

Synthesis, Characterization, and Thermal Degradation Studies of Copolymer Resin Derived from *p*-Cresol, Melamine, and Formaldehyde

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ABSTRACT: Copolymers (*p*-CMF) synthesized by the condensation of *p*-cresol and melamine with formaldehyde in the presence of an acid catalyst and using varied molar proportion of the reacting monomers. Copolymer resin compositions were determined on the basis of their elemental analysis. The number average molecular weight of these copolymers was determined by conductometric titration in nonaqueous media. Solution viscosity measurements in dimethyl sulfoxide (DMSO) were carried out to ascertain the characteristic functions and constants of the copolymer resins. The copolymer resins were further characterized by UV-visible absorption spectra in the nonaqueous medium, Infra-red (IR) spectra, and the nuclear magnetic resonance (NMR) spectra. Thermal studies of the resins were carried out to determine their mode of decomposition, the activation

energy (E_a), order of reaction (n), frequency factor (Z), entropy change (ΔS), free energy change (ΔF), and apparent entropy change (S^*). Thermal decomposition curves were discussed with careful attention of minute details. The Freeman-Carroll and Sharp-Wentworth methods have been used to calculate thermal activation energy and thermal stability. Thermal activation energy (E_a) calculated with these methods are in agreement with each other. The data from the Freeman-Carroll methods have been used to determine various thermodynamic parameters. The order of thermal stability of copolymers has been determined using TGA. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 859–868, 2008

Key words: synthesis; thermogravimetric analysis (TGA); resins

INTRODUCTION

Various copolymers can be synthesized by the condensation of a mixture of phenol or hydroxybenzoic acid, various amines, and formaldehyde.^{1,2} Various hydroxyl-benzoic acid-formaldehyde copolymers have been reported to find use as ion-exchangers.^{3,4} Literature survey reveals that ion exchange copolymer resins have been synthesized from salicylic acid, thiourea, and trioxane and also from *p*-hydroxybenzoic acid, urea, and formaldehyde.^{5,6} Ion-exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotic purification, and separation of radio isotopes and they find large scale applications in water treatment and pollution control purposes.^{7,8} Copolymer resins having good thermal stability have enhanced the scope for development of some polymeric materials. The study of the thermal degradation of copolymer resins have recently become a subject of interest. 2-Hydroxyacetophenone and its substituted derivatives have been condensed with formaldehyde to produce heat and light stabil-

izers.^{9,10} Joshi and Patel¹¹ have synthesized salicylic acid-urea-formaldehyde copolymers in view of the characteristics especially ion exchanging property and other industrial applications. In an earlier communication^{12–17} from this department a number of studies on such copolymers have been reported. However, no work seems to have been carried out on synthesis, characterization, ion exchange properties, and thermal stabilities of the copolymer resins from *p*-cresol, melamine, and formaldehyde. The present article describes the composition of these newly synthesized resins, their characterization by elemental analysis, average molecular weight (\bar{M}_n) determination, intrinsic viscosity in DMSO, IR spectra, UV-visible absorption spectra and NMR spectra, thermal analysis giving their relative thermal stabilities. The decomposition temperature has been discussed in terms of ΔF , ΔS , and S^* calculated by applying the Freeman-Carroll method. Kinetic parameters were determined by application of Freeman-Carroll and Sharp-Wentworth method.

EXPERIMENTAL

Starting materials

The important chemicals (starting materials) like *p*-cresol, melamine, and formaldehyde etc., used in the

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preparation of various new *p*-CMF copolymer resins were procured from the market and were of Analar or Chemically pure grade, and wherever necessary the purity was tested and confirmed by TLC.

