M in toluene at 60°C using BPO as the radical initiator. In most cases the total monomer concentration was 0.9 mol L⁻³ and the initiator concentration was 1% of the monomer weight. Conversions were kept to 1–7%. In Table I are presented the compositions determined for two samples of each of the terpolymers obtained. These compositions are an average value from calculations on the basis of the carbon, nitrogen, and oxygen contents. The maximum differences in compositions determined on the

TABLE I
Conditions and Results of the Copolymerization of Maleic Anhydride (A)
and *N*-Phenylmaleimide (M)^a

Monomer feed composition (mol %)		Yield (wt %)	Content of monomeric units in the copolymer (mol %)	
A	M		A	M
90	10	0.8	46.2	53.8
		2.8	45.9	54.1
80	20	1.3	45.2	54.8
		3.7	43.9	56.1
75	25	6.8	39.5	60.5
		4.2	38.6	61.4
70	30	3.3	33.4	66.6
		3.0	34.6	65.4
65	35	2.8	30.3	69.7
		4.1	32.2	67.8
60	40	4.5	28.7	71.3
		2.3	28.1	71.9
50	50	2.6	24.7	75.3
		4.2	25.6	74.4
40	60	3.4	22.4	77.6
		1.7	22.2	77.8
30	70	3.2	19.1	80.9
		1.3	18.3	81.7
20	80	4.0	15.7	84.3
		3.2	16.9	83.1
10	90	1.6	13.7	86.3
		2.6	14.7	85.3

^aTotal monomer concentration, 0.9 mol L⁻³; initiator, benzoyl peroxide, concentration 1% of the monomer mass; solvent, toluene; temperature, 60°C; time, 15–180 min.

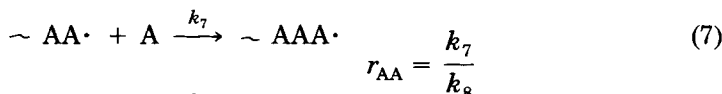
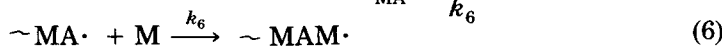
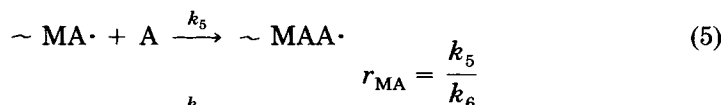
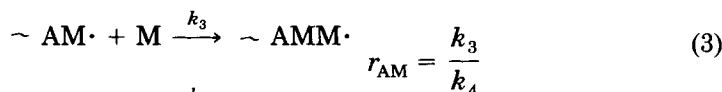
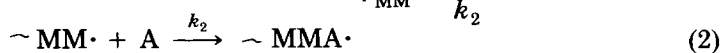
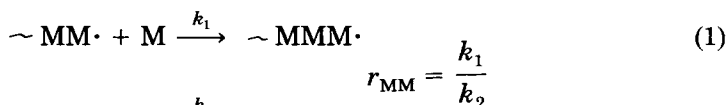
basis of the content of different elements as ca. 3% for one sample and ca. 4% for different samples. Thus, the maximum uncertainty for monomer contents can be estimated as $\pm 2\%$.

It should be noticed that the M content is higher than 50 mol% even when A is charged into the polymerization system in a nine-fold excess toward M.

The values of reactivity ratios determined according to the classical terminal copolymerization scheme using nonlinear least squares (NLLS) optimization routine are equal to: $r_M = 1.6657$ and $r_A = -0.0009$ with the standard error in the M monomeric unit (μ) mole fraction being 3.81% (Table II). The optimization of data at the very probable assumption that the A homopropagation does not proceed ($r_A = 0$) leads to only a slight change in the r_M value (1.6721) at practically the same sum of squares and slightly smaller standard error (3.72%) due to the smaller number of variables fitted in this calculation.

The value of r_M determined for this system is considerably smaller than that calculated from the $Q-e$ values using the Alfrey-Price equation. For example, when taking the $Q-e$ values recently recalculated by Greenley,¹³ then $r_M = 14.0414$ and $r_A = 0.0580$.

Somewhat smaller values of standard errors are obtained when optimizing the experimental data according to the penultimate μ model.¹⁴ In this model eight elementary chain growth reactions and four reactivity ratios are assumed.



