Spreadsheets in Copolymerization Studies

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ABSTRACT: A Lotus spreadsheet (LS) was utilized as part of a copolymerization study of methyl methacrylate (MMA) with N-phenylmaleimide (MP) and with some derivatives of MP, namely N-o-chlorophenylmaleimide (MOCP), N-p-tolylmaleimide (MPT), and N-o-tolylmaleimide (MOT). The use of LS provided a very rapid method to obtain values of copolymerization parameters which were in very good agreement with non-spreadsheet reported values. Further, a novel LS macro was developed which could be employed to ascertain the shape of the copolymer composition curve (copolymer composition as a function of monomer composition). Monomer reactivity ratios, r_1 and r_2, were determined as well as values of semi-empirical copolymerization parameters Q and e. An attempt was made to correlate the monomer structures used with the values of Q and e. An empirical decomposition temperature index (DTI) was also devised to measure the thermal stability of copolymers of MMA and MP as a function of MP content. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 891–900, 1997

Key words: spreadsheet; copolymerization parameters; maleimides; methyl methacrylate; thermal analysis

INTRODUCTION

In the past, spreadsheets were utilized primarily for business purposes.[1] Relatively recently, however, spreadsheets are playing an increasingly important role in scientific applications. Thus they have been used in the determination of kinetic parameters and mechanisms in thermal analysis,[2–5] in analytical chemistry,[6] and to forecast data consistency.[7] Spreadsheets allow the accurate analysis of data to occur rapidly, and process built-in data regression procedures and functions which are utilized in this article, as well as a Lotus spreadsheet (LS) macro.

The aim of this article is to extend the application of spreadsheets {[i.e., in particular Lotus 1-2-3 (versions 2.2 and 4 (Windows)]} to copolymerization studies. Thus, the LS will be employed to estimate parameters (r_1, r_2, Q, and e; to be described later) for copolymers resulting from the free radical reaction of methyl methacrylate (MMA) with N-phenyl maleimide (MP) and its derivatives, namely N-p-tolyl-, N-o-tolyl-, and N-o-chlorophenylmaleimide. Also, the LS will be used in the derivation of a macro to predict the shape of the curve resulting from a plot of copolymer composition versus monomer composition and to calculate molar ratios of monomeric content in the copolymers from parameters mentioned in the preceding. Furthermore, the experimental conditions utilized in the syntheses of the copolymers will be described along with empirical indices to measure their thermal stability.

THEORETICAL ASPECTS

The copolymer composition equation can be expressed as

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Table I   LSQ Values of r_1 and r_2 for the Copolymer System MP + MMA and a Macro to Predict the Copolymer Composition Curve