Synthesis of *p*-CMF copolymer resins

The new copolymer resin *p*-CMF-1 was synthesized by condensing *p*-cresol (1.08 g, 0.1 mol) and melamine (0.88 g, 0.1 mol) with 37% formaldehyde (11.1 mL, 0.3 mol) in a mol ratio of 1 : 1 : 3 in the presence of 2M 200 mL HCl as a catalyst at $(130 \pm 2)^\circ\text{C}$ for 5 h¹⁸ in an oil bath with occasional shaking to ensure thorough mixing. The separated copolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered, and then extracted with diethyl ether and then with petroleum ether to remove *p*-cresol-formaldehyde copolymer which might be present along with *p*-CMF copolymer. The copolymer was purified further by dissolving in 8% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual dropwise addition of ice cold 1 : 1 (v/v) concentrated hydrochloric acid/distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The copolymer sample *p*-CMF-1 thus obtained was filtered, washed several times with hot water, dried in air, powdered, and kept in vacuum desiccator over silica gel. The yield of the copolymer resin was found to be 75%.

Similarly other copolymer resins viz. *p*-CMF-2, *p*-CMF-3, and *p*-CMF-4 were synthesized by varying the molar proportions of the starting materials i.e., (2 : 1 : 4), (3 : 1 : 5) and (4 : 2 : 7), respectively.

The details of synthesis of copolymers along with color, melting point, yield, and elemental analysis are incorporated in Table I. Similarly the reaction and suggested structure of *p*-CMF-1 copolymer resin are depicted in Figure 1.

CHARACTERIZATION

All the newly synthesized and purified copolymers have been analyzed for carbon, hydrogen, and nitrogen at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. With the help of elemental data, the empirical formulae and the empirical weights have been assigned to the new copolymer resins.

The number average molecular weights (\overline{M}_n) were determined by conductometric titrations in nonaqueous medium such as dimethyl sulfoxide (DMSO) using ethanolic KOH as a titrant. Conductometric titration in nonaqueous media has been proved to be a simple yet effective method used by earlier research workers¹⁸⁻²⁰ for determination of number

TABLE I
Synthesis and Physical Data of *p*-CMF Copolymer Resins

Copolymer	Reactants			Catalyst 2M HCl (mL)	Yield (%)	Color	Melting point	Elemental Analysis wt (%)							
	<i>p</i> -Cresol (Mol)	Melamine (Mol)	Formaldehyde (Mol)					C		H		N			
<i>p</i> -CMF-1	0.1	0.1	0.3	200	75	Yellow	376	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
<i>p</i> -CMF-2	0.2	0.1	0.4	200	80	Yellow	385	51.98	50.84	5.41	4.96	30.00	29.22	21.15	20.68
<i>p</i> -CMF-3	0.3	0.1	0.5	200	75	Yellow	390	60.45	59.49	5.79	4.99	16.66	16.19	6.18	6.84
<i>p</i> -CMF-4	0.4	0.2	0.7	200	80	Yellow	396	64.28	63.82	5.95	5.80	11.29	10.93	6.18	6.84

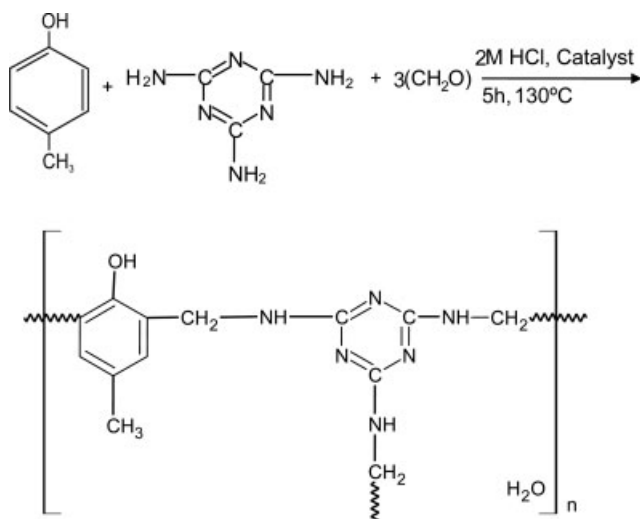


Figure 1 Reaction and suggested structure of representative *p*-CMF-1 copolymer resin.