The minimum value of the sum of squares in such a model was obtained for $r_{MM} = 1.0091$, $r_{AM} = 10.0179$, $r_{MA} = 0.0887$, and $r_{AA} = -0.0062$ with a standard error of 3.13% (Table II). When assuming that $r_{AA} = 0$ then practically the same sum of squares is obtained with the other parameters slightly changed: $r_{MM} = 1.0017$, $r_{AM} = 11.0025$, $r_{MA} = 0.0913$, and standard error of

TABLE II
Reactivity Ratios for the Terminal and Penultimate Model for Copolymerization
of Maleic Anhydride (A) with *N*-Phenylmaleimide (M)

Model	r_M	r_A	r_{MM}	r_{AM}	r_{MA}	r_{AA}	SS ^a	Sy ^b
Terminal	1.6657	-0.0009					0.0290	0.0381
	1.6721	0 ^c					0.0290	0.0372
Penultimate			1.0091	10.0179	0.0887	-0.0062	0.0176	0.0313
			1.0017	11.0025	0.0913	0 ^c	0.0176	0.0305
			1.1106	2.9072	0 ^c	0 ^c	0.0221	0.0333

^aSS = $\sum(Y_c - Y_e)^2$, where Y_c and Y_e are the calculated and experimental M or A mole fractions in the polymer, respectively.

^bSy = $[SS/(n - p)]^{0.5}$, where Sy is the standard error, and n and p are the number of data points and variables in the model, respectively.

^cFixed value.

3.05%. When assuming that r_{AA} and $r_{MA} = 0$ (no homopropagation of A), then $r_{MM} = 1.1106$ and $r_{AM} = 2.9072$ with a standard error of 3.33%.

The standard errors in the models studied are larger than the estimated uncertainty for copolymer composition ($\pm 2\%$), which may indicate that these models are not adequate for the description of the system studied. Such a possibility is indicated also by the fact that at an excess of A in the monomer feed the experimental data fit better to the models assuming a lack of homopropagation of this monomer, whereas at an excess of M a better approximation is obtained by the model in which the formation of AA diads is possible ($r_{MA} > 0$) (Fig. 1).

From our studies on the copolymerization of M and S¹² it appears that the M homopropagation is reversible. However, attempts to optimize experimental data obtained in this work on the basis of Lowry's models¹⁵ considering only the reversibility of M homopropagation did not lead to a decrease of the standard error. Taking into account that both M and A contain bulky and polar substituents it cannot be excluded that also other propagation reactions are reversible and the propagation and depropagation rate constants depend also on the kind of the penultimate mu. However, with such a mechanism the copolymerization models are difficult to apply quantitatively. We found that in reactions carried out at a four-fold excess of M in the monomer feed the M mu content in the products increases by ca. 4–5% when the total monomer concentration decreases to 0.2 mol L⁻³ whereas in the copolymerization of M and S, the dilution of the system led to a decrease in the M mu content in the products.¹² The greater reversibility of the A addition than of M homopropagation may be the reason for this.

Terpolymerization of A and S with Maleimides

In Table III are presented the compositions of terpolymers of A, S with maleimide, *N*-carbamylmaleimide, *N*-butylmaleimide, or M obtained at different initial monomer mole ratios. The reactions with the latter two maleimides were carried out in toluene, and for those with maleimide and *N*-carbamylmaleimide (which are weakly soluble in toluene) dimethylfor-

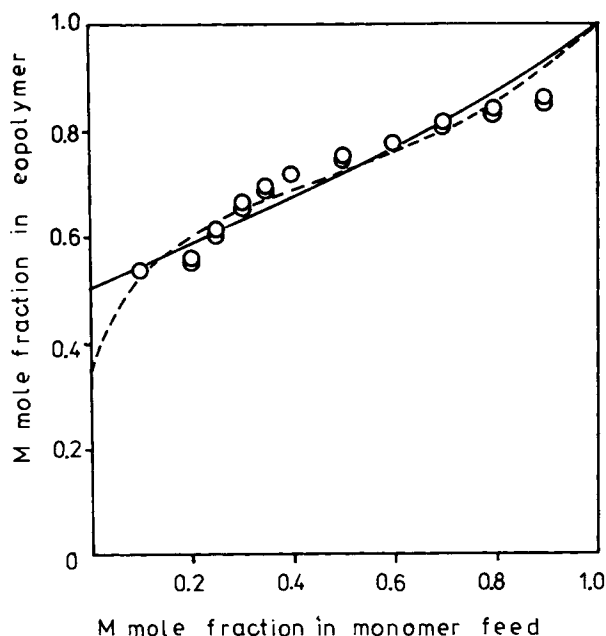
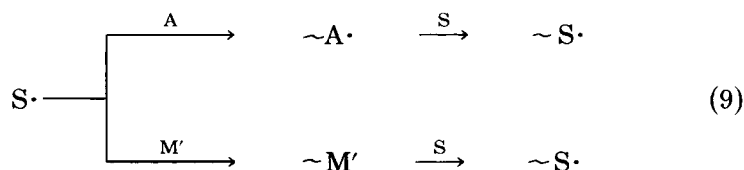


Fig. 1. Dependence of the poly[maleic anhydride (A)-co-phenylmaleimide (M)] composition on the M content in the monomer feed: (○) experimental data, (—) theoretical curve for the terminal model (when $r_A = 0$), (---) theoretical curve for the penultimate model (when $r_{AA} = 0$).

mamide was the solvent. In Table III are presented also the compositions predicted on the basis of classical terpolymerization equations^{16,17} and reactivity ratios in binary systems determined from the monomer Q and e values.¹³ From these calculations it appears that alternating copropagation of S with two competitive electron acceptors, A and maleimides (M'), should dominate in the system studied.



