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COPOLYMERIZATION OF MALEIMIDE MONOMERS CONTAINING HETEROCYCLIC GROUPS

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Key Words: Maleimide; Heterocyclic moieties; Copolymerization; Thermal stability

ABSTRACT

Thermal stable polymers were prepared by radical polymerization of two kinds of *N*-(substituted) maleimide containing heterocyclic groups. These monomers were readily copolymerized with styrene (ST), methyl methacrylate (MMA) and vinyl acetate (VA), and their reactivity ratios were determined by different methods. The Alfrey–Price *Q*–*e* values were determined from copolymerization analysis. The thermal behaviors of the polymers and copolymers were investigated by thermogravimetric method.

INTRODUCTION

Maleimide and its *N*-substituted derivatives are 1,2-disubstituted ethylenes. Their radical polymerization and copolymerization behaviors and thermal properties of the polymers have been extensively studied by many workers [1–11]. *N*-Cyclohexylmaleimide is especially useful as a heat-resistant reagent for common vinyl polymers [12]. Application of *N*-phenylmaleimide and *N*-(*p*-hydroxyphenyl) maleimide to acrylonitrile-butadiene-styrene (ABS) [13] and phenol resin [14], respectively, has been investigated.

Copolymerizations of *N*-substituted maleimides with various vinyl monomers have been investigated by many authors [15–21]. Specifically copolymerization with electron-donor monomers such as styrene (ST) and vinyl ether is well known to yield alternating copolymers over a wide range of comonomer compositions, and the copolymerization mechanism has been discussed by many workers [20, 21].

However, little information [22] is available on the polymerization and the copolymerization of *N*-(substituted) maleimide containing heterocyclic groups. In this article, *N*-(5-methyl isoxazole) maleimide (MMIXZ) and *N*-(5-methyl pyrazole) maleimide (MMPZ) were synthesized. The monomers were copolymerized with some vinyl monomers, and some of the resulting copolymers were thermally investigated.

EXPERIMENTAL

Materials

Maleic anhydride, 3-amino-5-methylisoxazole, 3-amino-5-methyl pyrazole, acetic anhydride, and fused sodium acetate (Aldrich) were used as received. Styrene, methyl methacrylate, and vinyl acetate (Aldrich) and all the reagents and solvents were purified by conventional methods.

N-(5-Methyl Isoxazole) Maleamic Acid

Maleic anhydride was dissolved in chloroform (or diethyl ether), and an equivalent amount of 3-amino-5-methyl isoxazole in the same solvent was added dropwise. The mixture was stirred at 35–40°C for 5–7 hours. The resulting product was filtered and washed with chloroform, then dried. The acid was crystallized from ethanol to obtain pure *N*-(5-methyl isoxazole) maleamic acid. Yield 98%, mp 181°C.

Elemental analyses. Found: C = 48.93, H = 4.02, and N = 14.22%. Calculated: 48.98, H = 4.08, and N = 14.29%.

^{1}H-NMR spectra of the prepared acid, DMSO using TMS as internal standard: 2.6 (s, 3H), 6.2 (s, 1H), 6.3–6.6 (t, 2H), and 10.99 (broad, 1H).

N-(5-Methyl Isoxazole) Maleimide (MMIXZ)

A mixture of *N*-(5-methyl isoxazole) maleamic acid (10 g), acetic anhydride (5.2 g), and sodium acetate (0.5 g) was heated at 80–90°C in a water bath for 30 minutes and the mixture was left at room temperature over night. The precipitated mixture was poured into cold water, filtered, and washed with water until it was free of acid. The maleimide was dried and purified by recrystallization from ethanol: yield 70%, mp 120°C.

Figure 1 shows the ^{13}C- and ^{1}H-NMR spectra of the prepared monomer.

Elemental analyses. Found: C = 53.56, H = 3.49, and N = 15.71%. Calculated: C = 53.93, H = 3.37, and N = 15.73%.

