



Copolymerization of *N-p*-Chlorophenylmaleimide with Vinyl Acetate: Evaluation of the Energy of Activation and Monomer Reactivity Ratios

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ABSTRACT

The copolymers (CPVAc) with various proportions of *N-p*-chloromaleimide (CMI) and vinyl acetate were prepared by free radical polymerization in tetrahydrofuran (THF) using 2,2'-azo-bis-isobutyronitrile (AIBN) as an initiator at 70±2°C. The series of copolymers (CPAVc1-CPAVc9) were characterized by FTIR and ¹H NMR spectroscopic methods. Solubility and viscosity parameters were studied for all the nine copolymers. The viscosity data were used to evaluate Huggins (KH), Kraemer (KK), Schulz-Blaschke (KSB), and Martin (KM) constants. Their energy of activation was calculated from thermogravimetric analyses of the copolymers using Broido's method and copolymer compositions were established by elemental analysis. The copolymer chains were comprised of the first monomer M₁(CMI) and the second monomer M₂(VAc). Units were distributed in a particular sequence for a definite chain length which was dependent on the feed composition of each monomer. The reactivity ratios of copolymerization were computed by using Fineman-Ross and Kelen-Tüdös methods and were found to be $r_1 = 1.177$ and $r_2 = 0.419$.

Key Words:

copolymerization;
N-p-chlorophenylmaleimide;
reactivity ratio;
activation energy;
vinyl acetate.

INTRODUCTION

Attention has been paid to synthesize the high performance polymeric materials with increased thermal stability. The polymer with heat resistance and good mechanical properties are the requirements of present day technology [1,2]. Among the thermally stable polymers with good mechanical proper-

ties, polyimides possess such properties [3]. The homopolyimides have certain disadvantages like insolubility and infusibility which make processing difficult. Copolymerization of maleimide is an alternative method for improving the polymer properties to meet specific requirements. Many such

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novel syntheses have been adopted for studying the control on degree of branching, molecular weights and macroscopic properties of block tercopolymers using atom transfer radical block copolymerization of methyl acrylate with polyvinyl acetate [4], higher alkyl methacrylates [5], and tertiary butyl methacrylates [6]. Therefore, to have a good knowledge of copolymerization parameters are theoretically and practically of outmost importance.

At the same time, solubility and viscosity of such copolymers are of great importance in understanding the processability of the polymers. There has been little interest focused on such basic properties which are of immense utility in the industrial applications. The sequential distribution of different monomers in a copolymeric chain depends upon the monomer feed ratio utilized during the copolymerization. The reactivity ratios in turn reflect the inherent tendencies of a radical to react with its related monomers relative to the comonomer. Hence the present work has been carried out to depict the importance of the basic properties of copolymers which in fact are dependent on their feed compositions.

In the present work, the free radical initiated copolymerizations of *N*-substituted maleimide with vinyl acetate were synthesized with varying feed compositions in THF at $70 \pm 2^\circ\text{C}$. The variation of the intrinsic viscosity and hence Huggins, Kraemer, Schulz-Blaschke, and Martin constants in different compositions of copolymers were evaluated. The energy of activation by Broido's method was computed from TGA data and the reactivity ratios have been determined by Finnmen Ross (FR) and Kelen-Tüdös (KT) methods.

EXPERIMENTAL

Materials

Maleic anhydride (SRL, extra pure) was recrystallized from chloroform and then further purified by the sublimation at 54°C . *p*-Chloroaniline (AR, BDH) was used as received. Vinyl acetate (AR, BDH) was purified by shaking it two to three times with 5% NaOH solution to remove hydroquinone inhibitor. It was then dried over anhydrous calcium chloride for 6 h and distilled. The head and tail fractions were discard-

ed. 2,2'-Azo-bis-isobutyronitrile (AIBN) obtained from Wilson Lab was crystallized from dry methanol and dried overnight at room temperature. Anhydrous sodium acetate (SRL, pure) was used as received. DMF, THF, acetic anhydride, methanol, etc. used in the present work were of analytical grade and of purity better than 99% and were used as received.

Preparation of Monomer (CMI)

N-p-chlorophenylmaleimide (CMI) was synthesized by the condensation reaction of maleic anhydride with *p*-chloroaniline followed by cyclodehydration using acetic anhydride and sodium acetate according to the modified method of Benicewicz [7]. *p*-Chloroaniline (0.1 mol) in 100 mL DMF solvent was added in a three neck 500 mL flat bottom flask to which condenser, thermometer, and an addition funnel were fitted and placed in a temperature bath. Maleic anhydride (0.1 mol) in 100 mL DMF was gradually added dropwise for 1 h at regular time interval while keep-