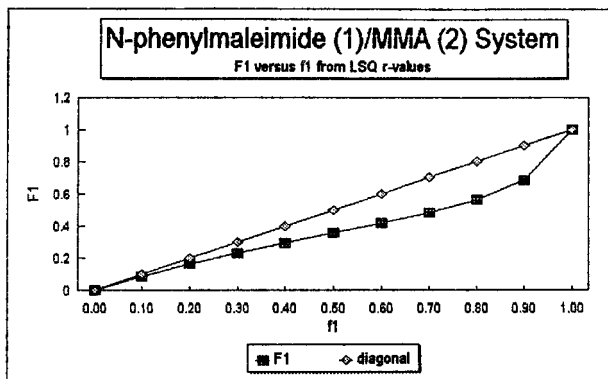|	A	B	C	D	E	F	G	H	I	J	K
1	This program estimates LSQ values of r_1 and r_2 for a co-monomer system and predicts the resulting copolymer composition based on these r-values using a										
2	macro: e.g., for N-o-chloro-phenylmaleimide (M1)/methyl methacrylate (M2):										
3											
4											
5			Y =	X =							
6			f1(1-2F1)/	f1 ^ 2(F1-1)/							
7	f1	F1	F1(1-f1)	F1(1-f1) ^ 2	f1(calc)	F1(calc)					
8	0.10	0.0825	1.125	−0.13730	0.00	0.000					
9	0.30	0.2186	1.103	−0.65655	0.10	0.080					
10	0.50	0.3301	1.029	−2.02939	0.20	0.152					
11	0.70	0.4607	0.398	−6.37332	0.30	0.218					
12	0.90	0.6479	−4.109	−44.01929	0.40	0.279					
13					0.50	0.338					
14					0.60	0.397					
15					0.70	0.459					
16					0.80	0.533					
17					0.90	0.648					
18					1.00	1.000					
19			Regression Ouput:								
20	Constant			1.190696083							
21	Std Err of Y Est			0.0579037906							
22	R Squared			0.9995103596							
23	No. of Observations			5							
24	Degress of Freedom			3							
25											
26	X Coefficient(s)		0.12039662		V	−0.211188					
27	Std Err of Coef.		0.0015385		w	−0.261188					
28					mr	0.8629867					
29											
30			\R{Let V,(1-ratio_r2)/(2-(ratio_r1+ratio_r2))}~								
31			{Let w,v-.05}~{Let MR,ratio_r1+(1-ratio_r2)*(1-w)/w}~								
32			{if v<0#OR#v>=1#AND#mr>1}F1 vs. f1 curve lies completely above diagonal!{Wait @Now+@time(0,0,9)}{ESC}{quit}								
33			{if v<0#OR#v>=1#AND#mr<1}F1 vs. f1 curve lies completely below diagonal!{Wait @Now+@time(0,0,9)}{ESC}{quit}								
34			{if v>0#OR#v<1#AND#mr<1}initial F1 vs. f1 curve lies below diagonal and then intersects it at f1 = V{Wait @Now+@time(0,0,9)}{ESC}								
35			{if v>0#OR#v<1#AND#mr>1}initial F1 vs. f1 curve lies above diagonal and then intersects it at f1 = v{Wait @Now+@time(0,0,9)}{ESC}								
36											
37											
38				RANGE NAMES							
39				MR	F28						
40				RATIO_r1	C26						
41				RATIO_r2	D20						
42				V	F26						
43				W	F27						
44				\R	B30						

Figure 1 F_1 versus f_1 from LSQ r-values for MMA(2) + MP(1).

$$(m_1/m_2) = [M1](r_1[M_1] + [M_2])/$$
$$[M_2](r_2[M_2] + [M_1]) \quad (1)$$

where r_1 and r_2 are monomer reactivity ratios, $[M_1]$ and $[M_2]$ denote the concentrations of two monomers in the feed, and m_1/m_2 is the molar ratio of the two monomer units in the copolymer.[8-11] Equation (1) can also be expressed in terms of mol fractions instead of concentrations. Thus, letting f_1 and f_2 denote mol fractions of M_1 and M_2 in the monomer feed, while F_1 and F_2 in the copolymer, it can be shown that

$$f_1(1 - 2F_1)/F_1(1 - f_1)$$
$$= r_2 + r_1[f_1^2(F_1 - 1)/F_1(1 - f_1)^2] \quad (2)$$

which was utilized in this article to estimate values of r_1 and r_2 from experimental data using a linear least-squares treatment (LSQ) (cf. Table I).

Values of r_1 and r_2 can be employed to ascertain the shape of the curve when F_1 is plotted against f_1. When monomer feed and copolymer compositions are equal (at low conversions), then $m_1/m_2 = [M_1]/[M_2]$ and eq. (1) yields

$$[M_1]_c/[M_2]_c = f_{1,c}/(1 - f_{1,c})$$
$$= (1 - r_2)/(1 - r_1) \quad (3)$$

where subscript c denotes the special conditions that were assumed. From eq. (3)

$$f_{1,c} = (1 - r_2)/[2 - (r_1 + r_2)] \quad (4)$$

Thus, for example, when $r_1 = 0.2$ and $r_2 = 0.3$, eq. (4) yields $f_{1,c} = F_{1,c} = \frac{7}{15}$, which indicates that the F_1 vs. f_1 curve crosses the diagonal at this value. When the values of $f_{1,c}$ become negative or physically unreal (e.g., $f_{1,c} > 1$), the F_1 vs. f_1 curves cannot cross the diagonal. There still remains how to determine what portions of the various curves

Table II   Various Copolymers and the Average and Standard for Their r_1, r_2 Values