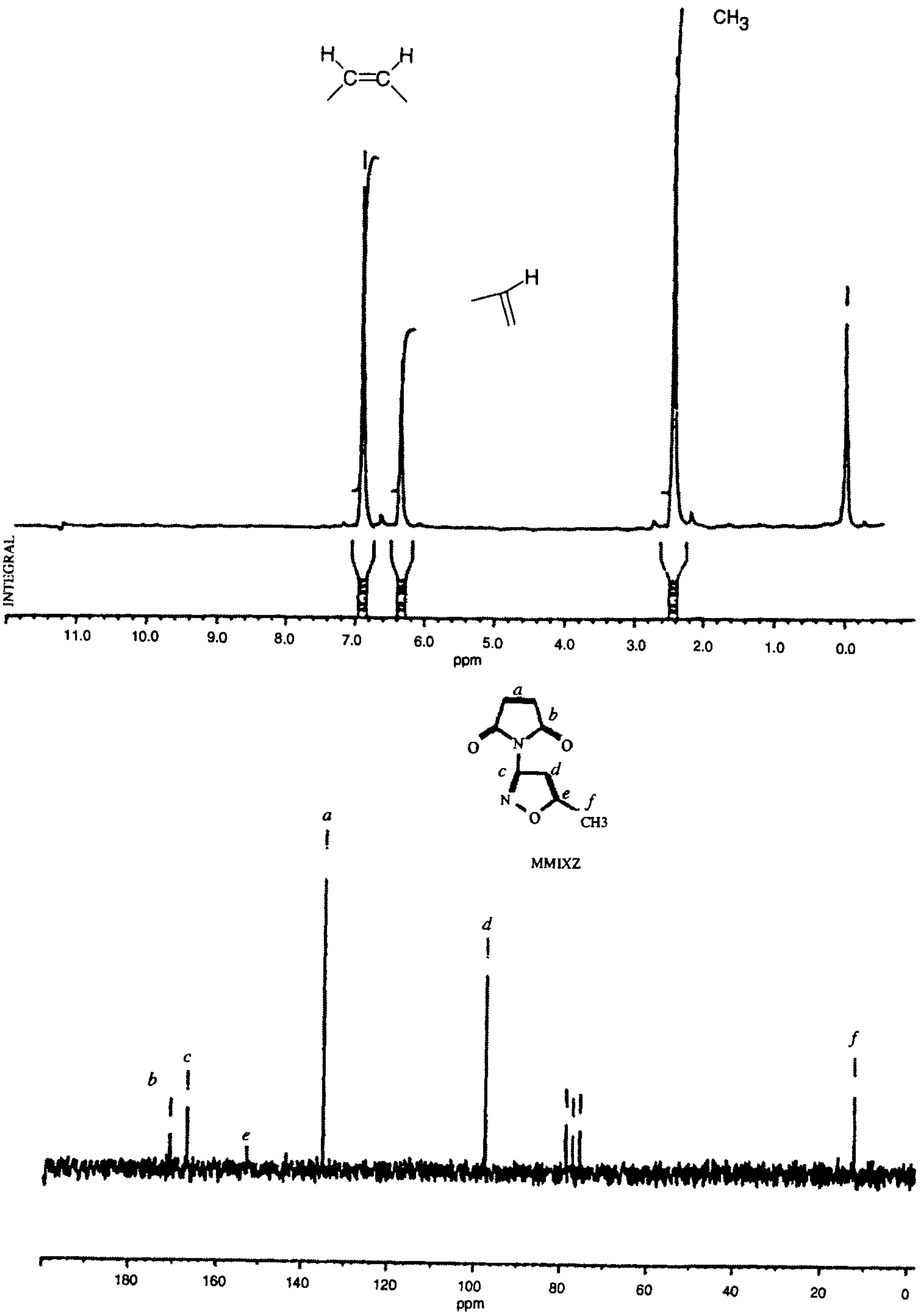

FIG. 1. ^{1}H- and ^{13}C-NMR spectra of MMIXZ monomer.

N-(5-Methyl Pyrazole) Maleimide (MMPZ)

This monomer was prepared by the same procedure as for the other monomer, mp 160°C (lit. 160–161°C) with a 85% yield. Spectral analysis (^{1}H- and ^{13}C-NMR spectra) confirmed the proposed structure and found it to be identical with what was reported in Ref. 22.

Elemental analyses. Found: C = 54.24, H = 4.23, and N = 19.04%. Calculated: C = 54.79, H = 4.11, and N = 19.04%.

Polymerization and Copolymerization Procedure

Radical solution polymerization and copolymerization of MMIXZ and MMPZ were carried out in sealed glass tubes with the proper solvent and initiator at 75°C. After polymerization or copolymerization for a given time, the contents of the tubes were poured into a large amount of ethanol to precipitate the polymer or the copolymer. The polymer and/or the copolymer was filtered, purified by the Soxhlet extraction method for 6 hours in ethanol, and dried under reduced pressure for 2–3 days.

Spectral Analysis

NMR spectra were recorded using a Bruker AC80 FTNMR. The elemental analyses were performed at the Microanalytical Unit of Kuwait University. The infrared spectra were obtained by the use of a Bruker IFS 25 FTIR spectrometer. The molecular weight (M_w) was determined by gel permeation chromatography (GPC) (Waters, 600) at 35°C in tetrahydrofuran (THF) as an eluent. The GPC was calibrated with standard polystyrene samples provided by Waters Co. Thermogravimetric analysis was carried out in a nitrogen stream with a heating rate of 20°C/min using a Shimadzu, DSC 50.

