

## Copolymerization of Indene with *N*-Phenylmaleimide

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**ABSTRACT:** The copolymerization of indene with *N*-phenylmaleimide has been investigated, and the monomer reactivity ratios in these solvents were estimated. A weak charge transfer complex (CTC) between the two monomers has been suggested by the NMR measurement. Kinetic studies of the copolymerization process of these monomers reveal a participation of this CTC in the propagation step.

**KEY WORDS** Copolymerization / Indene / *N*-Phenylmaleimide / Reactivity Ratio / Charge Transfer Complex /

Donor-acceptor interaction between monomer pairs affects greatly their copolymerization behavior.<sup>1,2</sup> This interaction leads usually to the formation of alternating copolymers. Indene (In) (an electron donor) has been copolymerized with maleic anhydride (MA) (an electron acceptor) and the kinetics of this process have been investigated by Kim *et al.*<sup>3</sup> who offered a mechanism for the propagation reaction. *N*-phenylmaleimide (NPMI) is also a strong electron acceptor, but contrary to maleic anhydride it can be polymerized easily by free radical mechanism. The present study was conducted to find out the characteristic features of the copolymerization of this donor-acceptor pair of monomers and to compare it with the In/MA system.

### EXPERIMENTAL

#### *Materials*

*N*-phenylmaleimide mp 85—87°C was prepared according to previously reported procedure.<sup>4</sup> Indene, Riedel-De Haeno AG-Seelze-

Hanover, was distilled under reduced pressure just before use. Solvents were purified according to conventional procedure.<sup>5</sup> Initiator, azobisisobutyronitrile (AIBN) (BDH) was recrystallized twice from methanol.

#### *Measurements*

<sup>1</sup>H NMR spectra were taken with a WN-90 Bruker spectrometer with Me<sub>4</sub>Si as an internal standard. To determine the equilibrium constants of the complex formation, NMR spectroscopy was used. The concentration of the acceptor (NPMI) was kept constant while the concentration of the donor (In) was changed. Rates of copolymerization were measured dilatometrically. The dilatometers, filled with monomer mixture, solvent and initiator were placed in a transparent Dewars flasks connected to a thermostat. The volume contraction was recorded as a function of time. The conversion was determined gravimetrically after separation of the copolymers.

The copolymers were precipitated in methanol, filtered, washed and reprecipitated again

from dioxane in methanol, and finally dried to reach a constant weight.

Elementary analyses were conducted at the Microanalytical Unit, Cairo University.

## RESULTS AND DISCUSSION

To determine the equilibrium constant of the CTC between In and NPMI, the chemical shift of the ethylenic protons was monitored as a function of the (In) concentration. Figure 1 shows  $^1\text{H}$  NMR spectra of the mixture of these two monomers with different composition in chloroform. A noticeable upfield chemical shift on increasing the indene concentration can be seen, and this was attributed to the complexation of NPMI and In molecules. The equation of Hana and Ashbaugh<sup>6</sup> was used for the determination of the equilibrium constant  $K$  of the CTC in the following form:

$$1/\Delta_{\text{obsd}} = \frac{1}{[\text{In}]} \cdot \frac{1}{K_{\text{comp}}} + 1/\Delta_{\text{comp}} \quad (1)$$

where

$$\Delta_{\text{obsd}} = \delta_{\text{fr}}^{\text{A}} - \delta_{\text{obsd}}^{\text{A}}$$

$$\Delta_{\text{comp}} = \delta_{\text{fr}}^{\text{A}} - \delta_{\text{comp}}^{\text{A}}$$

where  $\delta_{\text{fr}}^{\text{A}}$ ,  $\delta_{\text{obsd}}^{\text{A}}$ , and  $\delta_{\text{comp}}^{\text{A}}$  are the chemical shift values of the free, the observed and the complexed NPMI, respectively. The monomer concentrations were expressed in molality. Plots of  $1/\Delta_{\text{obsd}}$  against  $1/[\text{In}]$  gave a straight line as shown in Figure 2. The values of  $K$  are obtained, using the least square method, as the intercept over the slope of the straight line. Table I contains the obtained values of  $K$  for In/NPMI system in two solvents ( $\text{CCl}_4$  &  $\text{CHCl}_3$ ) as well as those for the In/MA system also in two solvents, namely,  $\text{CCl}_4$  (present study) and ethyl acetate values cited from literature.<sup>3</sup>

