

Copolymerization of *N*-Arylmaleimides with Vinyl Acetate

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ABSTRACT: Copolymerization of *N*- α -naphthylmaleimide with vinylacetate was investigated in different solvents. The solvent was found to play an important role in the reactivity of the maleimide due to molecular association of solvent/monomer molecules. The overall rate of copolymerization was found to increase as the ability of the solvent to associate with the maleimide increased. $ZnCl_2$ enhanced the reactivity of the maleimide due to a complex formation with growing radicals. The effect of substitution with a phenyl group on the reactivity of the double bond was also investigated.

KEY WORDS Copolymerization / *N*-Arylmaleimides-vinylacetate /
Reactivity Ratios / Solvent Effect / Zinc Chloride /

The polymerization of *N*-arylmaleimides was investigated in different solvents as well as in the presence of Lewis acid ($ZnCl_2$).¹ The rate changed markedly with the nature of solvent owing to molecular association of the solvent molecules with the maleimides. The rate also increased with the addition of $ZnCl_2$.

The purpose of this study has been to investigate the effect of these two factors on the copolymerization behavior of *N*-arylmaleimide with vinyl acetate. Benzene was found to induce large upfield chemical shifts of the ethylenic protons of *N*-substituted maleimides.² This was attributed to the formation of a 1:1 exo-stereospecific association of the solvent and solute molecules. Maleimides are known to be electron acceptors³ and vinyl acetate, as an electron donor. It should be expected that these two monomers can associate to form a charge transfer complex and then polymerize according to an alternating copolymerization scheme.^{4,5} The mutual competition between the solvent-maleimide interaction and the monomer association should therefore warrant investigation.

EXPERIMENTAL

Materials

Synthesis of maleimides was carried out in two stages according to the original method developed

by Searle.⁶ The final products were dried and purified by repeated recrystallization from aqueous ethanol. Melting points and analyses agreed well with the published literature data. Vinyl acetate (VAc) (Prolabo-France) was purified by distillation according to ordinary methods following removal of the inhibitor. Azobisisobutyronitrile (AIBN) (Fluka A.G.) was purified by recrystallization from methanol and then dried in the dark. Zinc chloride (Prolabo-France) was used as received. Solvents, of the highest grade available, were purified according to standard methods. The purity was checked with refractive index measurements.

Copolymerization

Polymerization ampoules of Pyrex glass were charged with the monomers, solvents and the initiator (AIBN), 0.2% by weight of the two monomers. The ampoules were then cooled and purified nitrogen gas was bubbled through the solution to eliminate dissolved oxygen. The ampoules were then sealed. Polymerization was carried out in a water bath thermostated at $70^\circ C \pm 0.1^\circ C$. Polymerization was brought to a stop by opening the glass ampoules and immediately pouring the contents into a large amount of ethanol or methanol. The precipitated materials were washed repeatedly with methanol or ethanol and dried at $60^\circ C$ until constant weights were attained. The

polymerization was homogeneous, except for that in acetonitrile where the polymers precipitated during the polymerization.

Rates of Copolymerization

Rates of copolymerization were determined using calibrated dilatometers immersed in a transparent Dewars flask connected to an ultra-thermostat. The dilatometers were charged under normal atmospheric conditions and oxygen was then eliminated by the usual cooling and thawing technique. The decrease in volume was followed as a function of time at constant temperature. After a required time, the dilatometer was connected to a vacuum line and the content was withdrawn and immediately precipitated in excess of ethanol. The copolymers were then filtered, washed, purified by reprecipitation from a dioxane solution into alcohol, and finally dried to constant weights. The rates were determined from the percent conversion and time of copolymerization.

Copolymer Analysis

Copolymer compositions were calculated on the basis of the nitrogen content of the copolymers. Nitrogen analysis was performed in the central microanalytical unit, Cairo University.

RESULTS AND DISCUSSION

The composition of the initial monomer mixtures and of the copolymers, and the conversions of the copolymers for the system α -naphthylmaleimide (α -NMI)/vinyl acetate (VAc) in different solvents are summarized in Table I. The data in Table I were analysed by the Fineman-Ross method⁷; the obtained reactivity ratios were used to construct theoretical copolymer composition curves. But the fit with the experimental points was poor. A better fit, however, was attained using the Kelen-Tüdös⁸ equation:

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

Here α is an arbitrary constant:

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

where

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

and

$$X = \frac{[M_1]}{[M_2]}, \quad Y = \frac{dM_1}{dM_2}$$

The apparent reactivity ratios of the two monomers were calculated from the straight lines in Figure 1 and are given in Table II. The continuous lines in Figures 2(a and b) are theoretical lines constructed using the reactivity ratio values in Table II. The points were obtained experimentally.