average molecular weight of phenol-formaldehyde resins.²¹ A plot of specific conductance against milliequivalents of base (ethanolic KOH) was made. There are several breaks and stepwise increase in the specific conductance in the plots due to stepwise neutralization of phenolic-OH group. From the plots, the amount of titrant added up to the first and last break were noted. The degree of polymerization (\overline{DP}) of the copolymer resin sample was obtained from the ratio of total milliequivalents of base required to reach the final stage of neutralization to the milliequivalents corresponding to the first break in the plots. From the value of degree of polymerization (\overline{DP}), the number average molecular weight (\overline{M}_n) of the copolymer has been calculated with the help of formula

$$\overline{M}_n = \overline{DP} \times \text{repeat unit weight.}$$

The intrinsic viscosity of all newly synthesized copolymers has been evaluated using Tuan-Fuoss viscometer²² fabricated in our research laboratory at different concentrations ranging from 1.00 to 0.031% of copolymer in DMSO at 30°C. Intrinsic viscosity $[\eta]$ was calculated from relevant plots of Huggins'²³ eq. (1) and Kraemer's²⁴ eq. (2) (Fig. 2).

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2.C \quad (1)$$

$$\ln \eta_r/C = [\eta] + K_2[\eta]^2.C \quad (2)$$

where η_r = relative viscosity, $[\eta] = \lim_{c \rightarrow 0}(\eta_{sp}/C)$, K_1 = Huggins' constant, K_2 = Kraemer's constant.

Electron absorption spectra of all newly synthesized copolymer resins were recorded in DMSO (spectroscopic grade) on Shimadzu double beam

spectrophotometer in the range of 200–850 nm at SAIF Punjab University, Chandigarh.

Infra-red spectra of four *p*-CMF copolymer resins were recorded on Perkin-Elmer-983 Spectrophotometer in KBr pallets in the wave number region of 4000–400 cm^{-1} at SAIF Punjab University, Chandigarh.

Nuclear magnetic resonance (NMR) spectra of newly synthesized copolymer resins have been scanned on Bruker Advanced 400 MHz NMR Spectrometer using $\text{DMSO-}d_6$ as solvent at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh.

TGA of all copolymer resins have been carried out by using Perkin-Elmer TGS-II Thermogravimetric Analyser at heating rate of 10°C per minute and in nitrogen atmosphere up to 800°C. The thermograms were recorded at Vishveshyarya National Institute of Technology, Nagpur. The thermograms were interpreted and analyzed to obtain information about the % weight loss at different temperatures. From the data obtained from thermograms the kinetic parameters and activation energy (E_a) have been calcu-