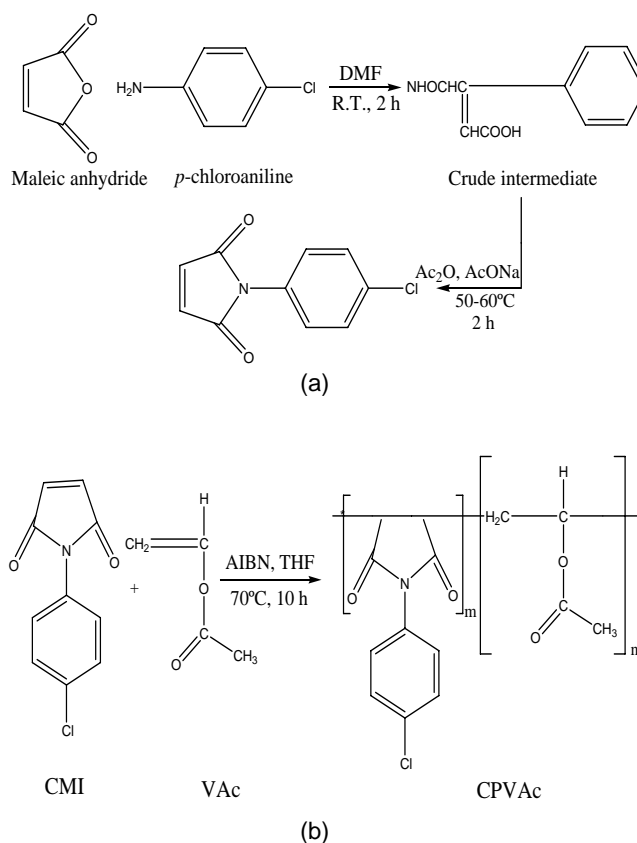


Figure 1. Structures of: (a) monomer CMI and (b) copolymer CPVAc.

ing the water bath temperature at 10°C.

When the reaction mixture turned yellow, the mixture was stirred for additional period of 3 h and the bath temperature was raised to 60°C and then 2.0 g anhydrous sodium acetate was added followed by acetic anhydride (0.12 mol) dropwise. The reaction was stirred for more 2 h till light yellow precipitate of CMI was obtained by adding the solution to ice-water bath. After recrystallization from methanol/water, pure CMI was obtained (mp:113.5°C and yield:75%) (Figure 1a).

Copolymerization

The free radical copolymerization method was adopted for the synthesis of copolymer of different compositions using AIBN as an initiator and THF as a solvent (35 mL). The polymerization reaction was carried out at 70±2°C for 12 h. The copolymers were precipitated in excess quantity of methanol and dried at 60°C under vacuum. Nine such copolymer samples (CPVAc1-CPVAc9) were synthesized using different feed ratios of monomers CMI and VAc. (Figure 1b)

Instrumentation Methods

Elemental Analyses

Elemental analyses (N%) of all polymer samples were carried out on Carlo Erba Elemental Analyzer Model 1106. It was carried out at the Department of Chemical Sciences, North Maharashtra University, Jalgaon. The N% has been used to calculate the feed composition of various copolymers.

Infrared Spectra

Fourier transform infrared spectra (FTIR) of solid samples of copolymers have been scanned on Perkin Elemer, FTIR spectrophotometer model, spectrum RXIFT-IR system at Gujarat Insecticide Limited, Ankleshwar (Gujarat, India). For preparation of the sample, highly purified and desiccated 1.0 g KBr and 4.0-5.0 mg of sample were mixed thoroughly and ground in a mortar. The finely ground mixture was then transferred to the mould and the pellets prepared in this manner were used to scan FTIR spectra of the copolymer samples by standard procedure.

The interpretations of the infrared spectra are based upon the empirical data obtained by assigning infrared absorption values to the structural units.

Nuclear Magnetic Resonance Spectra

¹H NMR spectra were taken in DMSO-D₆ solvent on Bruker-DPX-200 spectrometer at 200 MHz (RSIC, CDRI, Lucknow) with a sweep time of 10 min at room temperature. TMS was used as an internal reference.

Solubility

The solubility tests were conducted as follows: Samples of 30-40 mg of finely ground powder of copolymer samples were placed into small test tubes and 1 mL of each type of solvent was added and then stirred at 30±2°C for some time. A swollen gel which was an indication of polymer dissolution in the solvent was formed while shaking. Then, the gel was ultimately disintegrated leading to the formation of true solution. In some cases dissolution took a long time or it was necessary to raise the temperature.

Viscosity Measurements

The viscosity measurements of the copolymer solutions were carried out with Ubbelohde suspended level viscometer. All the measurements were performed at 30°C using appropriate set up of the thermostat. The flow time for definite volume of liquid (solution of copolymers) was measured. A definite and accurately weighed sample of each copolymer was dissolved in DMF and agitated to give a clear solution, which was diluted up to the mark.

RESULTS AND DISCUSSION

Solubility

Solubility is one of the important requirements for polymers in order to have an idea of processability. Hence the solubilities of the nine copolymers were tested in various organic solvents. It was found that the relative solubility of copolymers depends on the participating co-monomer and its composition [8].

All the nine copolymers were soluble in acetone, *p*-dioxane, dimethyl formadide, dimethyl sulphoxide, dimethyl acetate, ethyl acetate, and isobutyl acetate. They are partially soluble in carbon tetrachloride, chloroform, benzene, toluene, while they were totally insoluble in hexane, cyclohexane, methanol, ethanol, petroleum ether, and water.

