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Copolymerization of *N*-Arylmaleimides with Methyl Methacrylate

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NOTE

COPOLYMERIZATION OF *N*-ARYLMALEIMIDES WITH METHYL METHACRYLATE

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INTRODUCTION

Copolymerization parameters of a pair of monomers provide valuable information on the correlation between chemical structure and reactivity. Poly(methyl methacrylate) has been widely used in the field of plastics technology because of its crystal clear transparency and useful combination of mechanical, chemical, thermal, and electric properties [1]. Poly(*N*-arylmaleimides) and poly(*N*-alkylmaleimides) are well known for their thermal behavior [2-4]. Some reports on the synthesis of copolymers of methyl methacrylate with *N*-phenylmaleimide and *N*-mono(halophenyl)maleimide and their thermal behavior are available [5, 6]. The results of studies on the copolymerization of methyl methacrylates and three *N*-arylmaleimides are reported here.

EXPERIMENTAL

Materials

N-Arylmaleimides were synthesized by the literature method [7]. Their mp's are: phenylmaleimide (PMI), 90°C; *m*-chlorophenylmaleimide (*m*-ClPMI), 114°C; and *p*-chlorophenylmaleimide (*p*-ClPMI), 103°C. The *N*-arylmaleimides were characterized by NMR and IR. Methyl methacrylate

(MMA) (Sisco Chemicals) was freed from the inhibitor by repeated washing with 5% sodium hydroxide, followed by several washings with distilled water, and then drying over anhydrous calcium chloride for 3 days. The inhibitor-free MMA was stored in a dry bottle under nitrogen. Benzene was purified as described in the literature. AIBN (Merck) was recrystallized from chloroform three times before use.

Copolymerization

The copolymerization was carried out in benzene at 70°C by using AIBN as initiator with a monomer-to-initiator ratio of 50. The total concentration of the two monomers was 0.4 mol/L. In order to determine the time for 10% conversion, the reactions were carried out for different time intervals and the copolymers were precipitated with an excess of methanol, collected in pre-weighed G-3 crucibles, and dried in a desiccator over P_4O_{10} at room temperature. The times for 10% conversion were found by interpolation: MMA/PMI 3 h, MMA/*m*-ClPMI 2.3 h, and MMA/*p*-ClPMI 2.5 h.

To determine the reactivity ratios, the copolymerization was carried out starting with different mole ratios of the monomers and stopping the reaction by adding an excess of methanol before 10% conversion. The polymers were filtered, washed with methanol, and dried under vacuum over P_4O_{10}.

COPOLYMER COMPOSITION

The NMR spectra of the copolymers were recorded in $CDCl_3$ with a Perkin-Elmer R-32 unit. The mole ratios of the monomers in the copolymers were determined from the relative integrated areas of the peaks for phenyl (7.2-7.6 δ) and methoxy (3.6-3.7 δ) protons in the ^1H NMR spectra (Table 1).

RESULTS

When mol% MMA in the feed, $[M]_M$, is plotted against mol% MMA in the copolymers $[m]_M$, the curves for the systems MMA/*p*-ClPMI and MMA/*m*-ClPMI have an inflection point at $[M]_M = 0.75$, whereas the curve for MMA/PMI does not show any inflection point.

The reactivity ratios were determined by the Kelen-Tüdős (KT) [8] method (see Fig. 1). The Alfrey and Price [9] parameters Q_2 and e_2 of the *N*-aryl-maleimides were calculated by using the standard values of Q(0.74) and e(0.40) of MMA (Table 1).

TABLE 1. Copolymerization of Methyl Methacrylate with *N*-Arylmaleimides in Benzene at 70°C

MMA/PMI, mol% MMA			MMA/*p*-ClPMI, mol% MMA			MMA/*m*-ClPMI, mol% MMA		
Feed, $[M]_M$	Copolymer, $[m]_M$	Conversion, %	Feed, $[M]_M$	Copolymer, $[m]_M$	Conversion %	Feed, $[M]_M$	Copolymer, $[m]_M$	Conversion %
80.0	85.0	9.4	80.0	79.0	9.1	80.0	78.0	10.0
60.0	71.0	11.6	60.0	66.6	12.5	60.0	67.0	12.3
50.0	63.4	12.3	50.0	58.3	10.8	50.0	58.1	13.1
40.0	53.3	11.8	40.0	56.0	12.3	40.0	54.2	9.2
20.0	40.3	8.6	20.0	43.6	8.9	20.0	42.0	12.1
r_1	1.20			0.71			0.63	
r_2	0.38			0.14			0.14	
Q_2	0.58			1.07			1.31	
e_2	1.08			1.79			1.85	

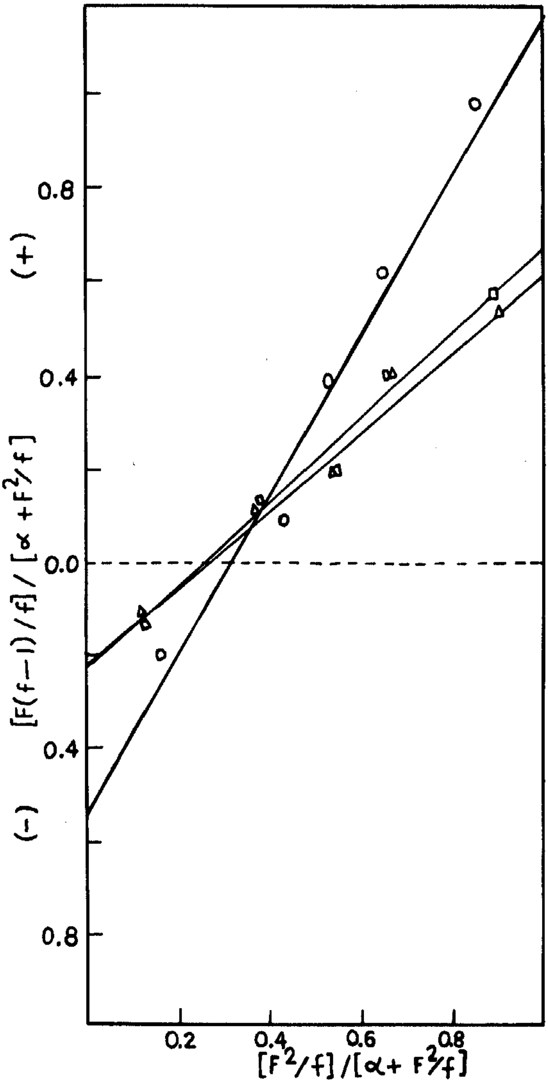

FIG. 1. Kelen-Tüdős plots for the determination of the reactivity ratios for MMA/PMI (○): MMA/*p*-ClPMI (△), and MMA/*m*-ClPMI (□).

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