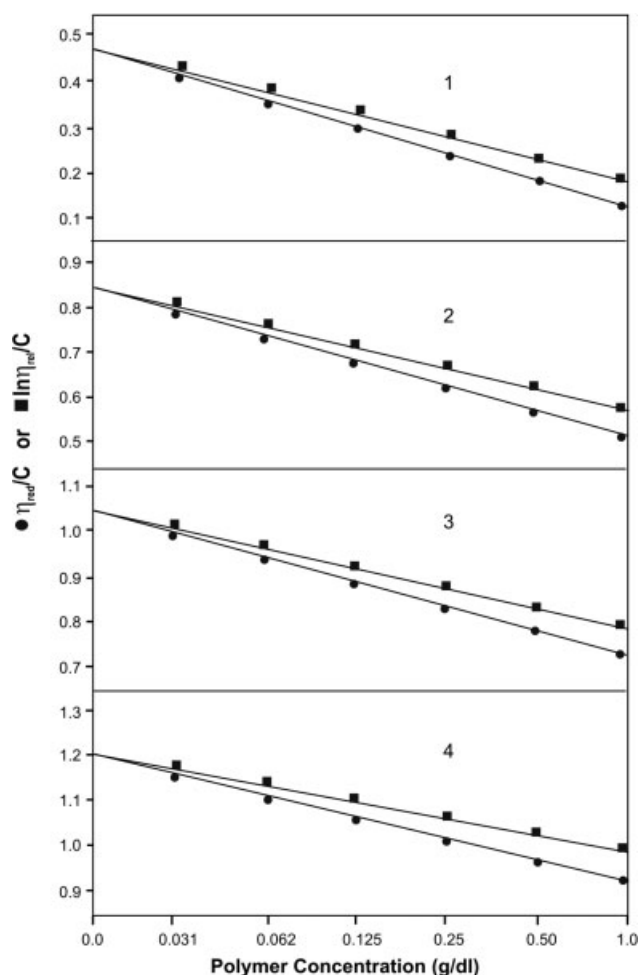


Figure 2 Viscometric plots of *p*-CMF copolymer resins. 1) *p*-CMF-1, 2) *p*-CMF-2,3) *p*-CMF-3, 4) *p*-CMF-4.

lated which help us to decide the thermal stability of copolymer resins. In the present investigation, Sharp-Wentworth and Freeman-Carroll methods have been used to determine the kinetic parameters of *p*-CMF copolymer sample.

Sharp-Wentworth method: In this method following expression is used.²⁵

$$\log \left[\frac{dc/dt}{\Delta(1-c)} \right] = \log(A/\beta) - E_a/2.303R - 1/T$$

where β is the linear heating rate. The graph of $\log \left[\frac{dc/dt}{\Delta(1-c)} \right]$ has been plotted. The graph is a straight line with E_a as slope and A as intercept. The linear relationship confirms that the assumed order (n) = 1 is correct.

Freeman-Carroll method: In this method following expression is used.²⁶

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = (-E_a/2.303R) - \frac{\Delta(1/T)}{\Delta \log W_r} + n$$

where dw/dt = rate of change of weight of copolymer sample with respect to time $W_r = W_c - W$, where W_c is the weight loss at the completion of the copolymer reaction or at definite time and W is the total weight loss up to time t . T is the temperature, R is the gas constant and n is the order of reaction. Hence the graph of

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} \text{ versus } \frac{\Delta(1/T)}{\Delta \log W_r}$$

should give on Y axis ($x = 0$) an intercept for the value of n , the order of reaction and the slope $m = -E_a/2.303R$. The detailed procedure is clearly laid out for one representative sample as an illustration.

RESULTS AND DISCUSSION

All the newly synthesized purified *p*-CMF copolymer resins were found to be yellow in color. The copolymers are soluble in solvents such as DMF, DMSO, and THF while insoluble in almost all other organic solvents. The melting points of these copolymers were found to be in the range of 376–396 K. These resins were analyzed for carbon, hydrogen, and nitrogen content. The details of synthesis of copolymers along with color, melting point, yield, and elemental analysis are incorporated in Table I. The copolymer which has been used in the present investigation was prepared by the reaction given in Figure 1.

The number average molecular weight (\overline{M}_n) of these copolymers has been determined by conductometric titration method in nonaqueous medium and using standard potassium hydroxide (0.05M) in absolute ethanol as a titrant. The results are presented in Table II. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 g of each copolymer. There are several breaks before the complete neutralization of all phenolic hydroxyl groups.²⁷ The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average one phenolic hydroxy group of each chain was neutralized.

From the plot, the first and final breaks were noted. The average degree of polymerization (\overline{DP}) and hence the number average molecular weight (\overline{M}_n) of all copolymers have been determined using the formula.

$$\overline{DP} = \frac{\text{Total milliequivalents of base required for complete neutralisation}}{\text{Milliequivalents of base required for smallest interval}}$$

$$\overline{M}_n = \overline{DP} \times \text{Repeat unit weight}$$

It is observed that the molecular weight of copolymers increases with increase in *p*-cresol content. This observation is in agreement with the trend observed by earlier workers.^{5,6}

Viscosity measurements were carried out at 300 K in freshly triple distilled DMSO using Tuan-Fuoss¹⁹ Viscomer, at six different concentrations ranging from 1.00% to 0.031%. Reduced viscosity versus concentration was plotted for each set of data. The intrinsic viscosity $[\eta]$ was determined by the corresponding linear plots (Fig. 2). Huggins' and Kraemmer's constants were determined by an expression 1 and 2.