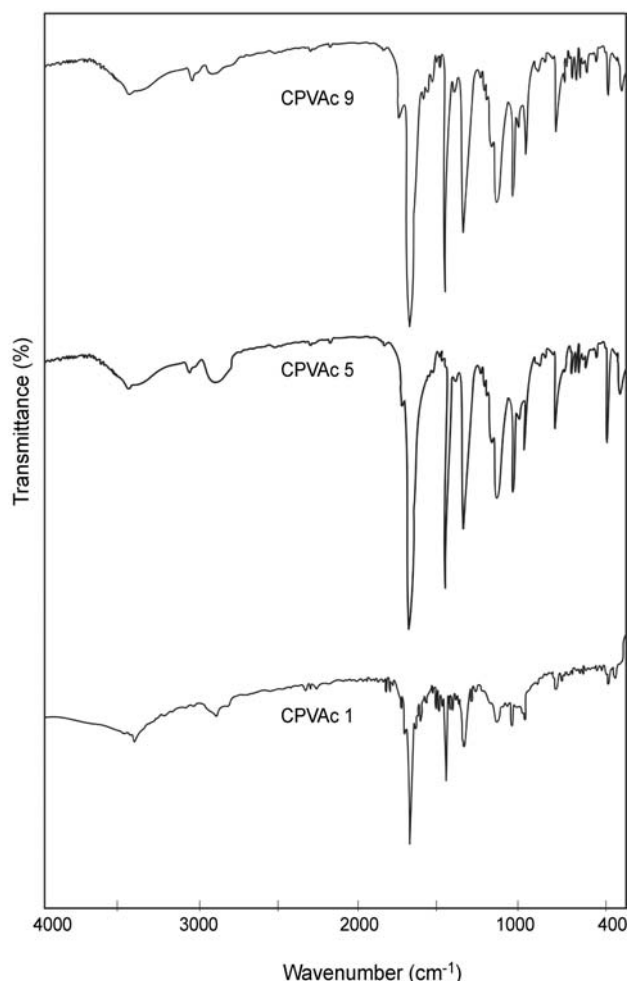


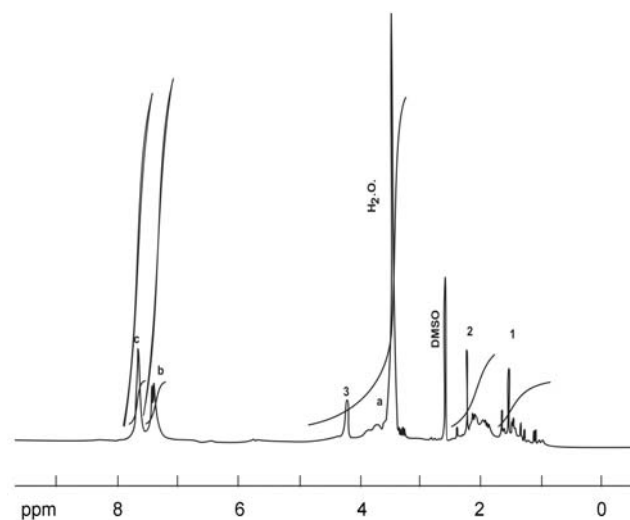
Figure 2. FTIR Spectra of copolymers.

Spectral Characterization

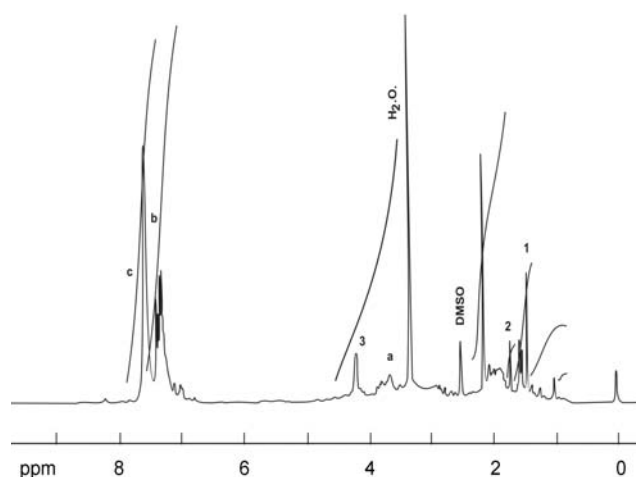
FTIR spectra of copolymers of CMI with vinyl acetate (CPVAc) show the characteristic absorption bands at 2969, 2954, and 2938 cm^{-1} [$\nu(\text{C-H})$ stretching of alkyl group in vinyl acetate segment], 1772-1716 cm^{-1} [$\nu(\text{C=O})$ stretching of imide group], 1600 and 1496 cm^{-1} [$\nu(\text{C=C})$ aromatic stretching], 1091 cm^{-1} [aromatic $\nu(\text{C-Cl})$ stretching], 835, 708, and 685 cm^{-1} [(C-H) bending of 1,4-disubstituted benzene]. The absence of the characteristic band at 948 cm^{-1} indicates that the polymer formation takes place via vinyl group [9].

The variation in all band intensities in different copolymer samples CPVAc1-CPVAc9 prepared using different feed ratios indicate different compositions of monomer in each copolymers.