	A	B	C	D	E	F	G	H
1								
2	MP		MPT		MOT		MOCP	
3	r1-values		r1-values		r1-values		r1-values	
4	0.1569		0.1359		0.1332		0.1204	
5	0.1568		0.1476		0.1292		0.1135	
6	0.1563		0.1362		0.1331		0.1204	
7								
8	0.1567	(avg)	0.1399	(avg)	0.1318	(avg)	0.1182	(avg)
9	0.0003	(std)	0.0054	(std)	0.0019	(std)	0.0033	(std)
10	————		————		————		————	
11	r2-value		r2-values		r2-values		r2-values	
12	1.1370		1.1045		1.1164		1.1293	
13	1.0750		1.1064		1.1376		1.1651	
14	1.0780		1.0567		1.1511		1.1907	
15								
16	1.0967	(avg)	1.0892	(avg)	1.1350	(avg)	1.1617	(avg)
17	0.0285	(std)	0.0230	(std)	0.0143	(std)	0.0252	(std)
18	0.1718	(r1r2)	0.1524	(r1r2)	0.1496	(r1r2)	0.1372	(r1r2)

Table III   Calculated *Q*- and *e*-Values for Various Copolymers Using LSQ *r*-Values

	A	B	C	D	E	F
1						
2	A) copolymer system: *N*-phenylmaleimide(1)(MP) and MMA(2)					
3						
4	Q2MMA	e2MMA	r1	r2		
5	0.64	0	0.156	1.078		
6						
7	r1r2	e1MP(calcd)	Q1MP(calcd)			
8	0.168	1.334	0.594			
9						
10	M1MP	M2MMA	m1/m2(exp)	m1/m2(calcd)		
11	10.00%	90.00%	0.092	0.095		
12	30.00%	70.00%	0.319	0.304		
13	50.00%	50.00%	0.547	0.556		
14	70.00%	30.00%	0.932	0.933		
15	90.00%	10.00%	2.150	2.149		
16			3.31E-04	<=sum of squares of differences		
17						
18	B) copolymer system: *N-p*-tolylmaleimide(1)(MPT) and MMA(2)					
19						
20	Q2MMA	e2MMA	r1	r2		
21	0.64	0	0.136	1.056		
22						
23	r1r2	e1MPT(calcd)	Q1MPT(calcd)			
24	0.144	1.393	0.606			
25						
26	M1MPT	M2MMA	m1/m2(exp)	m1/m2(calcd)		
27	10.00%	90.00%	0.093	0.097		
28	30.00%	70.00%	0.295	0.306		
29	50.00%	50.00%	0.537	0.553		
30	70.00%	30.00%	0.955	0.907		
31	90.00%	10.00%	1.988	1.990		
32			2.68E-03	<=sum of squares of differences		
33						
34	C) copolymer system: *N-o*-tolylmaleimide(1)(MOT) and MMA(2)					
35						
36	Q2MMA	e2MMA	r1	r2		
37	0.64	0	0.133	1.151		
38						
39	r1r2	e1MOT(calcd)	Q1MOT(calcd)			
40	0.153	1.370	0.556			
41						
42	M1MOT	M2MMA	m1/m2(exp)	m1/m2(calcd)		
43	10.00%	90.00%	0.092	0.089		
44	30.00%	70.00%	0.287	0.287		
45	50.00%	50.00%	0.517	0.527		
46	70.00%	30.00%	0.879	0.877		
47	90.00%	10.00%	1.949	1.948		
48			1.04E-04	<=sum of squares of differences		
49						

(continued)

Table III Continued

	A	B	C	D	E	F
50	D) copolymer system: *N-o*-chloro-phenylmaleimide(1)(MOCP) and MMA(2)					
51						
52	Q2MMA	e2MMA	r1	r2		
53	0.64	0	0.120	1.191		
54						
55	r1r2	e1MOCP(calcd)	Q1MOCP(calcd)			
56	0.143	1.395	0.537			
57						
58	M1MOCP	M2MMA	m1/m2(exp)	m1/m2(calcd)		
59	10.00%	90.00%	0.090	0.086		
60	30.00%	70.00%	0.280	0.278		
61	50.00%	50.00%	0.493	0.511		
62	70.00%	30.00%	0.854	0.847		
63	90.00%	10.00%	1.840	1.837		
64			3.98E-04	<=sum of squares of differences		

lie above or below the diagonal (also called the azeotropic line). This can be accomplished as in the following. When the F_1 vs. f_1 curves lie above the diagonal, $F_1/f_1 > 1$, and eq. (1) yields