According to the above relations, the plots of η_{sp}/C and $\ln \eta_{rel}/C$ against C were linear with slopes of K_1 and K_2 , respectively. By extrapolating linear plot to zero concentration, intercepts on the viscosity function axis give $[\eta]$ value in both plots. The calculated values of the constants K_1 and K_2 (Table II) in most cases satisfy the relation $K_1 + K_2 = 0.5$ favorably.^{28,29} It was observed that copolymer having higher (\overline{M}_n) shows higher value of $[\eta]$.

The UV-visible spectra (Fig. 3) of all the *p*-CMF copolymer samples in pure DMSO were recorded in the region 200–850 nm at a scanning rate of 100 nm min^{-1} and a chart speed of 5 cm min^{-1} . All the four *p*-CMF copolymer samples gave two characteristics bands at 200–230 nm and 280–320 nm. These observed positions for the absorption bands have

TABLE II
Molecular Weight Determination, Viscometric Data and IR Frequencies of the *p*-CMF Copolymers

Copolymer	Empirical formula of repeat unit	Empirical weight of repeat unit (g)	Average degree of polymerization (DP)	Average molecular weight (M_w)	Intrinsic viscosity η (dL/g)	Huggins' constant K_1	Kraemer's constant K_2	$K_1 + K_2$	Wave number (cm^{-1})	Important IR frequencies
p-CMF-1	$\text{C}_{13}\text{H}_{15}\text{N}_6\text{O}$	289	13.5	3901	0.482	0.272	0.224	0.496	3750–3751 b,st 3394–3398 b,st 1542–1548 b,st	>OH phenol >NH ₂ linkage (Imide) Aromatic ring
p-CMF-2	$\text{C}_{21}\text{H}_{23}\text{N}_6\text{O}_2$	410	15.5	6355	0.843	0.287	0.232	0.519	1475–1478 sh,st 1343–1383 sh,st 960sh,w	>CH ₂ bending (scissoring) >CH ₂ bending (twisting & wagging) 1,2-,3,5 substitution in benzene skeleton
p-CMF-3	$\text{C}_{28}\text{H}_{30}\text{N}_6\text{O}_3$	516	15.5	799	1.045	0.301	0.222	0.513	1001–1006 b,m 1142–1144 sh,m	
p-CMF-4	$\text{C}_{48}\text{H}_{50}\text{N}_{12}\text{O}_4$	858	16.0	13728	1.251	0.312	0.202	0.514	1308–1309 sh,m	

Sh, sharp; b, broad; st, strong; m, medium; W, weak.