RESULTS AND DISCUSSION

Homopolymerization

MMIXZ and MMPZ were polymerized in 1,4-dioxane and tetrahydrofuran (THF) or chloroform, respectively. The purified polymers were investigated by TGA, and their molecular weights were measured by GPC. The obtained molecular weights were 6400 and 6600 for MMIXZ and MMPZ, respectively. These low molecular weights are probably due to the use of a high concentration of the initiator (1 mol% AIBN). The kinetics of the free radical polymerization of MMIXZ will be reported later.

Copolymerization

The two prepared monomers (MMIXZ and MMPZ) were copolymerized with three monomers of commercial importance, styrene (ST), methyl methacrylate (MMA), and vinyl acetate (VA).

The monomer reactivity ratios of these systems were calculated by three methods: Fineman-Ross [23], Kelen-Tüdös [24], and the nonlinear least-squares [25, 26] methods.

A commercial program, Sigma Plot, provided by Jandel Scientific Company, was adapted for the calculations. The latter program is a very reliable and fast method for the determination of the monomer reactivity ratios using a nonlinear least squares approach.

Tables 1 and 2 summarize the copolymerization data of the investigated systems. The monomer-copolymer composition curves for all the investigated systems are shown in Figs. 2 and 3. The points are experimental while the curves are theoretical, constructed by the NLLS values of r_1 and r_2. Figures 4 and 5 demonstrate the calculation of the r_1 and r_2 values for the two monomers by the K-T method.

It is well-known that many maleimide derivatives undergo alternating copolymerization with styrene. A similar result was obtained for MMIXZ and MMPZ. The results of the monomer reactivity ratios for all the investigated systems by the different methods are reported in Tables 3 and 4.

Alfrey-Price [27] proposed the Q-e parameters as a semiempirical scheme. The Q value is related to the reactivity and the e value to the polarity of the monomer. This scheme is based on the Q and e values of styrene; $Q = 1$, $e = -0.80$, which is used as a comparative standard. For new monomers it is customary to calculate the Q-e parameters using several copolymerization systems. Generally, calculation makes use of the reactivity ratios of the new monomer with another monomer of known values of Q and e. However, two values are obtained for those parameters, and the choice of the correct one depends on the personal view. Greenley [28] proposed am improved treatment of the monomer reactivity ratios for the determination of a single value for the Q-e parameters.

The Alfrey-Price equations can be expressed as

$$r_1 = K_{11}/K_{12} = (Q_1/Q_2) \exp - e_1(e_1 - e_2)$$

This equation can be rearranged to the form [28]

$$\ln Q_1/r_1 - e_1^2 = \ln Q_2 - e_1 e_2$$

By using several copolymerization systems with known Q_1 and e_1 values and from the experimentally determined r_1 and r_2, the left hand side of the equation $\ln Q_1/r_1 - e_1^2$ vs e_1 can be plotted. A straight line is obtained with a slope equal to $-e_2$ and an intercept equal to $\ln Q_2$. An example of this type of calculation is given in Fig. 6. By this method, unique values for the Q and e parameters can be obtained instead of the two values usually obtained by using a single copolymerization system.

The Q and e values for the two monomers are calculated by this method and are summarized in Table 5. The e values of the two monomers are identical due to the similar electron density of the double bonds in both monomers. On the other hand, Q for MMIXZ is slightly bigger than that of MMPZ, probably due to the bulkier size of the latter due to the presence of the acetyl group attached to the nitrogen atom.

Characterization of the Polymers and Copolymers

The polymer and most of copolymers were colored and insoluble in hydrocarbons (e.g., cyclohexane, *n*-hexane, benzene, toluene) and hydroxylic solvents (e.g., ethanol, methanol, water), but soluble in DMF, THF, and DMSO.