Big differences in the reactivity ratio values when changing the copolymerization solvent are an indication of a deviation of this system from a terminal model. This deviation is illustrated in Figure 1, especially at a high content of α -NMI in the monomer mixture. The deviation of points from the straight line is higher for tetrahydrofuran (THF) than chloroform. The reactivity ratios for THF and chloroform were refined by the curve fitting method originally proposed by Alfrey *et al.*,⁹ using a programmable calculator.

A significant change in the reactivity ratio values on changing the copolymerization solvent was observed by Ledwith *et al.*¹⁰ for the copolymerization of *N*-vinylcarbazole and methyl methacrylate in precipitating copolymerization, in methanol compared with solution copolymerization in benzene. Simionescu *et al.*¹¹ observed considerable difference in the reactivity ratio values on changing the copolymerization solvent in the copolymerization of *N*-carbazoleethyl methacrylate with methacryloyloxyethyl 3,5-dinitrobenzoate. They ascribed these differences to the role of the reaction medium polarity in the intermonomeric charge transfer complex (CTC) formation and reactivity, and to the heterogeneity of the reaction medium. According to then, the heterogeneous medium favours complexation between the growing chain end and the adding monomer (or complex), enhancing an alternating tendency.

In the present study, it was found that the reactivity of α -NMI decreases in the order,

$$r_{\text{THF}} > r_{\text{chloroform}} > r_{\text{dioxane}} > r_{\text{acetonitrile}}$$

which is the same for the rate of homopolymerization of α -NMI in these solvents.¹⁾

The apparent alternating tendency, illustrated by

Polymerization of *N*-Arylmaleimides

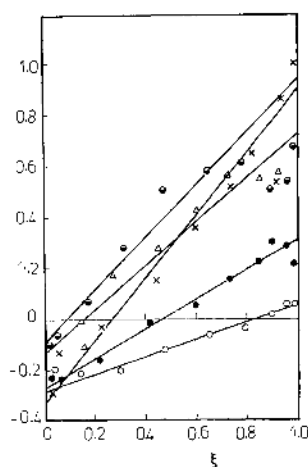
Table I. Copolymerization data for the system α -NMI (M_1)/VAc (M_2) in different solvents at 70°C

In dioxane					In dioxane + ZnCl ₂ 1% of the monomers				
Sample	<i>X</i>	Conversion	N ₂	<i>Y</i>	Sample	<i>X</i>	Conversion	N ₂	<i>Y</i>
		%	%				%	%	
1a	0.052	1.20	3.15	0.426	1b	0.052	3.86	3.20	0.440
2a	0.111	1.80	3.60	0.579	2b	0.111	—	3.99	0.770
3a	0.250	4.50	3.93	0.800	3b	0.250	7.74	4.30	0.970
4a	0.428	9.50	4.20	0.900	4b	0.428	6.60	4.50	1.150
5a	0.666	11.00	4.40	1.059	5b	0.666	3.20	4.69	1.390
6a	1.000	1.40	4.55	1.209	6b	1.000	3.42	4.90	1.710
7a	1.500	3.50	4.70	1.404	7b	1.500	3.90	5.10	2.187
8a	2.333	1.00	4.90	1.710	8b	2.330	2.40	5.15	2.330
9a	4.000	8.60	5.10	2.180	9b	4.000	9.40	5.55	4.810
10a	9.000	7.60	5.30	2.915	10b	9.000	1.80	5.78	10.100
In acetonitrile (heterogeneous system)					In THF				
Sample	<i>X</i>	Conversion	N ₂	<i>Y</i>	Sample	<i>X</i>	Conversion	N ₂	<i>Y</i>
		%	%				%	%	
1c	0.052	13.80	2.90	0.372	1d	0.052	7.60	3.70	0.620
2c	0.111	12.50	3.20	0.457	2d	0.111	6.30	4.10	0.830
3c	0.250	11.00	3.60	0.603	3d	0.250	8.20	4.45	1.110
4c	0.428	10.50	3.80	0.697	4d	0.428	7.90	4.70	1.390
5c	0.666	15.00	4.06	0.811	5d	0.666	7.20	4.90	1.720
6c	1.000	10.60	4.18	0.886	6d	1.000	5.60	5.00	1.930
7c	1.500	4.930	4.22	0.914	7d	1.500	6.50	5.10	2.190
8c	2.330	—	4.37	1.035	8d	2.330	8.90	5.14	2.330
9c	4.000	4.040	4.50	1.238	9d	4.000	13.50	5.42	3.600
10c	9.000	1.200	4.77	1.509	10d	9.000	5.50	5.72	7.320
In chloroform (temperature 60°C)									
Sample	<i>X</i>	Conversion	N ₂	<i>Y</i>					
		%	%						
1e	—	—	—	—					
2e	—	—	—	—					
3e	0.250	12.00	4.10	0.832					
4e	0.428	12.00	4.60	1.267					
5e	0.666	—	4.70	1.404					
6e	1.000	32.00	4.90	1.720					
7e	1.500	4.00	5.10	2.180					
8e	2.330	1.25	5.20	2.500					
9e	4.000	9.00	5.40	3.470					
10e	—	—	—	—					

$X = M_1/M_2$, $Y = dM_1/dM_2$
 [AIBN] = 0.2% by weight of the two monomers.