$$r_1 + (1 - r_2)[(1 - f_1)/f_1] > 1 \qquad (5)$$

whereas, when the curve lies below the diagonal

$$r_1 + (1 - r_2)[(1 - f_1)/f_1] < 1 \qquad (6)$$

Thus, when $r_1 = 0.2$ and $r_2 = 0.3$ (see the preceding), the value of the LHS of eqs. (5 and 6) becomes $1.25 > 1$, when the value of f_1 is taken as 0.4 (below the value where $f_{1,c} = \frac{7}{15}$). Then, it can be stated that, for the preceding values of r_1 and r_2, the initial F_1 vs. f_1 curve lies above the diagonal, then crosses the diagonal and then lies below the diagonal until the value of $f_1 = 1$. Analogous considerations apply when the curve crosses the diagonal and the LHS of eqs. (5 and 6) possesses a value < 1. Now the initial portion of the curve (prior to intersecting the diagonal) lies below the diagonal. The previous considerations have been utilized to devise the macro listed in Table I.

In an attempt to combine the effects of resonance stabilization and polarity on the relative reactivities of various monomers with various free radicals in a semi-quantitative manner, the Q–e scheme was devised [e.g., see ref. 11]. In this article, the Q-value was correlated with the degree of resonance among covalent forms, while the e-value was correlated with the electron-donating

or electron-attracting character of substituents at the double bond. Electron-donating groups, which activate the benzene ring, are expected to afford negative e-values. The following expressions could be obtained based on various assumptions made:

$$-(e_1 - e_2)^2 = \ln(r_1 r_2) \qquad (7)$$

$$Q_1 = r_1 Q_2 / \exp[-e_1(e_1 - e_2)] \qquad (8)$$

Values of e and Q were calculated from eqs. (7) and (8) using base values of Q and e for MMA.[11]

Another expression used in this article to estimate values of m_1/m_2 from given values of Q and e is ref. 11.

$$\frac{m_1}{m_2} = \frac{\begin{array}{l}(M_1)^2 Q_1^2 \exp(-e_1^2) \\ + (M_1)(M_2)Q_1 Q_2 \exp(-e_1 e_2)\end{array}}{\begin{array}{l}(M_2)^2 Q_2^2 \exp(-e_2^2) \\ + (M_1)(M_2)Q_1 Q_2 \exp(-e_1 e_2)\end{array}} \qquad (9)$$

Equation (9) was employed in Tables III and V.

EXPERIMENTAL [12]

Raw Materials

The benzoyl peroxide initiator (BPO) was purified by two crystallizations from chloroform. Maleic anhydride was recrystallized from chloroform prior to use. Aniline, *p*-toluidine, *o*-toluidine, and *o*-chloroaniline were purified by distillation in the

presence of zinc dust. Various solvents employed were further refined according to standard procedures.

Methyl methacrylate (MMA) was freed from hydroquinone by washing it with 5% aqueous NaOH solution three times, followed by several washings with distilled H_2O. The resulting MMA was then dried with anhydrous Na_2SO_4, followed by its distillation under reduced pressure, discarding the head and tail fractions.

Synthesis of *N*-arylmaleimides

Four *N*-arylmaleimides were prepared utilizing a modified procedure reported by Searle.[13] The following aryl derivatives were synthesized: phenyl, *p*-tolyl, *o*-tolyl, and *o*-chlorophenyl. Yields varied from 60 to 77%; melting points and elemental analyses observed were in good agreement with reported and calculated values, respectively.

Copolymerization of MMA with *N*-arylmaleimides (NAM)

A total of 0.02 mol of MMA and NAM, in different compositions, were placed into an ampule (50 mL), and 15 mL of cyclohexanone was added along with 12.1 mg of BPO. The ampule was kept at 0°C, flushed with nitrogen, and then attached to a long air condenser, which was flushed with nitrogen. The ampule was then maintained at 70 ± 0.1°C in an oil batch for 2.5–3 h in order to obtain the relatively low conversions of ∼ 5–10%. In each copolymerization, the copolymer was precipitated with methanol. The resulting white solid was dissolved in methyl ethyl ketone or chloroform, the solution then filtered and added to excess methanol. The resulting precipitate was washed with methanol and then vacuum dried.