TABLE 1. Radical Copolymerization of MMIXZ (M_1) with MMA (M_2), or VA (M_2), and ST (M_2) in 1,4-Dioxane at 75°C

Run	M_2	M_1 in monomer, mol%	Conversion, %	*N*, %	M_1 in copolymer, mol%
1	MMA	5.08	7.22	1.04	3.97
2		9.99	10.23	1.96	7.69
3		14.89	10.94	2.72	10.94
4		20.04	11.32	3.50	14.46
5		25.08	12.61	4.12	17.35
6		30.14	13.6	4.81	20.76
7		36.95	12.36	6.30	28.61
8		50.01	12.08	7.98	38.55
9		59.87	10.58	8.60	42.53
10		69.96	14.19	9.72	50.24
11		79.63	9.42	10.85	58.73
12		88.7	12.23	11.08	60.51
13		94.69	23.96	12.82	75.64
1	ST	9.76	7.62	8.02	38.79
2		19.88	7.28	8.83	44.02
3		30.19	9.48	9.26	46.98
4		40.15	10.09	9.33	47.43
5		49.69	13.44	9.51	48.74
6		60.13	11.94	9.70	50.05
7		69.52	8.53	9.55	49.02
8		80.40	11.63	9.86	51.24
9		84.53	12.82	9.99	52.15
1	VA	10.07	19.62	10.02	48.63
2		20.10	22.37	10.86	55.13
3		29.32	20.99	10.95	55.86
4		40.25	27.12	11.24	58.25
5		51.28	23.52	11.81	63.25
6		60.06	18.03	12.02	65.08
7		70.62	21.17	12.88	73.40
8		80.74	25.49	13.56	80.55
9		90.44	21.39	14.31	89.29

TABLE 2. Radical Copolymerization of MMPZ (M_1) with MMA (M_2), VA (M_2), and ST (M_2) in Chloroform and DMF at 75°C

Run	M_2	M_1 in monomer, mol%	Conversion, %	*N*, %	M_1 in copolymer, mol%
1	MMA	10	15	3.16	9
2		21	17	5.60	17
3		30	18	7.13	23
4		41	15	9.25	32
5		49	17	10.45	38
6		59	20	11.79	45
7		69	20	12.90	52
8		74	20	13.51	57
9		85	17	15.19	69
10		100	11	18.26	100
1	ST	9.84	9.77	10.58	39.55
2		20.17	9.78	11.46	44.49
3		30.31	12.81	11.86	46.86
4		39.95	11.80	12.16	48.64
5		49.49	14.30	12.28	49.39
6		60.50	19.05	12.43	50.34
7		69.94	21.08	12.28	49.32
8		79.3	22.42	12.57	51.21
9		90.39	15.01	13.46	57.16
1	VA	9.92	18.33	12.31	67.41
2		19.94	18.96	13.24	72.51
3		29.79	15.08	13.56	74.26
4		39.53	20.68	14.09	77.13
5		50.33	24.12	14.57	79.76
6		59.85	21.36	15.21	83.27
7		70.06	20.20	16.09	88.09
8		79.83	19.92	16.43	89.97
9		90.41	17.28	17.25	94.45

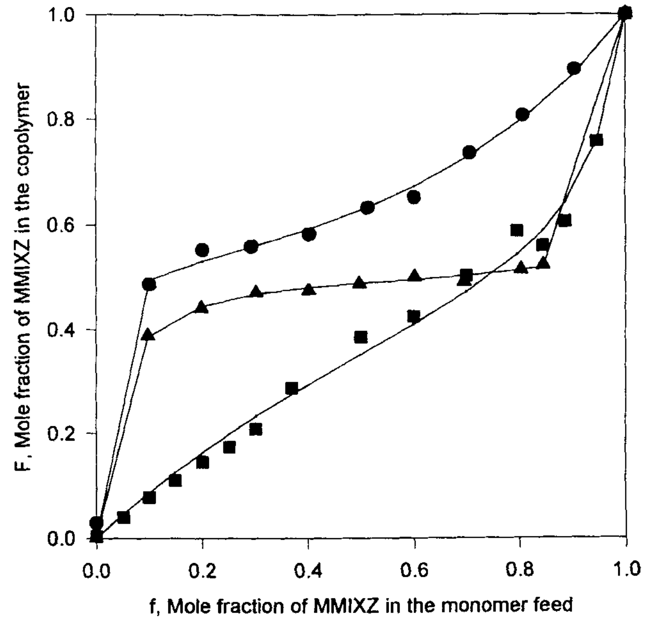

FIG. 2. Copolymer composition diagram of MMIXZ with (■) MMA, (▲) ST, and (●) VA.

