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Copolymerization and Monomer Reactivity Ratios of N-*p*-chlorophenyl Maleimide with Ethyl Acrylate

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The free radical copolymerisation of N-*p*-chlorophenyl maleimide (CMI) with ethyl acrylate (EA) has been carried out in tetrahydrofuran (THF) at 70°C. The copolymers were characterized by infrared and ^{1}H-NMR spectroscopic methods. The copolymer compositions were established by elemental analysis. The reactivity ratios of copolymerisation were computed by using Finnmen-Ross and Kelen-Tudos methods and were found to be $r_1 = 1.106$ and $r_2 = 0.352$. Thermogravimetric analysis of the copolymers were carried out in nitrogen atmosphere at a heating rate of 10°C/min. The solubility parameters of all the copolymers were determined.

Key Word: Copolymerization, Monometer, Reactivity, N-*p*-Chlorophenyl maleimide, Ethyl acetate.

INTRODUCTION

The homopolyimides have certain disadvantages like insolubility, infusibility which make processing difficult. Copolymerisation is an alternative method for improving the polymer properties to meet specific requirements. Knowledge of copolymerisation parameters is theoretically and practically of great importance. The correlation between reactivity and monomer structure can be studied conveniently by copolymerizing a homologous series of a monomers with a reference monomer.

The free radical initiated copolymerization of N-substituted maleimide with various vinyl monomers were investigated to modify the polymer properties[1,2]. In continuation to our studies[3] on the N-arymaleimides copolymers with methyl acrylate, the present study deals with the copolymerization of N-*p*-chlorophenyl maleimide (CMI) with ethyl acrylate (EA) initiated by AIBN in THF at 70°C. The reactivity ratios have been determined by Finnmen-Ross (FR)[4] and Kelen-Tudos (KT)[5] methods.

EXPERIMENTAL

Preparation of monomer

N-*p*-chlorophenyl maleimide was synthesized from maleic anhydride and *p*-chloroaniline in two stages according to the original method developed by Searle[6]. After recrystallization from carbon tetrachloride, N-*p*-chlorophenyl maleimide gave yellow needles, m.p. 113.5°C.

Copolymerization

The free radical copolymerization method was adopted for the synthesis of copolymer of different compositions using AIBN as an initiator and THF as

solvent. The polymerization reaction was carried out at 70°C for 12 h. The polymer was precipitated in excess quantity of methanol. Each of copolymer samples was dried at 60°C under vacuum.

RESULTS AND DISCUSSION

Solubility

Solubility is one of the important requirements for polymer and hence the solubilities of the copolymer were tested in various organic solvents. It is found that the relative solubility of copolymers depends on the participating co-monomer and their composition.

All the type of copolymers are soluble in acetone, dioxane, dimethyl formamide, dimethyl sulphoxide, dimethyl acetate, ethyl acetate and isobutyl acetate. They are partilly soluble in carbon tetrachloride, chloroform, benzene and toluene. These are totally insoluble in hexane, cyclohexane, methanol, ethanol, petroleum ether and water.

Characterization

IR spectrum of copolymer sample of CMI with ethyl acrylate (CPEA 5) shows the characteristic absorption bands (cm^{-1}) at 2969, 2954, 2938 (C—H stretching of alkyl group in ethyl acetate segment), 1772–1716 (C=O stretching, imide, amide and ester group), 1600, 1496 (aromatic C=C stretching), 1091 (aromatic C—Cl stretching), 835, 708, 685 (C—H bending, 1,4-disubstituted benzene). The absence of characteristic band at 948 cm^{-1} indicates the polymer formation *via* vinyl group[7].

The ^{1}H-NMR spectrum of copolymer sample of CMI with ethyl acrylate (CPEA 5) exhibits the peak at δ = 7.20–7.60 ppm corresponds to the two types of aromatic protons of the CMI segments in the copolymer chain. The δ = 7.40–7.58 ppm (broad) is due to two aromatic protons *meta* to N of imide group and the δ = 7.27–7.31 ppm (broad) is due to the two aromatic protons *ortho* to N of the imide group. The broad peak observed at δ = 3.61–3.76 ppm is assigned to 2H of methane (—CH—CH) protons of copolymer main chain. The broad peak observed in the range δ = 1.18–1.23 ppm is of 3H of methyl (—CH_3) group, δ = 1.70–1.85 ppm is of 2H of methylene (—CH_2) group, δ = 2.04–2.27 ppm is of 1H of methine (—CH) group and at δ = 4.06–4.11 ppm is of 2H of (—OCH_3) group.

Copolymer composition

The copolymer composition of samples were determined by N% analysis, since CMI monomer (M_1) contains nitrogen while other monomer ethyl acrylate do not have any nitrogen. Thus the N% in the copolymer can safely be used to estimate the copolymer composition[8–10]. In the present investigation the copolymer composition (w% and mole ratio) has been determined by N% consideration.