In order to estimate copolymer compositions, the micro Kjeldahl method was employed to estimate the percent nitrogen. In this manner, the amount of MMA and of NAM in each copolymer could be calculated.

RESULTS AND DISCUSSION

The polymerization of MMA with *N*-arylmaleimides to yield various copolymers is depicted below:

R=H, p-CH₃, o-CH₃, o-Cl
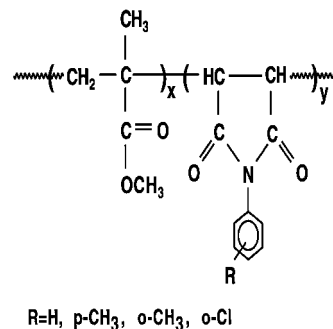
Other copolymers synthesized consisted of MMA and derivatives of MP, such as *N-o*-chlorophenylmaleimide, *N-p*-tolylmaleimide, and *N-o*-tolylmaleimide. These derivatives were designated as MOCP, MPT, and MOT, respectively. The thermal behavior of copolymers of MP + MMA has been previously described.[14,15] However, reactivity ratios were not determined, and a thermal stability index (DTI) utilized in the present paper was not employed in the cited references. The copolymerization parameters for MP/MOT and MP/MOCP systems have not been reported. Also, spreadsheets were not mentioned.

In Table I, eq. (2) was used to estimate values of r_1 and r_2 for MP using a LS and data[12] for f_1 and F_1 (subscript 1 designates MP) (see columns A–D). The regression output is indicated in rows 19–28. In this manner, values of $r_1 = 0.156$ and $r_2 = 1.078$ were obtained. After obtaining these values, the macro (rows 30–44) was employed and indicated that the F_1 vs. f_1 curve was below the diagonal, as found (see Fig. 1). In this manner, values of r_1 and r_2 for the other copolymers synthesized were found using the LS and a least-squares treatment (LSQ). All these copolymers possessed F_1 vs. f_1 curves which also lay completely below the diagonal. Table II summarizes the r_1 and r_2 values, calculated via LSQ, in rows 6 and 14 for the various copolymers. Thus, for example, in this table, $r_1 = 0.1204$ and $r_2 = 1.191$ for MOCP. In Table I, columns E and F display calculated values of f_1 and F_1 based on the LSQ values of r_1 and r_2 obtained for the MP copolymer. The agreement between experimental values in rows A8–A12 and B8–B12 and those calculated was found to be good. The same could be said for all the other copolymers. Besides the LSQ values of r_1 and r_2 obtained in Table II for the various copolymers, two other sets of r_1 and r_2 values were obtained for the various copolymers (see rows 4, 5.12, and 13). These resulted from procedures[12]

to calculate r_1 and r_2 values which did not utilize spreadsheets, i.e., the Kelen–Tudos and Fineman–Ross methods. In Table II, average values of r_1 and r_2 are listed along with standard deviations for three sets of r_1, r_2 values (see rows 8, 9 and 16, 17). The products of the average values of r_1, r_2 are listed in row 18. Other procedures have been described for obtaining r_1, r_2 values, refs. 16 and 17, for example.

In Table III, Q and e values for the various copolymers were calculated using LSQ r-values, eqs. (7) and (8), and base values for MMA of Q = 0.64 and e = 0.[11] Thus, for the MP system, it was found that $Q(\text{MP})$ = 0.594 and $e(\text{MP})$ = 1.334 (cf. Cells C8 and B8). Values of e and Q for MPT, MOT, and MOCP are to be found in Cells B24 and C24, B40 and C40, B56 and C56, respectively. These Q–e values were utilized to calculate m_1/m_2 values using eq. (9); for example, see columns C11–C15 and D11–D15 for MP. The agreement between experimental and calculated values was found to be good for all the copolymers examined. Table IV lists the cell contents for the MP + MMA system (cf. Table III).

In Table V, Q and e values for the various copolymers were also calculated, as in Table III, using average r-values (cf. Table II). The values obtained are comparable with those obtained using LSQ r-values (cf. Table III). However, based on the sum of the squares of the differences between experimental and calculated values of m_1/m_2 (compare Cells C32, C48, and C64 in Tables III and V), the spreadsheets LSQ r-values provided better agreement. This indicates that the use of average r-values from spreadsheet and two non-spreadsheet procedures did not improve the agreement more than when spreadsheet r-values were used alone.