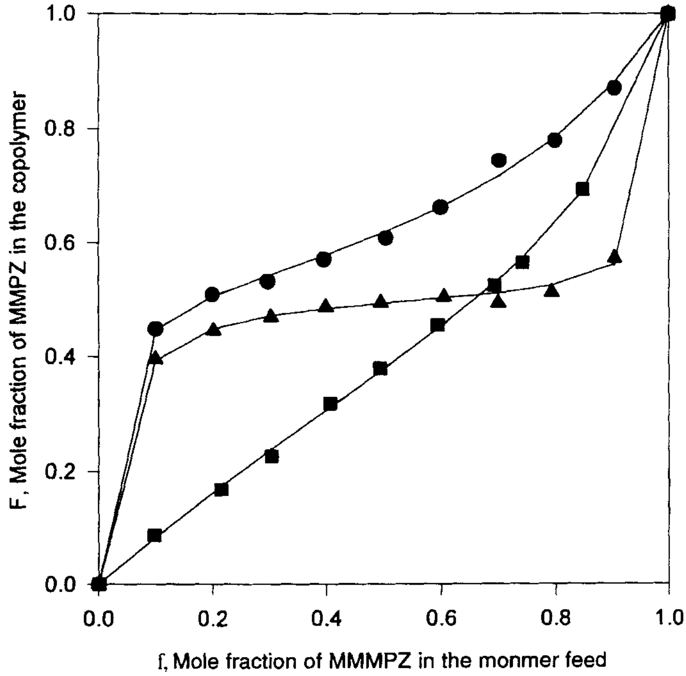

FIG. 3. Copolymer composition diagram of MMPZ with (■) MMA, (▲) ST, and (●) VA.

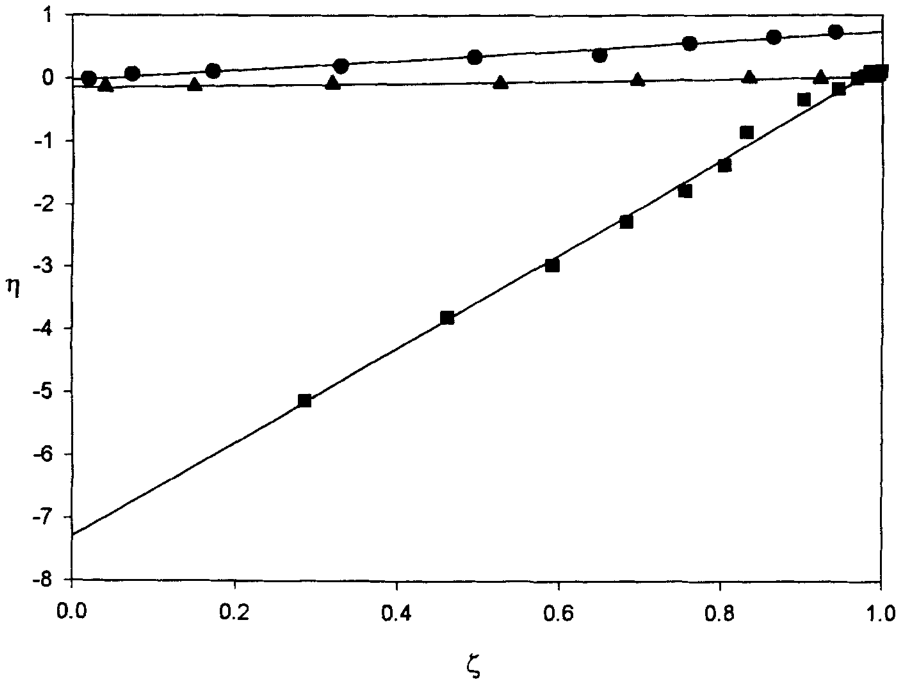

FIG. 4. Kelen-Tüdös plot for the systems MMIXZ with (■) MMA, (▲) ST, and (●) VA.

The ^1H spectrum of poly(MMIXZ): DMSO, 6.36 (broad, 1H), 4.2–4.1 (broad, 2H), 2.44 (s, 3H). ^{13}C NMR: DMSO, C_a (43.1), C_b (174.5), C_c (171.8), C_d (99.3), C_e (152.9), C_f (12.3).

The absorption due to the carbon-to-carbon double bond in the monomer (C_a 134.9) disappeared, indicating that radical polymerization proceeded via an opening of the double bond (vinyl polymerization) to give poly(substituted maleimide). Similar results were also observed for the copolymer. Further evidence for this mechanism is found from IR spectra. The IR spectra show that the band at 1400 cm^{-1}, which is due to the stretching vibration of C=C, disappeared in the polymer of MMIXZ.

These polymaleimides are different from ordinary flexible vinyl polymers; they did not melt below their decomposition temperature.

Thermal Stability of the Polymers and Copolymers

Poly(MMIXZ) and poly(MMPZ) show good thermal stability. They did not show any change in appearance when heated in air up to 300°C. Furthermore, thermogravimetric analysis (TGA) was carried out in a nitrogen stream. From the thermograms, no apparent loss could be observed below 350°C. These polymers and copolymers showed an excellent stability similar to those of poly(*N*-phenylmaleimide), and poly(*N*-alkylphenyl maleimide).