The weight percentage of monomer CMI in copolymer was calculated as

$$WM_1\% = \frac{N\% \text{ in copolymer}}{N\% \text{ in } M_1} \times 100$$

The no. of moles n_1 and n_2 of monomers M_1 and M_2 are given by

$$N_1 = WM_1\%/MW_1$$

$$N_2 = WM_2\%/MW_2$$

which will give mole ratio of monomer M_1 and M_2 as

$$\text{Mole ratio} = n_1/n_2$$

and mole fraction F_1 of monomer in copolymer was determined as

$$F_1 = n_1/(n_1 + n_2)$$

The results of copolymer samples have been summarized in Table-1. It is evident that as mole fraction of CMI in feed is increased, the mole ratio of CMI in copolymer also increases. The dependence of copolymer composition (F_1) on feed ratio (X_1) is shown in Fig. 1. As the composition of monomer in copolymer is different from that of feed ratio, this suggests that the copolymer composition is not azeotropic.

This study reveals that copolymers formed are not alternate copolymers but are random copolymers.

Reactivity ratio

The reactivity ratios of CMI and EA were estimated from the monomer feed ratios by the application of methods like Finnmen-Ross (F-R)[4] and Kelen-Tudos (K-T)[5]. Table-2 shows the F-R and K-T parameters for the copolymers. The reactivity ratios r_1 and r_2 are the slope and the intercept on y-axis respectively (F-R plot) and the intercept at $\xi = 1$ gives r_1 and the intercept at $\xi = 0$ gives r_2/α ($\alpha_{cal.} = 0.628$) (K-T plot). The values from the F-R plot and K-T plot (Fig. 2 and Fig. 3) are presented in Table-3. The reactivity ratio of CMI r_1 is greater than r_2. This result shows higher reactivity ratio of CMI as compared to acrylate; the copolymers formed will, therefore, be richer in CMI.