It was previously indicated that Q-values can be related to resonance effects, while e-values are related to electron-donating and electron-attracting effects (in the following, it should be remembered that such postulated effects are based on a semi-empirical hypothesis). Based on the preceding, the following observations may be made. The Q-values (Table III) for MP, MPT, MOT, and MOCP are, respectively, 0.594, 0.606, 0.556, and 0.537. Resonance effects in MPT would be expected to be greater than for MP due to possible hyperconjugative effects of the methyl group. For the ortho-substituted derivatives, MOT and MOCP, stearic factors could exist, which would decrease the degree of resonance leading to lower

Table IV   Cell Contents for the MP(1)+MMA(2) System

A:A2: [W14] ′A) copolymer system: N-phenylmaleimide(1)(MP) and MMA(2)
A:A4: [W14] ″Q2MMA
A:B4: [W14] ″e2MMA
4:C4: [W13] ″r1
A:D4: [W11] ″r2
A:A5: [W14] 0.64
A:B5: [W14] 0
A:C5: (F3) [W13] 0.1563
A:D5: [W11] 1.078
A:A7: [W14] ″r1r2
A:B7: [W14] ″e1MP(calcd)
A:C7: [W13] ″Q1MP(calcd)
A:A8: (F3) [W14] +C5*D5
A:B8: (F3) [W14] @SQRT(−@LN(A8))
A:C8: (F3) [W13] +C5*A5/(@EXP(−B8 ˆ 2))
A:A10: [W14] ″M1MP
A:B10: [W14] ″M2MMA
A:C10: [W13] ″m1/m2(exp)
A:D10: [W11] ″m1/m2(calcd)
A:A11: (P2) [W14] 0.1
A:B11: (P2) [W14] 0.9
A:C11: (F3) [W13] 0.0924
A:D11: (F3) [W11] (A11 ˆ 2*C8 ˆ 2*@EXP(−(B8) ˆ 2)+A11*B11*C8*A5)/(B11 ˆ 2*A5 ˆ 2+A11*B11*C8*A5)
A:A12: (P2) [W14] 0.3
A:B12: (P2) [W14] 0.7
A:C12: (F3) [W13] 0.2417/0.7583
A:D12: (F3) [W11] (A12 ˆ 2*C8 ˆ 2*@EXP(−(B8) ˆ 2)+A12*B12*C8*A5)/(B12 ˆ 2*A5 ˆ 2+A12*B12*C8*A5)
A:A13: (P2) [W14] 0.5
A:B13: (P2) [W14] 0.5
A:C13: (F3) [W13] 0.547
A:D13: (F3) [W11] (A13 ˆ 2*C8 ˆ 2*@EXP(−(B8) ˆ 2)+A13*B13*C8*A5)/(B13 ˆ 2*A5 ˆ 2+A13*B13*C8*A5)
A:A14: (P2) [W14] 0.7
A:B14: (P2) [W14] 0.3
A:C14: (F3) [W13] 0.932
A:D14: (F3) [W11] (A14 ˆ 2*C8 ˆ 2*@EXP(−(B8) ˆ 2)+A14*B14*C8*A5)/(B14 ˆ 2*A5 ˆ 2+A14*B14*C8*A5)
A:A15: (P2) [W14] 0.9
A:B15: (P2) [W14] 0.1
A:C15: (F3) [W13] 2.15
A:D15: (F3) [W11] (A15 ˆ 2*C8 ˆ 2*@EXP(−(B8) ˆ 2)+A15*B15*C8*A5)/(B15 ˆ 2*A5 ˆ 2+A15*B15*C8*A5)
A:C16: (S2) [W13] @SUMXMY2(C11 . . C15, D11 . . D15)
A:D16: [W11]′ <=sum of squares of difference

See Table III.