The copolymerization composition data obtained in  $\text{CHCl}_3$  and cyclohexane (as an inert solvent; heterogeneous copolymerization) are summarized in Table II. Figures 3 and 4

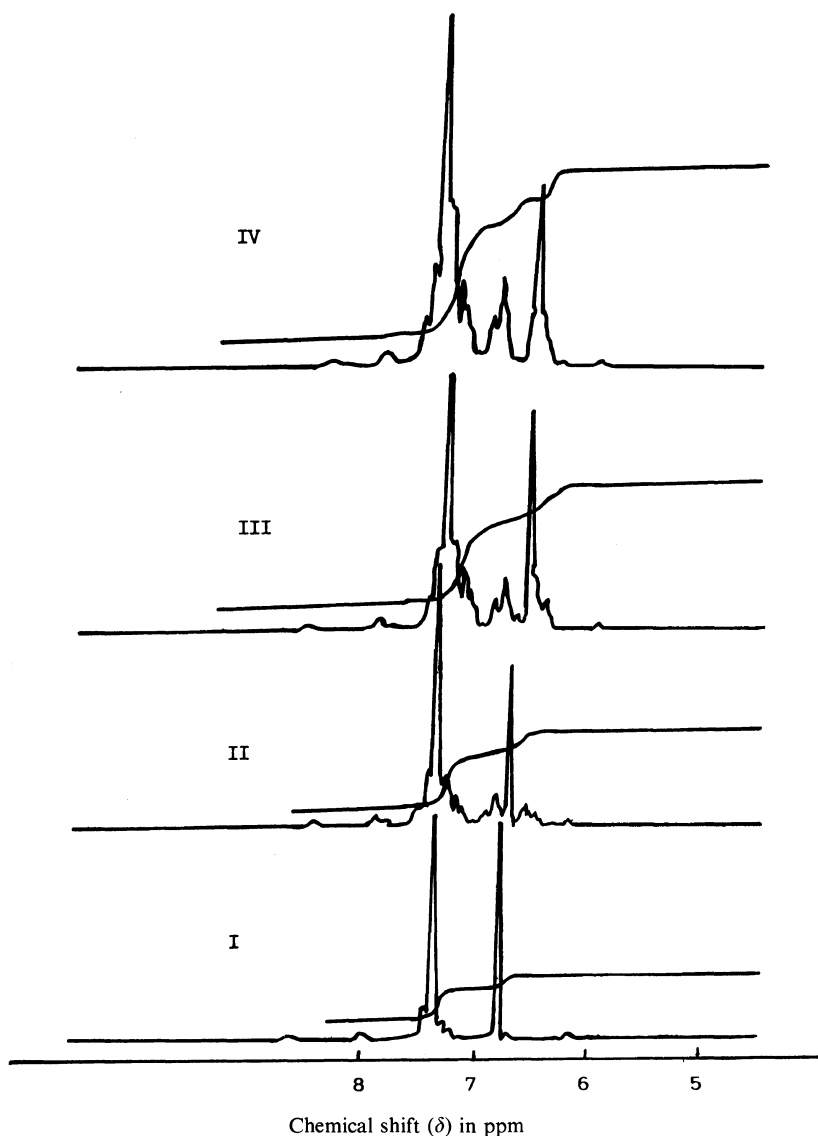
represent the copolymer composition diagram and the corresponding Kelen-Tüdös<sup>7</sup> plots, respectively. The apparent monomer reactivity ratios were determined from the slopes and intercepts of Figure 4:

$$r_{(\text{In})} = 0.247, r_{(\text{NPMI})} = 0.382 \text{ in chloroform.}$$

and

$$r_{(\text{In})} = 0.717, r_{(\text{NPMI})} = 0.63 \text{ in cyclohexane.}$$

The effect of solvent on the monomer reactivity ratios has been investigated by several authors.<sup>8-10</sup> The change in the reactivity ratios with the solvent nature was attributed to the role of the medium polarity on the intermonomeric charge-transfer complex.<sup>9</sup> The heterogeneity of the reaction medium leads also to variation of the reactivity ratio values and to an enhancement of the alternating tendency.<sup>10</sup> The latter suggestion has also been adapted in the present study. The alternating tendency in the present system is less pronounced than that of styrene/MA system.<sup>3</sup> This could be due to the steric factors. MA forms alternating copolymers with vinyl acetate and vinyl ethers.<sup>4</sup> Its inability towards homopolymerization increases the cross propagation reaction, in addition to the formation of relatively strong CTC with these comonomers (mostly donors). On the other hand, although NPMI is a strong acceptor, it can be homopolymerize, reducing thus the extent of alternation. The copolymerization of NPMI with styrene,<sup>11</sup> vinyl acetate,<sup>10</sup> and vinyl ethers<sup>12</sup> proceeds with the formation of alternating copolymers but with lower extent of alternation than that of the corresponding MA systems. The alternating copolymerization has attracted the attention of many research groups. The following three postulates have been presented to explain this phenomenon. The first is the cross-reaction of free monomer due to either difference in polarity between monomer pairs or charge-transfer interaction between a growing polymer radical and a monomer molecule.<sup>13</sup> The second postulate is



**Figure 1.** NMR spectra of the In/NPMI mixtures in chloroform: I, NPMI only; II, NPMI + In (3.3 molal); III, NPMI + In (2.22 molal); IV, NPMI + In (1.66 molal).

the homopolymerization of a CTC formed between monomer pairs.<sup>14</sup> The third mechanism is the combination of the aforementioned two postulates which has been given by Shirota *et al.*<sup>15</sup>

According to the latter mechanism, the overall initial copolymerization rate  $R_p$  consists of two parts:

A contribution due to the polymerization of the free monomers  $R_p(f)$

$$R_p(f) = A(x)[M_1], \quad (2)$$

and a second part due to the participation of a CTC  $R_p(CT)$

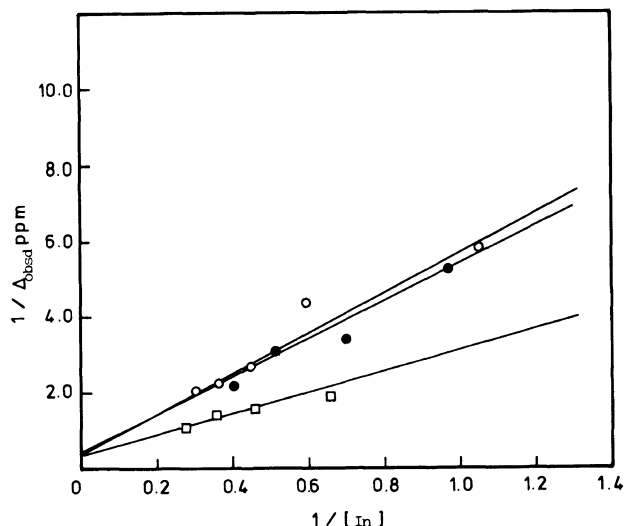


Figure 2. Relation between  $1/\text{obsd}$  and inverse concentration of In: □, MA/In, in  $\text{CCl}_4$ ; ○, In/NPMI, in  $\text{CHCl}_3$ ; ●, In/NPMI, in  $\text{CCl}_4$ .

Table I. Equilibrium constants of the CTC for the In and NPMI monomers, in different solvents

System	Solvent	$K$	$t/^\circ\text{C}$
In/MA	Ethyl acetate	0.32 <sup>a</sup>	25
	Ethyl acetate	0.16 <sup>a</sup>	45
	$\text{CCl}_4$	0.35	25
In/NPMI	$\text{CHCl}_3$	0.042	25
	$\text{CCl}_4$	0.087	25

<sup>a</sup> Data cited from ref 3.

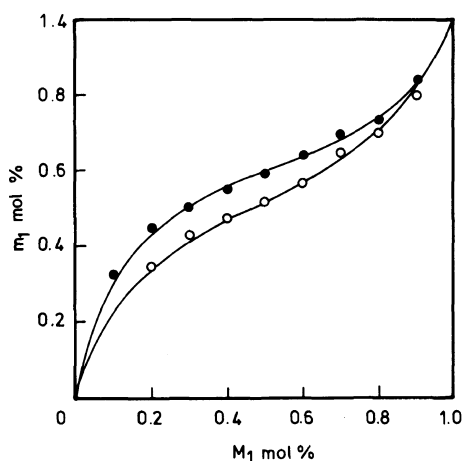


Figure 3. Copolymer composition diagram for In/NPMI system in: ○,  $\text{CHCl}_3$ ; ●,  $\text{CCl}_4$ .