Table II. Apparent reactivity ratios for copolymerization of α -NMI (M_1) and VAc (M_2) in different solvents

Solvent	K-T method		$r_1 \times r_2$	F-R method	
	r_1	r_2		r_1	r_2
Dioxane	0.3060	0.0780	0.0230	0.2160	0.0730
Dioxane + ZnCl ₂	0.8070	0.0596	0.0480	0.6020	0.0230
Acetonitrile	0.0530	0.1830	0.0097	0.0600	0.1680
THF	0.9430	0.0247	0.0230	0.8200	0.0200
Chloroform ^a	0.7160	0.0503	0.0360	0.7800	0.0400

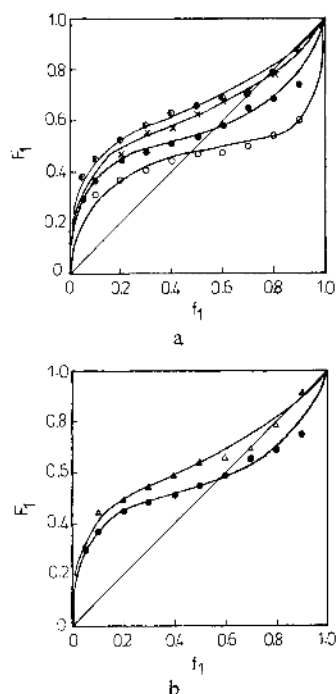
^a Temperature, 60°C.**Figure 1.** Diagram for radical copolymerization of α -NMI (M_1) with VAc (M_2) in different solvents at 70°C with AIBN as the initiator; curves are drawn using the reactivity ratios depicted in Table I: ●, dioxane; ◐, THF; ○, acetonitrile; △, chloroform (copolymerization temperature was 60°C); ×, dioxane + ZnCl₂ (1% of the two monomers).

the reactivity ratios product, follows a different order:

Acetonitrile > dioxane > THF > chloroform

The high tendency for alternation in acetonitrile ($r_1 \cdot r_2 = 0.009$) may possibly have been due in part to the heterogeneity of the medium and partly to the stronger participation of the CTC of the two monomers in the copolymerization mechanism.

In the first part of this work¹⁾ it was shown that the susceptibility of the solvents undergoes covalent association with the α -NMI which increases in the same order as that of the reactivity. When the

**Figure 2.** Kelen-Tüdös plots. a: (●), dioxane; (◐), THF; (○), acetonitrile; (×), chloroform. b: (●), dioxane; (△), dioxane + ZnCl₂.

solvent has a small tendency to associate with the solute molecules, the monomers have a better chance to participate as CTC in the copolymerization. Figure 2 also gives a clearer illustration of this assumption.

The overall rate of copolymerization $d[M_1 + M_2]/dt$ was found to be higher in THF than in dioxane for all monomer mole fraction mixtures. Figure 3 illustrates the logarithm of the rate of copolymerization of α -NMI and VAc in THF at 60°C (at

Table III. Copolymerization of *N*-arylmaleimides (M_1) and vinylacetate (M_2) in dioxane at 70°C with AIBN as the initiator

2CMI-VAc			NPMI-VAc			4CMI-VAc		
f_1	$\frac{N_2}{\%}$	F_1	f_1	$\frac{N_2}{\%}$	F_1	f_1	$\frac{N_2}{\%}$	F_1
0.05	3.60	0.3834	0.05	4.20	0.3570	0.05	3.75	0.3780
0.10	3.60	0.3840	0.10	4.60	0.4057	0.10	4.20	0.4530
0.20	4.20	0.4916	0.20	5.05	0.4620	0.20	4.40	0.4900
0.30	4.40	0.5326	0.30	5.60	0.5440	0.30	4.55	0.5190
0.40	4.45	0.5430	0.40	5.80	0.5730	0.40	—	—
0.50	4.55	0.5650	0.50	6.00	0.6050	0.50	4.50	0.5400
0.60	4.77	0.6100	0.60	6.10	0.6210	0.60	4.75	0.5590
0.70	4.96	0.6534	0.70	5.90	0.5880	0.70	4.90	0.5920
0.80	5.10	0.7010	0.80	6.10	0.6210	0.80	5.00	0.6140
0.90	5.50	0.8202	0.90	6.40	0.6720	0.90	5.10	0.6382
1.00 ^a	6.00	1.0000	1.00	7.95	1.0000	1.00	6.30	—

^a Nitrogen of the homopolymers (average of 4 values).