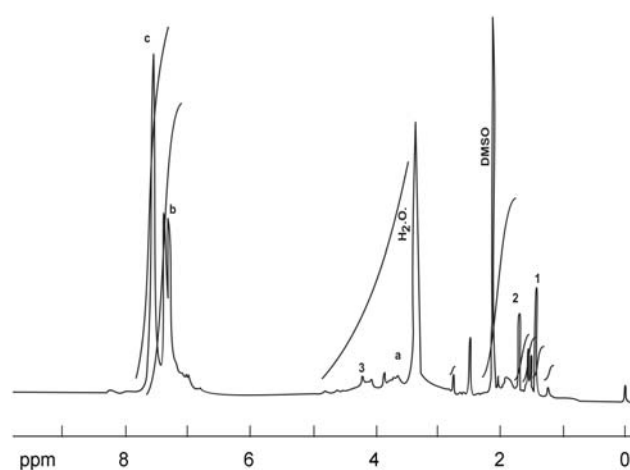
The weak shoulder at 1772 cm^{-1} progressively increases as imide content increases from copolymer



(a)



(b)



(c)

Figure 3. ^1H NMR Spectra of copolymers: (a) CPVAc1; (b) CPVAc5; (c) CPVAc9.

samples 1-9. Figure 2 shows FTIR spectra of copolymers CPVAc1, CPVAc5, and CPVAc9.

The ¹H NMR spectra of nine copolymers exhibit the peak at δ = 7.1-7.6 ppm corresponding to the two types of aromatic protons of the CMI segment. The δ = 7.53-7.54 ppm (broad) is due to the two aromatic protons meta to nitrogen of imide group and δ = 7.31-7.40 ppm (broad) is due to the two aromatic protons ortho to nitrogen of the imide group. The broad peak observed at δ = 3.68-3.88 ppm corresponds to 2H -(CH-CH) protons in copolymer main chain and 3H of acetate segment. The broad peak observed in the range δ = 1.8-2.0 ppm is the only H of methine (-CH) group. The peak in the range δ = 1.5-1.8 ppm is due to 2H of methylene -(CH₂) group. The ¹H NMR spectra of copolymers CPVAc1, CPVAc5, and CPVAc9 are shown in Figure 3.

Viscosity Measurements

The solution viscosity is basically a measure of the size of extension in space of polymer molecules. Measurements of solution kinematics viscosity are generally made by comparing the efflux time "t" required for specified volume of polymer solution to flow through a capillary tube with corresponding efflux time "t₀" of the solvent. From the kinematic viscosity of the solution, ν, and of the solvent, ν₀, the relative, η_{rel}, specific, η_{sp}, reduced, η_{red}, and inherent, η_{inh}, viscosities can be evaluated as follows:

$$\eta_{rel} = \nu/\nu_0 = t/t_0 \quad (1)$$

$$\eta_{sp} = \nu/(\nu_0 - 1) = \eta_{rel} - 1 \quad (2)$$

$$\eta_{red} = \eta_{sp}/C \quad (3)$$

$$\eta_{inh} = (\ln \eta_{red})/C \quad (4)$$

The viscosities of the copolymers CPVAc2, CPVAc5, and CPVAc9 in Table1 increase with the increase in concentration of the copolymer solutions.

Intrinsic Viscosity

In order to quantify a viscosity function of a copolymer in a solvent, which may be independent of the concentration, the limiting value of reduced viscosity (η_{sp}/C) or that of the inherent viscosity (ln η_{rel}/C) at

Table 1. Viscosity data of copolymer CPVAc in DMF at 30±2°C.

C	[η] _{rel}	[η] _{sp} (dL/g)	[η] _{red} (dL/g)	[η] _{inh} (dL/g)
CPVAc2				
0.20	1.0484	0.0484	0.2421	0.2364
0.40	1.0977	0.0977	0.2442	0.2329
0.60	1.1484	0.1484	0.2473	0.2306
0.80	1.2002	0.2002	0.2502	0.2280
1.00	1.2530	0.2530	0.2530	0.2255
CPVAc5				
0.20	1.0403	0.0403	0.2016	0.1975
0.40	1.0818	0.0818	0.2045	0.1965
0.60	1.1249	0.1249	0.2081	0.1960
0.80	1.1696	0.1696	0.2120	0.1958
1.00	1.2154	0.2154	0.2154	0.1950
CPVAc9				
0.20	1.0316	0.0316	0.1501	0.1556
0.40	1.0640	0.0640	0.1600	0.1550
0.60	1.0972	0.0972	0.1620	0.1546
0.80	1.1314	0.1314	0.1643	0.1543
1.00	1.1660	0.1660	0.1660	0.1563

infinite dilution is chosen and this is termed as intrinsic viscosity [η].