However, in actual systems, at an equimolar amount of S and electron acceptor monomers, products are formed containing less than 50 mol% of S mu, which indicates that also the addition of A and M' to macroradicals terminated by their mu proceeds besides alternating propagation by eq. (9). The A mu content in the products obtained is much larger than that expected. This monomer shows a higher reactivity in chain growth reactions than either maleimide, *N*-butylmaleimide, or *N*-carbamylmaleimide.

In reactions with M, at a large excess of S in the monomer feed, the relative reactivities of both electron acceptor monomers are similar. Under these conditions alternating propagation dominates in the system [eq. (9)], and the rate of addition to S macroradicals is decisive of the content of

TABLE III
 Terpolymerization of Styrene (S), Maleic Anhydride (A), and Maleimides (M')^a

Maleimide	Monomer feed (mol %)			Yield (wt%)	Terpolymer composition (mol %) (theoretically predicted)		
	S	M'	A		S	M'	A
<i>N</i> -phenylmaleimide ^b	80	10	10	3.0	50.7	24.9	24.4
	50	25	25	1.0	46.5	27.9	25.6
					(50.5)	(34.5)	(15.0)
	50	10	40	3.7	44.2	14.0	41.8
					(50.4)	(18.0)	(31.4)
	50	40	10	10.1	43.9	42.0	14.1
					(50.6)	(44.7)	(9.0)
<i>N</i> -butylmaleimide ^b	17	66	17	7.1	36.2	47.3	16.5
					(50.1)	(44.9)	(5.0)
	17	17	66	7.5	43.7	17.9	38.4
					(50.1)	(18.5)	(31.4)
	50	25	25	3.4	46.1	16.5	37.4
					(50.8)	(25.0)	(24.2)
	50	10	40	0.7	47.0	9.9	43.1
Maleimide ^c					(50.8)	(10.1)	(39.1)
	50	40	10	7.8	46.8	34.2	19.0
					(50.8)	(39.6)	(9.6)
	17	66	17	4.3	47.1	38.7	14.2
					(50.2)	(39.9)	(10.0)
	50	25	25	5.6	45.8	14.3	39.9
					(51.0)	(18.0)	(31.0)
<i>N</i> -carbamylmaleimide ^c	50	10	40	4.5	45.0	5.4	49.6
					(51.0)	(6.2)	(42.8)
	50	40	10	6.0	47.1	30.8	22.1
					(51.2)	(34.1)	(14.7)
	17	66	17	1.5	41.1	34.8	25.1
	50	25	25	4.0	43.3	23.4	33.3
	50	10	40	4.6	43.6	13.2	43.2
	50	40	10	9.1	43.3	35.7	21.6
	17	66	17	7.2	43.0	46.2	10.8

^aTotal monomer concentration, 0.9 mol L⁻³; initiator, benzoyl peroxide; temperature, 60°C.^bInitiator, 1 wt % with respect to the monomer mass; solvent, toluene.^cInitiator, 8 wt % with respect to the monomer mass; solvent, *N,N*-dimethylformamide.

electron-acceptor mu. These macroradicals are characterized by strong nucleophilic properties and probably the interactions between the radical single occupied molecular orbital (SOMO) and monomer lowest unoccupied molecular orbital (LUMO) are decisive of the active complex energy and electron acceptor addition rate constant. These interactions should be more effective the lower is the LUMO energy. The energetic level of that orbital is the lowest the higher the monomer resonance stabilization and the stronger the substituent negative induction effect. The values of e and Q indicate that the induction effects are stronger in an A molecule and M is characterized by larger resonance stabilization, and it is possible that the energetic levels of LUMO in both monomers are similar. On the other hand, the level of the highest occupied molecular orbital (HOMO) should be considerably higher in

a M molecule, since an increase of the resonance effect leads to a rise in energy of this orbital, and an increase of the negative induction effect to a decrease of that energy. This is probably one of the reasons of the higher reactivity of M in the addition to macroradicals terminated by this μ or a A μ . These radicals are characterized by strong electrophilic properties, due to which their SOMO energy is low and the SOMO-HOMO interactions are very important in the addition reactions.

Other maleimides studied in this work are characterized by a lower resonance stabilization than M and probably this is the reason of their lower reactivity than M, both in the addition to S macroradicals as well as to electrophilic macroradicals. On the basis of the composition of the terpolymers obtained it can be presumed that the resonance stabilization in maleimide molecules decreases in the order:



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