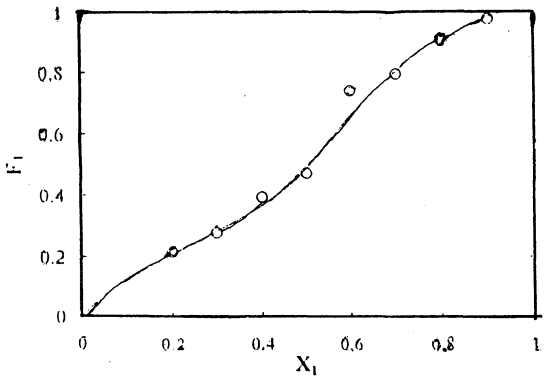

Fig. 1. Feed composition (X_1) vs. copolymer composition

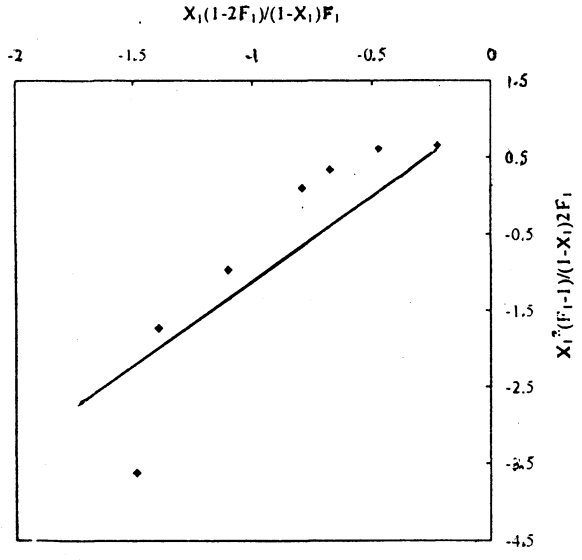

Fig. 2. Finemann-Ross plot for copolymer CPEA

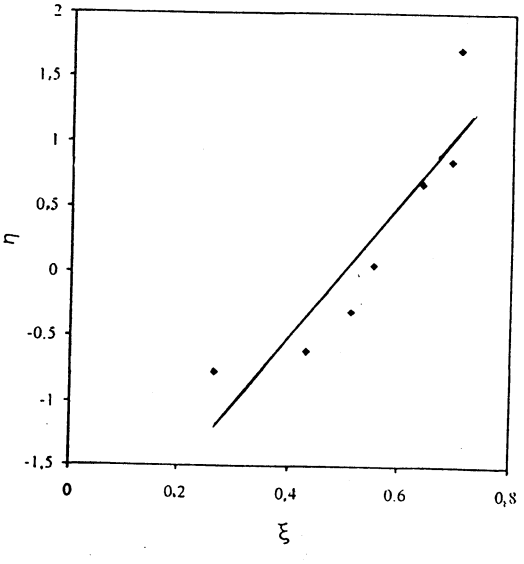

Fig. 3. Kelen-Tudos plot for copolymer CPEA

TABLE-1
FEED AND COPOLYMER COMPOSITION

Polymer code	Feed mol. fraction		N %	Copolymer wt % of CMI	Composition F_1
	CMI	EA			
CPEA 1	0.1	0.9	—	—	—
CPEA 2	0.2	0.8	2.45	36.35	0.216
CPEA 3	0.3	0.7	3.02	44.01	0.280
CPEA 4	0.4	0.6	3.90	57.86	0.398
CPEA 5	0.5	0.5	4.41	65.43	0.476
CPEA 6	0.6	0.4	5.76	85.46	0.740
CPEA 7	0.7	0.3	6.00	89.02	0.796
CPEA 8	0.8	0.2	6.45	95.70	0.915
CPEA 9	0.9	0.1	6.67	98.96	0.979

Thermogravimetric analysis

The thermal stability data of the copolymers are measured by TGA in nitrogen atmosphere. All the copolymers degrade in three steps. For the copolymer samples of CMI with ethyl acrylate of ratio 8 : 2 (CPEA 2) (Fig. 4) initial decomposition begins at 350°C which continues up to 440°C. About 63.61% weight loss is observed during the first step degradation. The second step degradation starts from 510 to 630°C with about 9.81% weight loss is found at 419 and 580°C for first and second steps respectively.

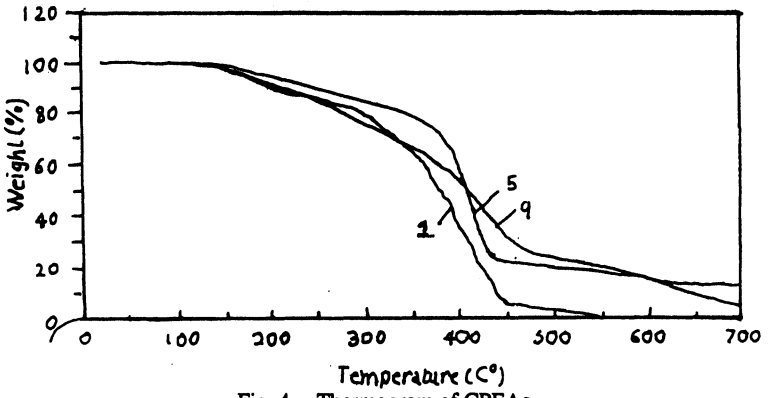

Fig. 4. Thermogram of CPEAs

CPEA 5 ratio 5 : 5 (Fig. 4) exhibits thermal stability up to 345°C. The first decomposition step involves a weight loss of 33.03% and proceeds up to 440°C. The maximum rate of weight loss occurs at 427°C. The second decomposition step begins from 540 to 690°C involving a weight loss of 11.10%. The maximum rate of weight loss in this step occurs at 660°C.

CPEA 9 ratio 1 : 9 (Fig. 4), the first decomposition step involving a weight loss of about 53.72%, begins at 345°C and proceeds up to 450°C. The second decomposition step begins from 540 to 690°C involving weight loss of about 22.67%. The maximum rate of weight loss in this step occurs at 600°C.

TABLE-2
PARAMETERS FOR F-R METHOD[4] AND K-T METHOD[5] TO DETERMINE REACTIVITY RATIOS OF MONOMERS

Code	Mole ratio feed	Mole fraction of CMI		F-R method		K-T method	
		X_1	F_1	$\frac{X_1(1-2F_1)}{(1-X_1)F_1}$	$\frac{X_1^2(F_1-1)}{(1-X_1)^2F_1}$	η	ξ
CPEA 1	1 : 9	0.1	—	—	—	—	—
CPEA 2	2 : 8	0.2	0.215	0.651	–0.227	–0.771	0.265
CPEA 3	3 : 7	0.3	0.280	0.613	–0.472	–0.612	0.431
CPEA 4	4 : 6	0.4	0.398	0.342	–0.672	–0.306	0.512
CPEA 5	5 : 5	0.5	0.476	0.101	–0.790	0.058	0.551
CPEA 6	6 : 4	0.6	0.740	–0.973	–1.101	0.686	0.637
CPEA 7	7 : 3	0.7	0.796	–1.735	–1.395	0.858	0.689
CPEA 8	8 : 2	0.8	0.915	–3.628	–1.486	1.116	0.703
CPEA 9	9 : 1	0.9	0.979	–8.807	–1.737	3.723	0.734

TABLE-3
Monomer reactivity ratio r_1 and r_2

Method	M_1	M_2
	CMI —CO—EA	
	r_1	r_2
FR	1.106	0.352
KT	0.997	0.265

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