Multiple Viscosity Measurements Method

The equations of Huggins [10], Kraemer [11], Schulz-Blaschke [12], and Martin [13] are the most often used equations for the determination of [η].

$$-\eta_{sp}/C = [\eta] + KH [\eta]^2 C \quad \text{Huggins} \quad (5)$$

$$-\ln \eta_{rel}/C = [\eta] + KK [\eta]^2 C \quad \text{Kraemer} \quad (6)$$

$$-\eta_{sp}/C = [\eta] + KSB [\eta] \eta_{sp} \quad \text{Schulz-Blaschke} \quad (7)$$

$$-\ln(\eta_{sp}/C) = \ln [\eta] + KM [\eta] C \quad \text{Martin} \quad (8)$$

where, KH, KK, KSB, and KM represent the Huggins, Kraemer, Schulz-Blaschke, and Martin constants given for each respective polymer-solvent-

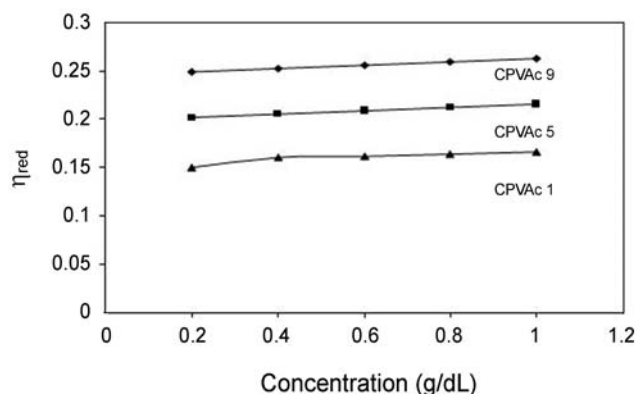


Figure 4. Huggins plot for copolymers.

temperature system. The values of $[\eta]$ and constants KH, KK, KSB, and KM in DMF solvent at $30 \pm 2^\circ\text{C}$ are obtained by applying the method of least squares. The linear plots of Huggins, Kraemer, Schulz-Blaschke, and Martin equations are shown in Figures 4, 5, 6, and 7; respectively. The viscosity data of only three copolymers CPVAc2, CPVAc5, and CPVAc9 are given in Table 1. The $[\eta]$ of only three copolymers CPVAc2, CPVAc5, and CPVAc9 and the corresponding constants are given in Table 2.

When, $[\eta] = 0.2378, 0.1993, \text{ and } 0.1561$; it shows that the value of $[\eta]$ depends upon the composition of copolymer samples. In all cases, the increase in mole ratio of CMI decreases the value of $[\eta]$ which apparently indicates that by increasing CMI feed ratio, one obtains the copolymer of lower molecular weight.

Thermal Characterization

The thermograms of CPVAc1, CPVAc5, and CPVAc9

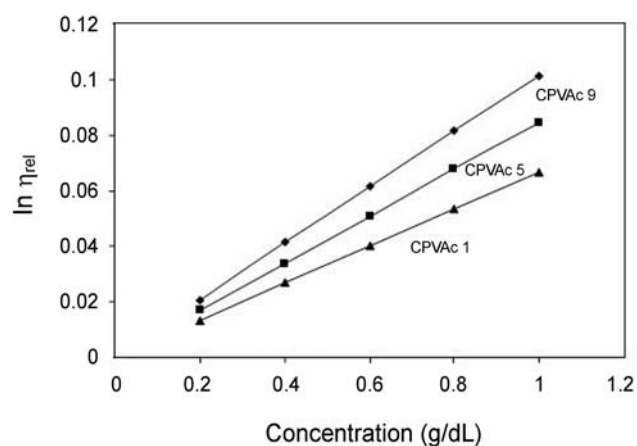


Figure 5. Kraemer plot for copolymers.

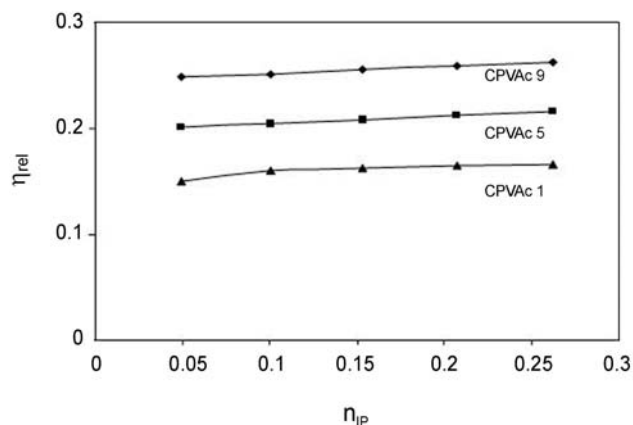


Figure 6. Schulz-Blaschke plot for copolymers.

are shown in Figure 8. Thermal data obtained from TGA are presented in Table 3. All the copolymers of CPVAc degrade in three steps (Figure 8). The thermal stability of CPVAc2 is exhibited up to 220°C . The first step degradation starts at the same temperature which extends up to 265°C with about 11.41% weight loss. The second step decomposition involves 35.90% weight loss within the range of 290°C to 450°C . The third step decomposition involves 22.8% weight loss within the range of 465°C to 625°C .

The copolymer CPVAc5 starts to degrade at 230°C and extends up to 272°C with about 6.88% weight loss. The weight loss of 40.39% occurs within the range of 310°C to 490°C in the second step. The third step decomposition is followed by 33.33% weight loss within the range of 510°C to 660°C .