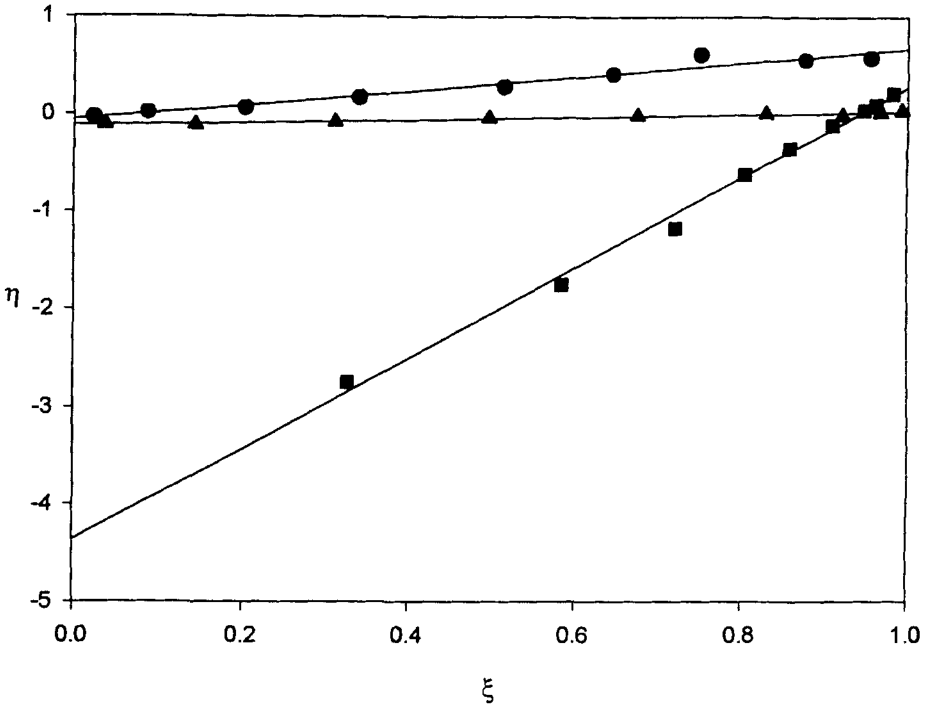

FIG. 5. Kelen-Tüdös plot for the systems MMPZ with (■) MMA, (▲) ST, and (●) VA.

TABLE 3. MMIXZ Reactivity Ratios Calculated by Different Methods

		M_2		
	Method	MMA	ST	VA
r_1	F-R	0.178	0.0164	0.755
	K-T	0.192	0.0139	0.730
	NLLS	0.130	0.0158	0.706
r_2	F-R	1.257	0.0678	0.0149
	K-T	1.272	0.0660	0.0187
	NLLS	1.084	0.0646	0.0117

TABLE 4. MMPZ Reactivity Ratios Calculated by Different Methods

		M_2		
	Method	MMA	ST	VA
r_1	F-R	0.234	0.016	0.653
	K-T	0.261	0.024	0.668
	NLLS	0.304	0.031	0.672
r_2	F-R	1.059	0.058	0.035
	K-T	1.088	0.060	0.039
	NLLS	1.141	0.061	0.036

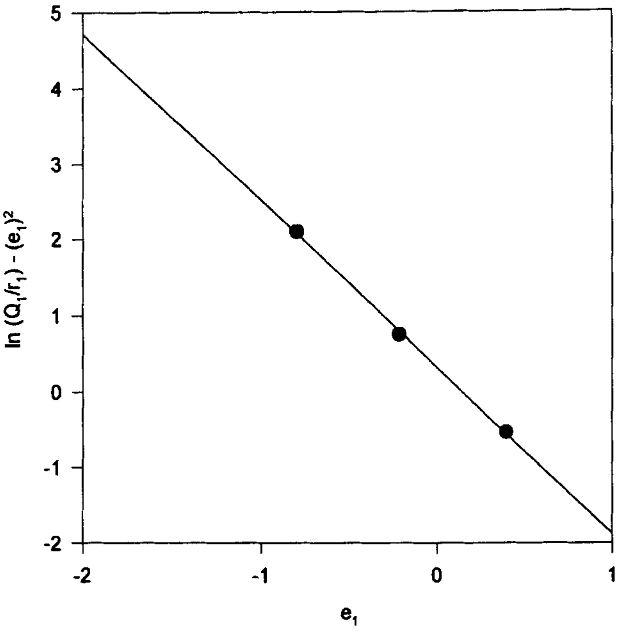

FIG. 6. Plot for the determination of Q_2 and e_2 for MMIXZ.