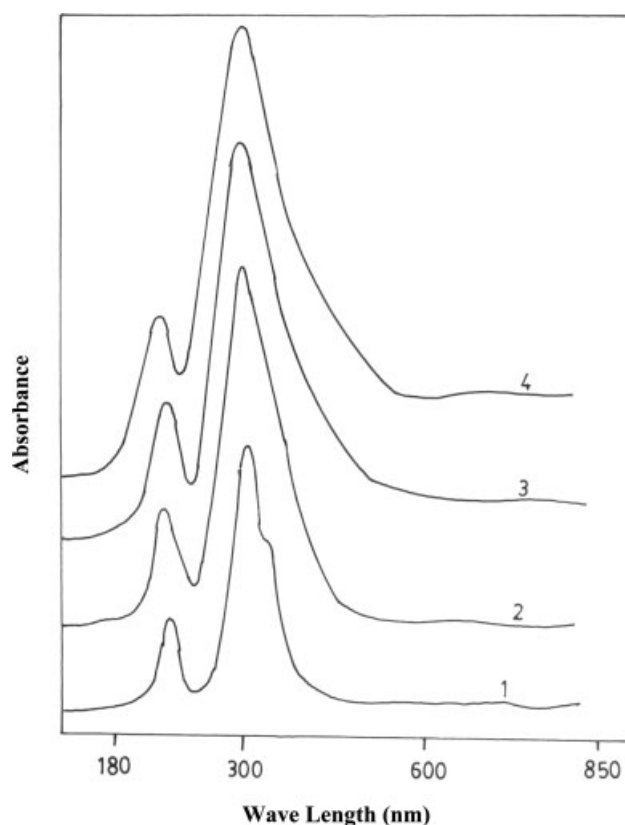


Figure 3 Electronic absorption spectra of *p*-CMF copolymer resins. 1) *p*-CMF-1, 2) *p*-CMF-2, 3) *p*-CMF-3, 4) *p*-CMF-4.

different intensities. The more intense band is due to $\pi \rightarrow \pi^*$ transition and the less intense is due to $n \rightarrow \pi^*$ transition. $\pi \rightarrow \pi^*$ transition indicates the presence of aromatic nuclei and $n \rightarrow \pi^*$ transition indicates the presence of $-\text{NH}$ and $-\text{OH}$ group. The hyperchromic effect is due to the presence of $-\text{OH}$ and $-\text{NH}$ groups, which act as auxochrome.^{30,31} From the spectra of *p*-CMF copolymer resins it is observed that ϵ_{max} value gradually increases in the order of $p\text{-CMF-1} < p\text{-CMF-2} < p\text{-CMF-3} < p\text{-CMF-4}$. The increasing order of ϵ_{max} values may be due to introduction of more and more aromatic ring and auxochromes phenolic $-\text{OH}$ and $-\text{NH}$ groups in the repeated unit of the copolymer resins. The observation is in good agreement with proposed structures of above copolymer resins.

The IR spectral data are tabulated in Table II and IR spectra of all four *p*-CMF copolymers are depicted in Figure 4. The IR spectral studies revealed that all these copolymers gave rise to nearly similar pattern of spectra. A broad absorption band appeared in the region 3751 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl ($-\text{OH}$) groups exhibiting intramolecular hydrogen bonding.³² A sharp strong peak at $1548\text{--}1542 \text{ cm}^{-1}$ may be

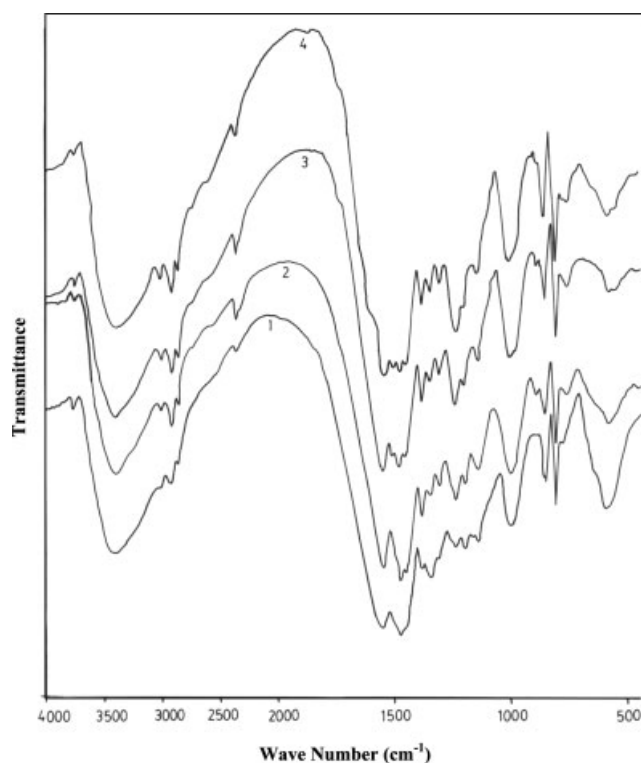


Figure 4 Infra red spectra of *p*-CMF copolymer resins. 1) *p*-CMF-1, 2) *p*-CMF-2, 3) *p*-CMF-3, 4) *p*-CMF-4.