Table V   Calculated Q- and e-Values for Various Copolymers Using Average r-Values

	A	B	C	D	E	F
1						
2	A) copolymer system: N-phenylmaleimide(1)(MP) and MMA(2)					
3						
4	Q2MMA	e2MMA	r1	r2		
5	0.64	0	0.1567	1.097		
6						
7	r1r2	e1MP(calcd)	Q1MP(calcd)			
8	0.172	1.327	0.584			
9						
10	M1MP	M2MMA	m1/m2(exp)	m1/m2(calcd)		
11	10.00%	90.00%	0.092	0.094		
12	30.00%	70.00%	0.319	0.300		
13	50.00%	50.00%	0.547	0.552		
14	70.00%	30.00%	0.932	0.929		
15	90.00%	10.00%	2.150	2.148		
16			3.91E-04	<=sum of squares of the difference		
17						
18	B) copolymer system: N-p-tolylmaleimide(1)(MPT) and MMA(2)					
19						
20	Q2MMA	e2MMA	r1	r2		
21	0.64	0	0.140	1.089		
22						
23	r1r2	e1MPT(calcd)	Q1MPT(calcd)			
24	0.152	1.371	0.588			
25						
26	M1MPT	M2MMA	m1/m2(exp)	m1/m2(calcd)		
27	10.00%	90.00%	0.093	0.094		
28	30.00%	70.00%	0.295	0.299		
29	50.00%	50.00%	0.537	0.546		
30	70.00%	30.00%	0.955	0.905		
31	90.00%	10.00%	1.988	2.016		
32			3.43E-03	<=sum of squares of the differences		
33						
34	C) copolymer system: N-o-tolylmaleimide(1)(MOT) and MMA(2)					
35						
36	Q2MMA	e2MMA	r1	r2		
37	0.64	0	0.1318	1.135		
38						
49	r1r2	e1MOT(calcd)	Q1MOT(calcd)			
40	0.150	1.378	0.564			
41						
42	M1MOT	M2MMA	m1/m2(exp)	m1/m2(calcd)		
43	10.00%	90.00%	0.092	0.090		
44	30.00%	70.00%	0.287	0.290		
45	50.00%	50.00%	0.517	0.530		
46	70.00%	30.00%	0.879	0.880		
47	90.00%	10.00%	1.949	1.941		
48			2.39E-04	<=sum of squares of the differences		
49						

(continued)

Table V Continued

	A	B	C	D	E	F
50	D) copolymer system: *N-o*-chloro-phenylmaleimide(1)(MOCP) and MMA(2)					
51						
52	Q2MMA	e2MMA	r1	r2		
53	0.64	0	0.118	1.62		
54						
55	r1r2	e1MOCP(calcd)	Q1MOCP(calcd)			
56	0.137	1.410	0.551			
57						
58	M1MOCP	M2MMA	m1/m2(exp)	m1/m2(calcd)		
59	10.00%	90.00%	0.090	0.088		
60	30.00%	70.00%	0.280	0.283		
61	50.00%	50.00%	0.493	0.517		
62	70.00%	30.00%	0.854	0.851		
63	90.00%	10.00%	1.840	1.826		
			7.92E-04	<=sum of squares of the differences		

values of Q than for MP or MPT. The e-values for MP, MPT, MOT, and MOCP (see Table III) are, respectively, 1.334, 1.393, 1.370, and 1.395. Based on electron-attracting effects (inductive), it may be expected that MOCP would possess the highest value of e, as observed. The resulting difference in the e-values for MPT and MOT may be due to a greater influence on the inductive effect by stearic factors, as in the case of MOT, in comparison with

MPT. It may be expected that the inductive effect of the methyl group is much smaller than that of tertiary nitrogen. This could account for the similar e-values obtained for various substituent groups.