The first step degradation starts at 230°C for copolymer CPVAc9 with 19.10% weight loss and

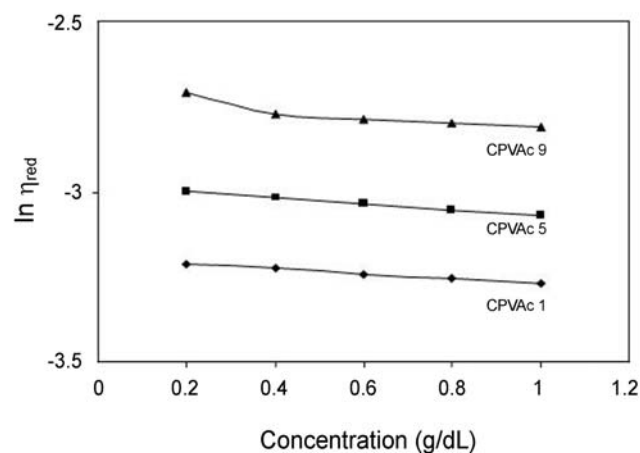


Figure 7. Martin plot for copolymers.

Table 2. $[\eta]$ of copolymer CPVAc and constants.

Copolymer code	$[\eta]$	KH	$[\eta]$	KK	$[\eta]$	KSB	$[\eta]$	KM
CPVAc2	0.2378	0.3710	0.2378	0.1330	0.2378	0.3650	0.2379	0.3594
CPVAc5	0.1992	0.2898	0.1992	0.2080	0.1994	0.2610	0.1992	0.2886
CPVAc9	0.1561	0.3899	0.1561	0.1180	0.1561	0.3652	0.1562	0.3649

Table 3. Thermal characteristics of CPVAc copolymers.

Copolymer code	Step	T_1	T_{max}	T_{50}	T_f	ipdt
CPVAc2	I	220	235	400	265	400
	II	290	385		450	
	III	465	545		625	
CPVAc5	I	230	255	425	272	419
	II	310	400		490	
	III	510	625		660	
CPVAc9	I	230	260	430	310	422
	II	340	400		490	
	III	520	580		660	

extends up to 310°C. The second step decomposition of 32.05% weight loss occurs within the range of 340°C to 490°C, and finally the third step decomposition involving 28.20% weight loss lies within the range of 520°C to 660°C.

As the CMI monomer content has increased, the

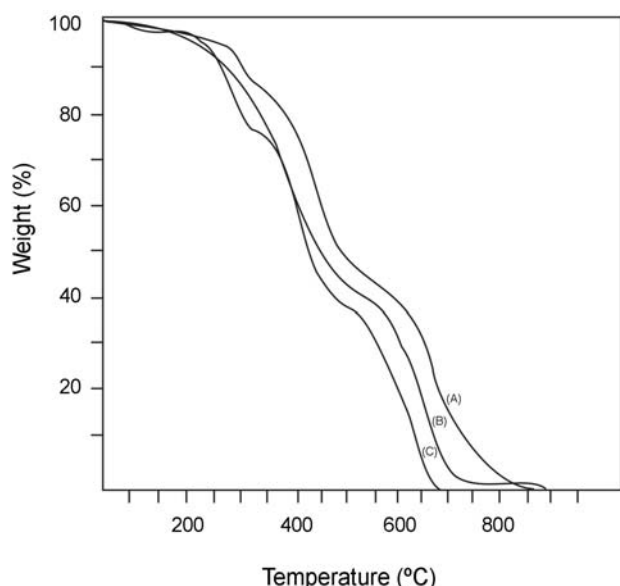


Figure 8. Thermograms of copolymers: (a) CPVAc1; (b) CPVAc5; (c) CPVAc9.

stability has steadily shown improvement. Thus, the CPVAc2 with minimum content of CMI was stable up to 625°C whereas, CPVAc9 was stable up to 660°C due to higher content of CMI.

Semi-quantitative Estimation of Thermal Stability

The values of integral procedural decomposition temperature (ipdt) [14], as a means of summing up the whole shape of the normalized data curves of TGA, are also calculated to obtain a more semi-quantitative data regarding the relative thermal stabilities (Table 3).

Evaluation of Kinetic Parameters

The thermogravimetric analyses provide some information in evaluating kinetic parameters of various thermal decomposition reactions and materials. Broido [15] has suggested a simple and sensitive graphical method of treating TGA data. For typical calculations for CPVAc5 copolymer, the relevant plot of three-step degradation of CPVAc5 copolymer is shown in Figure 9. The straight lines are due to the linear regression analysis of the experimental data. The values of energy of activation (E_a) of various degradation steps involved were evaluated from the

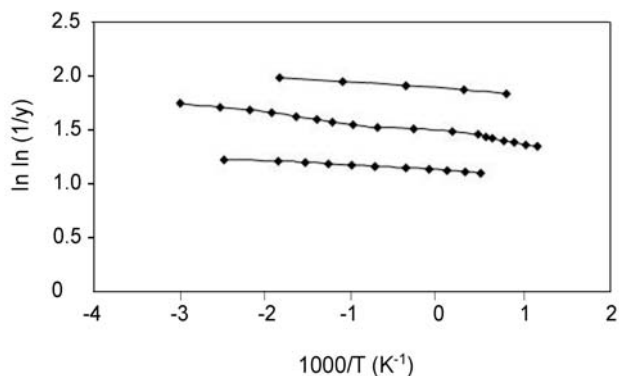


Figure 9. Broido plot for CPVAc5 copolymer.

slopes of the least square plots of the relevant data.