Table II. Copolymerization data for the System In/NPMI in  $\text{CHCl}_3$  and cyclohexane at  $65^\circ\text{C}$  using AIBN ( $5 \times 10^{-3} \text{ mol l}^{-1}$ ) as initiator<sup>a</sup>

mol% of In in monomer feed	In cyclohexane		In $\text{CHCl}_3$	
	N%	Copolymer composition/mol%	N%	Copolymer composition/mol%
		NPMI		NPMI
10	7.25	85.87	7.00	81.24
20	6.60	74.40	6.35	70.56
30	6.3	71.30	6.00	63.35
40	6.00	66.80	5.20	57.85
60	5.40	59.60	4.60	48.57
70	4.95	52.70	4.40	43.50
80	4.60	47.56	3.6	36.88
90	3.4	33.10		

<sup>a</sup> Conversion was kept below 10%.

$$R_p(\text{CT}) = A(x) \cdot K \left[ \frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}} \cdot x \right] [M_1]^2 \quad (3)$$

$$\begin{aligned} R_p &= R_p(f) + R_p(\text{CT}) \\ &= A(x)[M_1] + A(x)K[k_{1c}/k_{12} \\ &\quad + (k_{2c}/k_{21})x][M_1]^2 \end{aligned} \quad (4)$$

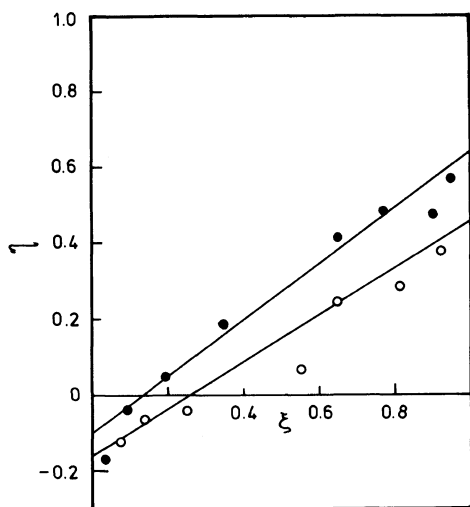


Figure 4. Kelen-Tüdös plots for In/NPMI system in  $\text{CCl}_4$  (●) and  $\text{CHCl}_3$  (○).

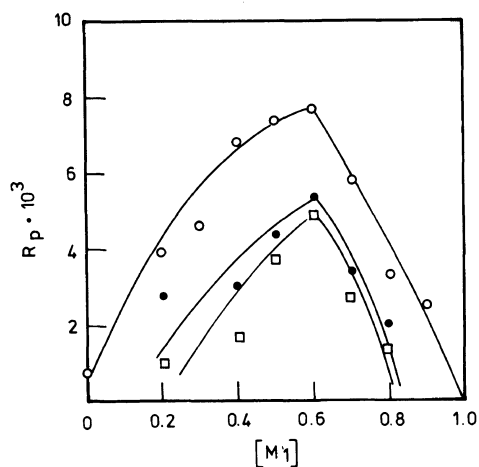


Figure 5. Rate of polymerization of In/NPMI system as a function of monomer ratio at different total monomer concentration 2 (○), 1.5 (●), 1 (□) in  $\text{mol l}^{-1}$ .

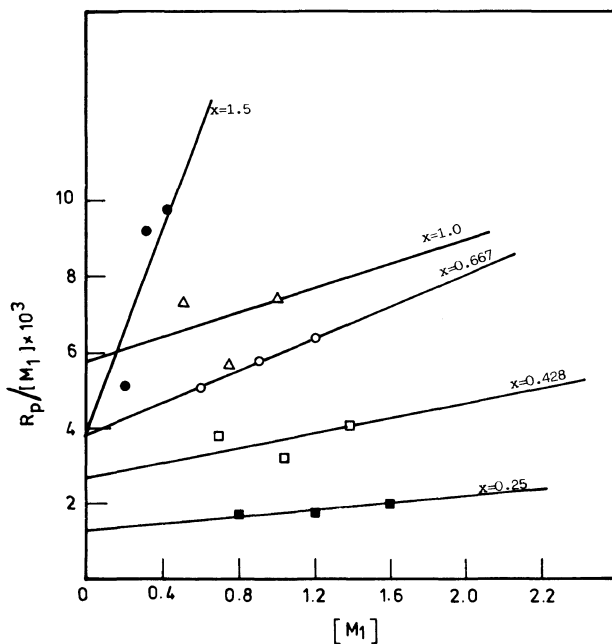


Figure 6.  $R_p/[M_1]$  vs.  $[M_1]$  at various  $x = [M_2]/[M_1]$ .