Figure 2 depicts T_g curves for the MP copolymers [the MP content (mol fraction) for curves MP1, MP3, MP5, and MP7 were, respectively, 0.085, 0.242, 0.354, and 0.483].[12] A thermal sta-
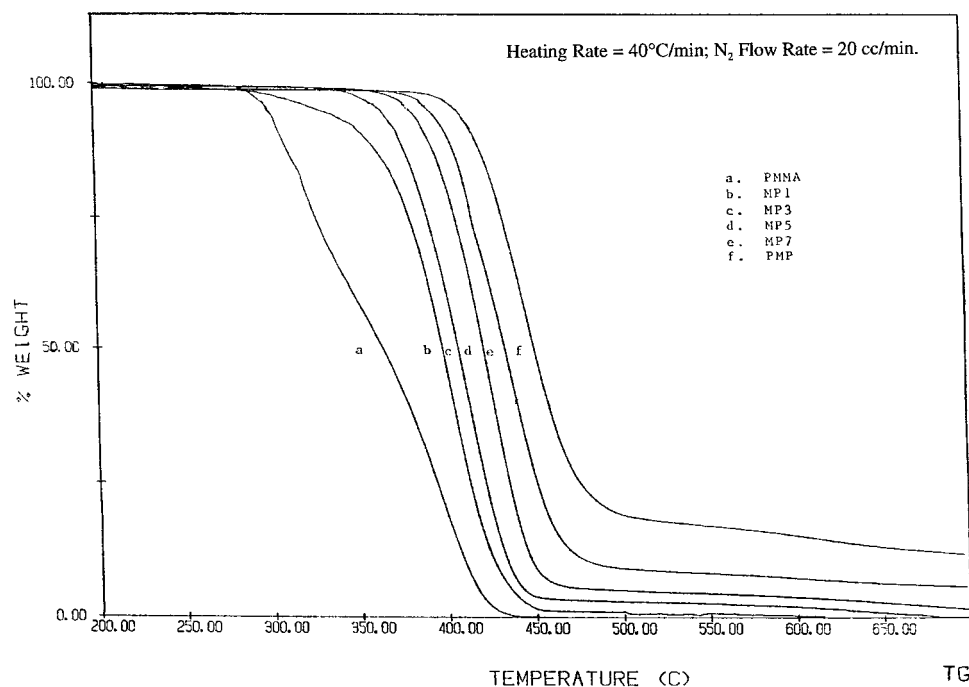

Figure 2 TG curves for various compositions of the copolymer MMA + MP.
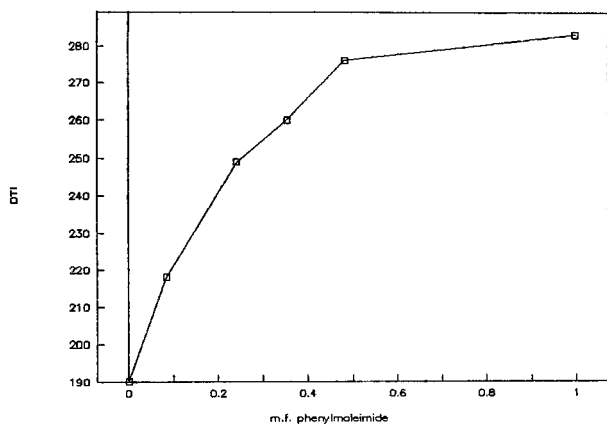
Figure 3 DTI versus mol fraction MP in the copolymer MMA + MP.

bility index was devised based on work done by Doyle.[18] Thus, T^* was set equal to $640A^* + 50$ in order to carry out measurements in the temperature range (°C) 50–690. Then an arbitrary index called decomposition temperature index (DTI) was utilized such that DTI = $640A^*K^* + 50$. From the preceding, DTI values for PMMA, MP1, MP3, MP5, MP7, and MP were found to be 190, 218, 249, 260, 276, and 283, respectively (using weight measurements). Figure 3 depicts a plot of these values versus the mol fraction (m_1/f_1) of MP. From this figure, it can be seen that the DTI value increases until a value of m_1/f_1 is ~ 0.5, after which there is very little change in the DTI value as m_1/f_1 increases to 1. From Figure 2 it can also be observed that, as the content of MP in the copolymer increased, there was also an increase in the residual char yield, which was also observed by Choudhary et al.[14] The increase in char formation is also attributed to a number of factors including the aromaticity of the polymer chain.[19,20]

CONCLUSIONS

A Lotus spreadsheet was successfully utilized to provide a rapid method to obtain values of copolymerization parameters, namely r_1, r_2, Q and e, for the free radical copolymerization of methyl methacrylate with N-phenyl-, N-p-tolyl-, N-o-tolyl-, and n-o-chlorophenylmaleimide in cyclohexanone. The values obtained were in very good

agreement with non-spreadsheet reported values. Also, a novel LS macro developed during this study was successfully employed to ascertain the shape of the copolymer composition curve (copolymer composition versus monomer composition). The Q and e values obtained seemed to correlate well with the monomer structures. With respect to thermal stability of copolymers, an empirical decomposition temperature index (DTI) was also devised and utilized for an MMA/MP copolymer system which showed that DTI value increases until the mole fraction of MP in copolymer is ~ 0.5, after which there is insignificant change as the mol fraction of MP approaches 1.

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