TABLE 5. Value of *Q* and *e* for the Monomers

Monomer	*Q*	*e*
MMIXZ	1.363	2.20
MMPZ	0.923	2.27

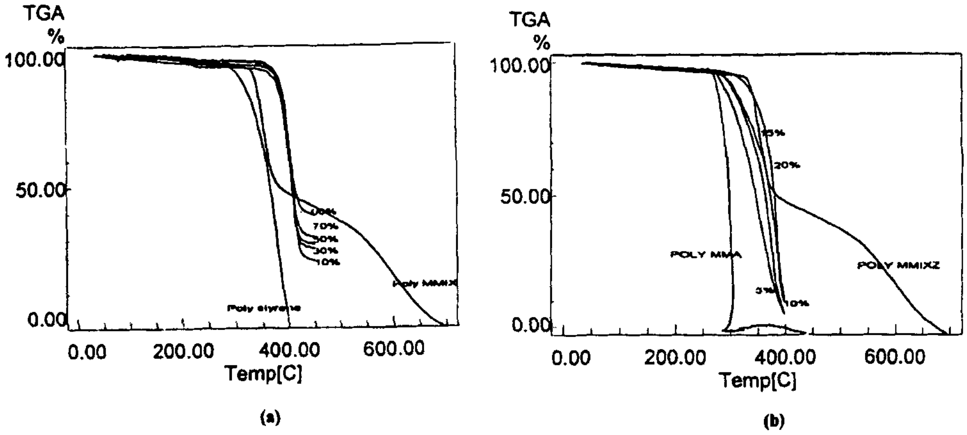

FIG. 7. (a) TGA curves of polystyrene, polyMMIXZ, and their copolymers. (b) TGA curves of polymethyl methacrylate, polyMMIXZ, and their copolymers.

Figures 7(a) and 7(b) show the thermogravimetric behavior of the copolymers of MMIXZ with ST and MMA, respectively. The polystyrene and polymethyl methacrylate start to decompose at around 300°C and degrade completely at 400°C. The homopolymer of maleimide isoxazole begins to degrade at around 350°C and performs a two-stage decomposition, losing about 50% of its weight at 400°C. The other 50% decomposes completely at about 650°C.

On the other hand, the copolymers with ST show improvement over the two respective homopolymers. The decomposition of copolymers containing 10–90% MMIXZ starts at 400°C and follows a one-stage decomposition pattern. The weight loss decreases with an increasing MMIXZ content in the copolymer. A similar behavior has been observed for the MMA copolymer series, especially at a low

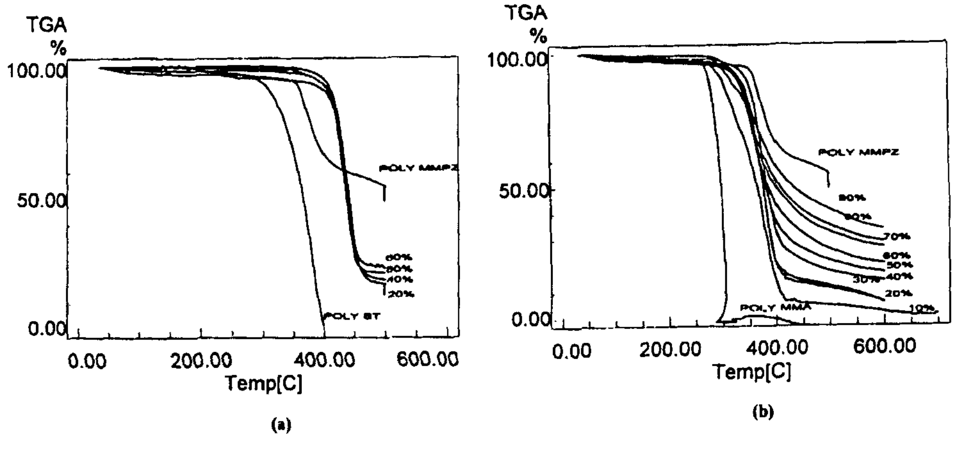

FIG. 8. (a) TGA curves of polystyrene, polyMMPZ, and their copolymers. (b) TGA curves of polymethyl methacrylate, polyMMPZ, and their copolymers.

molar concentration of MMIXZ in the copolymer with MMA. This illustrates that the incorporation of even 10% MMIXZ in either the polystyrene or polymethyl methacrylate chain improves both the starting point of decomposition as well as the residual amount of the polymer remaining at a higher temperature.

Very similar results and improvement of the thermal stability were found for the other copolymers of ST and MMA with MMPZ as shown in Fig. 8(a) and 8(b).