$A(x)$  is a function of the rate of initiation (which is considered to be independent upon the monomer feed ratios), the rate constants of the bimolecular homo- and cross-termination reactions, and the rate constants of addition

reactions. Here,  $x$  is the monomer feed ratio,  $[M_2]/[M_1]$ .  $K$  is the equilibrium constant of the CTC,  $k_{1c}$  is the rate constant of the CTC addition to the donor (In) end of the growing chain and  $k_{2c}$  is the analogous expression for

**Table III.** Overall initial copolymerization rate  $R_p$  and the value of  $R_p/[M]$  for each given monomer feed molar ratio and the rate of the free monomer  $R_p(f)$  and the charge-transfer complex monomer  $R_p(CT)$  as a function of the monomer concentrations for the In/NPMI system

$x = M_2/M_1$	Total monomer concentration mol l <sup>-1</sup>	[In]=[M <sub>1</sub> ] mol l <sup>-1</sup>	$R_p \times 10^3$	$R_p/[M_1] \times 10$	$R_p(f) \times 10^3$	$R_p(CT) \times 10$
0.25	2.0	1.6	3.3	2.0	2.1	1.1
	1.5	1.2	2.1	1.7	1.5	0.6
	1.0	0.8	1.4	1.8	1.0	0.3
0.428	2.0	1.4	5.8	4.1	3.8	2.0
	1.5	1.05	3.4	3.2	2.9	1.1
	1.0	0.7	2.7	3.8	1.9	0.5
0.667	2.0	1.2	7.6	6.3	4.6	3.0
	1.5	0.9	5.2	5.8	3.4	1.7
	1.0	0.6	5.0	8.3	2.3	0.8
1.00	2.0	1.0	7.4	7.4	5.7	1.6
	1.5	0.75	4.3	5.7	4.3	0.9
	1.0	0.5	3.7	7.4	2.9	0.4
1.50	2.0	0.8	6.9	8.6	0.8	7.4
	1.5	0.6	3.0	5.0	0.6	4.1
	1.0	0.4	1.6	4.0	0.4	1.8
4.00	2.0	0.4	3.9	9.8	1.6	3.0
	1.5	0.3	2.7	9.1	1.2	1.7
	1.0	0.2	1.0	5.0	0.8	0.8

the acceptor and (NPMI).

The overall initial copolymerization rate  $R_p$  for the investigated system in  $\text{CHCl}_3$  was measured under a constant initiator concentration at each given monomer feed ratio,  $x$ . The data obtained for this system are plotted in Figure 5. A plot of  $R_p/[M_1]$  vs.  $[M_1]$  for each  $x$  value gives a straight lines as shown in Figure 6.  $M_1$  stands for In and  $M_2$  for NPMI. The slope of each line when divided by the intercept gives a function  $F(x)$ <sup>15</sup>:

$$F(x) = K[k_{1c}/k_{12} + (k_{2c}/k_{21})]x \quad (5)$$

When  $F(x)$  is plotted against  $x$ , a straight line should therefore be obtained. However, due to the scattering of points in Figure 6 the uncertainties in the slopes and intercepts are quite high, and accumulate in the plot of  $F(x)$  vs.  $x$  giving a poor straight line relation. Using the data in Table II, a straight line was obtained with a negative intercept which could be approximated to zero, since a negative value has

no physical significance, with a slope of 1.27. In this way  $k_{1c}/k_{12} = 0$ . In other words, the chain with indene radical end can not attack CTC monomer. The slope  $K(k_{2c}/k_{21}) = 1.27$  and  $K = 0.042$ , one gets a value of 30.2 for  $k_{2c}/k_{21}$ . This means that the CTC prefers to be attacked by NPMI radical. In this way one should not expect a high alternation tendency in this system.

The last two columns in Table III represent the contribution of the free monomer and the CTC in the overall rate of copolymerization. The data indicate a high participation of the CTC although its concentration is very small.

Further discussion will be reported in the near future.

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