The E_a of the three copolymers of CMI-co-VAc (CPVAc2, CPVAc5, and CPVAc9) are tabulated in Table 4 and can be compared with E_a of the homopolymers. The E_a of the first step for all the three copolymers of vinyl acetate is as much as E_a value of the first step of PCMIs. Thus, the maleimide content improves the thermal stability of copolymers at different feed ratios.

Copolymer Composition

The copolymer compositions of samples were determined by N% analysis, since CMI monomer (M_1) contains nitrogen while vinyl acetate monomer does not have any nitrogen. Thus, the N% in the copolymers can safely be used to estimate the copolymer composition [16,17].

In the present investigation, the copolymer composition (wt% and mole ratio) has been determined by N% consideration. The weight percentage of monomer CMI in copolymer was calculated as follows:

$$WM_1 = \frac{\text{N\% in copolymer}}{\text{N\% in } M_1} \times 100 \quad (9)$$

Table 4. Activation energy (E_a) in kcal/mol of thermal degradation of homo and copolymers.

Polymer	Step I	Step II	Step III
PVAc	57.24	33.00	-
PCMI	22.39	50.11	-
CPVAc2	44.43	23.70	68.09
CPVAc5	36.46	29.48	42.42
CPVAc9	29.78	58.83	59.09

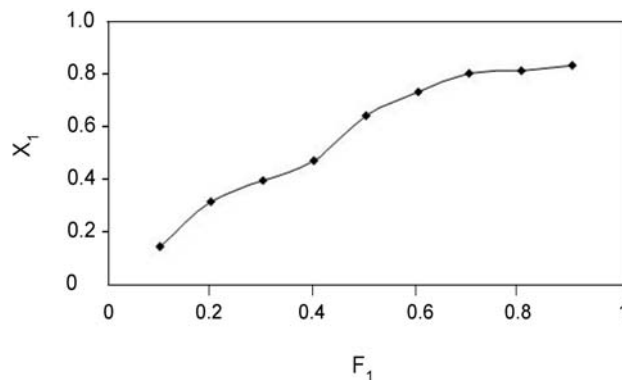


Figure 10. Feed composition ratio of copolymers.

The number of moles, n_1 and n_2 of monomers, M_1 and M_2 are given:

$$n_1 = WM_1\% / MW_1 \quad (10)$$

$$n_2 = WM_2\% / MW_2 \quad (11)$$

and would give the molar ratio of monomers M_1 and M_2 as:

$$\text{Mole ratio} = n_1 / n_2 \quad (12)$$

The results of copolymer samples have been summarized in Table 5. It is evident that as mole fraction of CMI in feed is increased, the mole ratio of CMI in copolymer has also increased.

The dependence of copolymer composition (F_1) on feed ratio (X_1) is shown in Figure 10. As the composition of monomer in copolymer is different from that of feed ratio, this suggests that the copolymer composition is not azeotropic.

Reactivity Ratio

The reactivity ratios of monomers CMI and VAc are estimated from the monomer feed ratios by application of methods like Finmen-Ross (FR) [18] and Kelen-Tüdös (KT) [19].

Table 6 shows the data of FR and KT parameters for the copolymers. The reactivity ratios r_1 and r_2 are the slope of FR plot and its intercept on y-axis, respectively. The intercept at $\xi = 1$ gives r_1 and the intercept at $\xi = 0$ gives r_2/α ($\alpha_{cal} = 0.628$) for KT plot. FR and KT plots are shown in Figures 11 and 12, respectively. The values from FR and KT plots

Table 5. Feed and copolymer composition.

Copolymer code	Feed (mol fraction)		Yield (%)	N (%)	Copolymer (wt%) of CMI	Composition F_1
	CMI	VAc				
CPVAc1	0.1	0.9	17	1.96	29.1	0.145
CPVAc2	0.2	0.8	19	3.54	52.5	0.314
CPVAc3	0.3	0.7	24	4.14	61.4	0.397
CPVAc4	0.4	0.6	35	4.61	68.3	0.472
CPVAc5	0.5	0.5	45	5.46	81.0	0.638
CPVAc6	0.6	0.4	56	5.84	86.6	0.729
CPVAc7	0.7	0.3	64	6.10	90.5	0.798
CPVAc8	0.8	0.2	66	6.15	91.2	0.812
CPVAc9	0.9	0.1	68	6.68	92.4	0.828

Table 6. Parameters of FR and KT methods to determine reactivity ratios of copolymers.