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REFERENCES

[1] P. O. Tawney, R. H. Snyder, R. P. Conger, K. A. Leibbrand, C. H. Stiteler, and A. R. Williams, *J. Org. Chem., 26,* 15 (1961).

[2] R. C. P. Cubbon, *Polymer, 6,* 419 (1965).

[3] M. Yamada, I. Takase, and T. Mishima, *Kobunshi Kagaku, 32,* 348 (1966); *24,* 326 (1967); *26,* 393 (1969).

[4] T. Oishi and N. Kimura, *Kobunshi Ronbunshu, 32,* 380 (1975); *33,* 141, 685 (1976). T. Oishi, T. Ishikawa, and T. Kimura, *Ibid., 36,* 751 (1979). T. Oishi and M. Fujimoto, *J. Polym. Sci., Polym. Chem. Ed., 22,* 2789 (1984).

[5] K. B. Olson and G. B. Butler, *Macromolecules, 17,* 2480, 2486 (1984).

[6] S. A. Jones and D. A. Tirrell, *Ibid., 19,* 2080 (1986); *J. Polym. Sci., Polym. Chem. Ed., 25,* 3177 (1987); G. S. Prementine, S. A. Jones, and D. A. Tirrell, *Macromolecules, 22,* 770 (1989); S. A. Jones and D. A. Tirrell, *J. Polym. Sci., Part A: Polym. Chem., 25,* 1177 (1987).

[7] A. A. Mohamed, F. H. Jebrael, and M. Z. Elsabee, *Macromolecules, 19,* 32 (1986).

[8] J. M. Barrales-Rienda, J. I. Gonzalez de la Campa, and J. G. Ramoss, *J. Macromol. Sci.—Chem., A11,* 267 (1977).

[9] T. Otsu, A. Tatsumi, and A. Matsumoto, *J. Polym. Sci., Polym. Lett. Ed., 24,* 113 (1986).

[10] T. Otsu, A. Matsumoto, T. Kubota, and S. Mori, *Polym. Bull., 23,* 43 (1990).

[11] A. Matsumoto, T. Kuboto, and T. Otsu, *Macromolecules, 23,* 4508 (1990).

[12] S. Tsunoda, T. Yamada, Y. Haruta, and T. Oishi, Jpn. Tokkyo Koho JP 62109811 (1987); F. Sato, Jpn. Kokai Tokkyo Koho JP 62156115 (1987).

[13] Y. Koinuma, K. Doninai, and K. Kato, Jpn. Kokai Tokkyo JP 0215863, (1990); *Chem. Abstr., 113*(24), 213375Q.

[14] A. Matsumoto, K. Hasegawa, A. Fukuda, and T. Otsu, *Polym. Prepr. Jpn., 39,* 1366 (1990).

[15] J. Iroh, J. P. Bell, and D. A. Scola, *J. Appl. Polym. Sci., 41,* 735 (1990); K. Hanayama, T. Asahi, and N. Ozuru, Kokai Tokkyo Koho JP 0258512, (1990); *Chem. Abstr.*, 192156B (1990).

[16] T. Oishi, T. Kawamoto, and M. Fujimoto, *Polym. J.*, p. 613 (1990).

[17] A. Matsumoto, Y. Oki, and T. Otsu, *Ibid.*, p. 23 (1991).
[18] M. Z. Elsabee, M. W. Sabaa, H. F. Naguib, and K. Furuhata, *J. Macromol. Sci.—Chem.*, *A24*, 1207 (1987).
[19] M. Z. Elsabee, M. W. Sabaa, and S. Mokhtar, *Polym. J.*, *15*, 429 (1983).
[20] M. Otsuka, K. Matsuoka, K. Takmoto, and M. Imoto, *Kogyo Kagaku Zasshi*, *73*, 1062 (1970).
[21] K. G. Olson and G. B. Butler, *Macromolecules*, *16*, 707 (1983).
[22] B. Boulevin and F. Malek, *Eur. Polym. J.*, *30*, 93 (1994).
[23] M. Fineman and S. D. Ross, *J. Polym. Sci.*, *5*, 259 (1950).
[24] T. Kelen, F. Tüdös, and B. Turcsanyi, *Polym. Bull.*, *2*, 71 (1980).
[25] D. W. Behnken, *J. Polym. Sci.*, *A2*, 645 (1964).
[26] P. W. Tidwell and G. A. Mortimer, *Ibid.*, *A3*, 369 (1965).
[27] T. Alfrey, J. J. Bohrer, and H. Mark, *High Polymers*, Interscience, New York, NY, 1952, p. 3.
[28] R. Z. Greenley, *J. Macromol. Sci.—Chem.*, *A9*(4), 505 (1975).

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