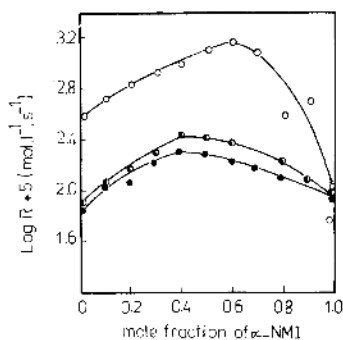


Figure 3. Initial copolymerization rates versus the monomer feed molar ratio, $[AIBN] = 1.9 \times 10^{-3} \text{ mol l}^{-1}$; monomer concentration = 2 mol l^{-1} ; temperature, 70°C, for THF temperature, 60°C. Solvent: ●, dioxane; ○, THF; ○, dioxane + $ZnCl_2$ (1% of the two monomers).

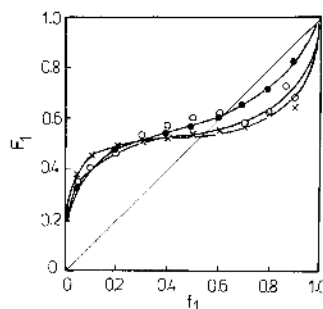


Figure 4. Diagram for radical copolymerization of NPMI (○), 2CMI (●), 4CMI (×), with VAc (M_2) in dioxane at 70°C, $[AIBN] = 0.2\%$ of the two monomers; curves are drawn using the reactivity ratios in Table IV.

70°C, the THF solution boils in the dilatometer) and in dioxane at 70°C (the rate is significantly lower at 60°C) as a function of the monomer mixture composition. The overall monomer concentration was 2 mol l^{-1} . $[AIBN] = 1.89 \times 10^{-3} \text{ mol l}^{-1}$. A more detailed analysis of the kinetics of the copolymerization of this system is now in progress.

Furthermore, the interaction of Lewis acids with the maleimides was investigated by the addition of $ZnCl_2$ to the α -NMI/VAc system in dioxane. Although no complex formation was detected spectroscopically between α -NMI and $ZnCl_2$,¹ its

presence was found to increase the rate of homopolymerization of the maleimide monomer. Here again it was found that the rate of copolymerization of α -NMI with VAc in dioxane increases on addition of $ZnCl_2$ for all monomer mixtures used (Figure 3). The reactivity ratios are also affected by the presence of $ZnCl_2$ and increased to $r_{2-NMI} = 0.807$ (Table II). This again confirms the assumption that $ZnCl_2$ must associate with the growing maleimide radical and not the monomer.

Substitution of a phenyl ring on the maleimide should also affect the reactivity of its double bond. Three more maleimides: *N*-phenylmaleimide

Table IV. Apparent reactivity ratio values for *N*-arylmaleimides (M_1) and vinyl acetate (M_2)^a in dioxane

M_1	r_1	r_2	Q_1	e_1	$r_1 \cdot r_2$
2CMI	0.368	0.0296	0.550	1.908	0.0108
NPMI	0.198	0.0550	0.296	1.906	0.0108
4CMI	0.184	0.0216	0.717	2.131	0.0039
α -NMI	0.306	0.0780	0.252	2.152	0.0230

^a $Q_2=0.026$; $e_2=-0.220$.

(NPMI), *N*-(2-chlorophenyl)maleimide (2CMI), and *N*-(4-chlorophenyl)maleimide (4CMI) were polymerized with vinyl acetate using dioxane as the solvent and AIBN as the initiator in 0.2% by weight of the two monomers in all cases. The copolymerization conditions and analysis are summarized in Table III. The reactivity ratios and the Q - e values for the 4 maleimides monomers were calculated by the K-T method using the least squares technique and are given in Table IV. The reactivity ratios of NPMI and VAc in benzene were reported by Barrales Rienda¹² to be $r_{\text{NPMI}}=1.69$ and $r_{\text{VAc}}=0$. This suggests that benzene molecules associate with the maleimide π -cloud more strongly than dioxane and that the benzene complex is more reactive than that of the dioxane. The stronger association of benzene with α -NMI was confirmed by dipole moment measurements. The details of these calculations will be published

later. If ZnCl_2 is added to NPMI/VAc in dioxane, the value of r_{NPMI} increases to 1.02, and r_{VAc} becomes 0.03, approaching the values reported for the same system in benzene without ZnCl_2 .

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