Copolymer code	Mole ratio feed	Mole fraction of CPVAc		FR method		KT 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
CPVAc1	1 : 9	0.1	0.145	0.544	-0.073	-0.919	0.123
CPVAc2	2 : 8	0.2	0.314	0.296	-0.137	-0.452	0.208
CPVAc3	3 : 7	0.3	0.397	0.222	-0.279	-0.279	0.350
CPVAc4	4 : 6	0.4	0.472	0.079	-0.497	-0.078	0.489
CPVAc5	5 : 5	0.5	0.638	-0.433	-0.567	0.398	0.522
CPVAc6	6 : 4	0.6	0.729	-0.942	-0.836	0.695	0.617
CPVAc7	7 : 3	0.7	0.798	-1.743	-1.378	0.910	0.726
CPVAc8	8 : 2	0.8	0.812	-3.074	-3.074	0.728	0.877
CPVAc9	9 : 1	0.9	0.828	-7.130	-16.826	0.411	0.970

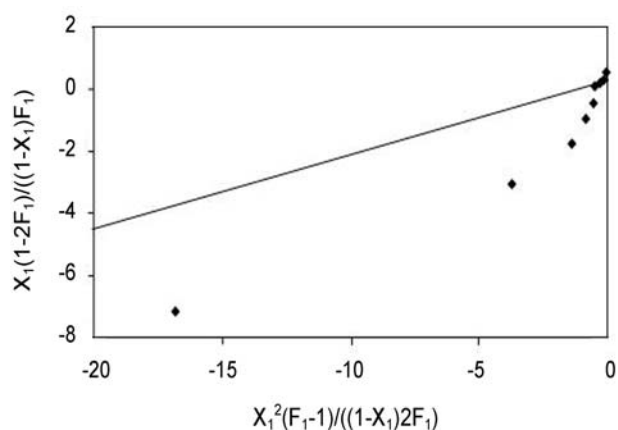


Figure 11. Finmen-Ross plot for copolymers.

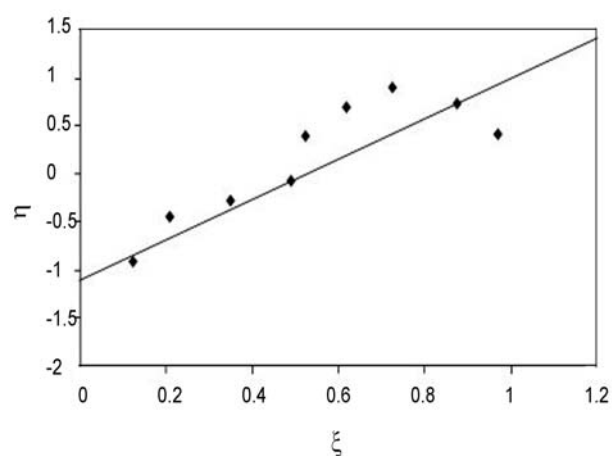


Figure 12. Kelen- Tüdös plot for copolymers.

Table 7. Monomer reactivity ratios (r_1 and r_2) and Q and e values by Alfrey-Price equation.

Copolymer	Finemann-Ross Method		Kelen-Tüdös Method		Mean		Q*		E*	
	r_1	r_2	r_1	r_2	r_1	r_2	O	R	O	R
CMI-co-VAc	0.991	0.290	1.363	0.549	1.177	0.419	0.0296	0.026	0.039	-0.88
CMI-co-EA	1.106	0.352	0.997	0.265	1.051	0.308	0.077	0.41	1.119	0.55
CMI-co-BA	0.798	0.310	1.215	0.606	1.006	0.458	0.060	0.38	1.311	0.85

(*) O = observed ; R = reserved.

are presented in Table 6.

The reactivity ratios r_1 and r_2 in copolymerization reactions can be fruitfully discussed in terms of monomer structures. The effect of resonance stability or of steric hindrance on reactivity can be established using Alfrey-Price equation [20]. Vinyl acetate copolymers with the monomers (r_1) such as *N*-(2-5-dichlorophenyl)maleimide or *N*-(2-cyanophenyl)maleimide exhibit monomer reactivity ratios r_1 greater than r_2 [21]. The CMI copolymer with ethyl acetate and butyl acetate has been studied earlier [22, 23] which has also shown the similar trend. Alfrey-Price used empirical parameters Q and e to represent the resonance stability of monomer M_1 and polarity of the radical M_1^* . For VAc arbitrarily, these parameters are taken as $Q = 0.026$ and $e = -0.88$. The values of Q and e are shown in Table 7. The result shows higher ratio of CMI as compared to the acetate. Thus, the resulting copolymer formed is therefore richer in CMI.

CONCLUSION

The copolymers derived from CMI and VAc with different ratios show that the reactivity ratio of CMI, r_1 is greater than r_2 . This result shows higher reactivity of CMI as compared to vinyl acetate. Thus, copolymers formed will therefore be rich in CMI. The study reveals that copolymers formed are not alternate copolymers but are random copolymers. The values also showed that maleimide content improves thermal stability of copolymers of different feed ratios. But the viscosity parameters suggest that as CMI feed is increased, the molecular weight of copolymer has dropped. Therefore, a selective ratio can be chosen for a required property of the copolymer.

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