ascribed to aromatic skeletal ring. The bands obtained at $1478\text{--}1475\text{ cm}^{-1}$ and $1383\text{--}1343\text{ cm}^{-1}$ suggest the presence of methylene (--CH_2) bridge.³³ The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium/weak absorption bands appeared at 960, 1000, 1130–1150, and 1309–1308 cm^{-1} , respectively.^{34,35} The presence of sharp and strong band at $3398\text{--}3394\text{ cm}^{-1}$ indicates the presence of --NH bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.

The NMR spectra of all four *p*-CMF copolymers were scanned in $\text{DMSO-}d_6$ solvent. The spectra are given in Figure 5 and the spectral data are given in Table III. From the spectra it is revealed that all *p*-CMF copolymers gave rise to different pattern of

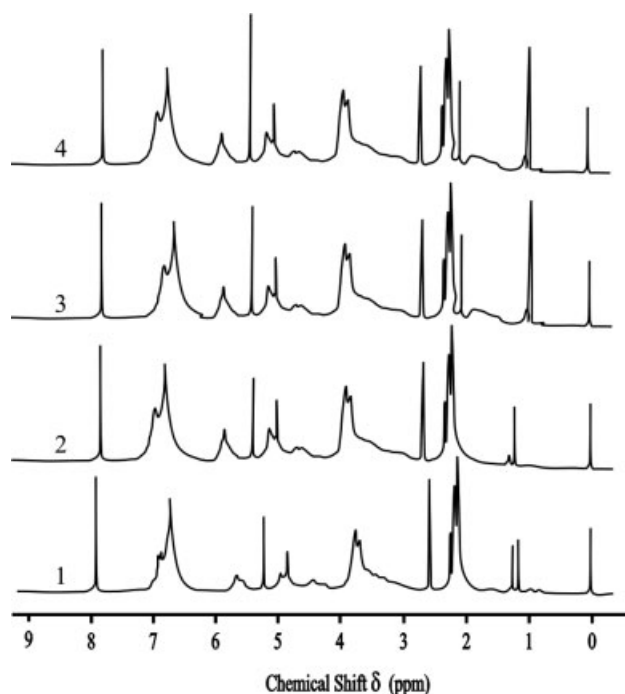


Figure 5 Nuclear Magnetic Resonance spectra of *p*-CMF copolymer resins. 1) *p*-CMF-1, 2) *p*-CMF-2, 3) *p*-CMF-3, 4) *p*-CMF-4.

^1H -NMR spectra, since each of *p*-CMF copolymer possesses set of proton having different electronics environment. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature. All the *p*-CMF copolymer samples show an intense weakly multiplet signals at 2.12 (δ) ppm that may be attributed to methyl proton of Ar--CH_3 group. The medium singlet at 2.24 (δ) ppm may be due to methylene proton of Ar--CH_2 bridge. The singlet obtained in the region 3.09 (δ) ppm may be due to the methylene proton of $\text{Ar--CH}_2\text{--N}$ moiety. The signals in the region 5.19 (δ) ppm are attributed to protons of --NH bridge. The weak multiplet signals (unsymmetrical pattern) in the region of 6.67 (δ) ppm may be attributed to aromatic proton (Ar--H). The signals in the range at 7.33–7.76 (δ) ppm may be due to phenolic hydroxyl protons. The much down-field chemical shift for phenolic --OH indicates

TABLE III
 ^1H NMR Spectral Data of *p*-CMF Copolymer Resins

Observed Chemical Shift (δ) ppm				Nature of proton assigned	Expected chemical shift (δ) ppm
<i>p</i> -CMF-1	<i>p</i> -CMF-2	<i>p</i> -CMF-3	<i>p</i> -CMF-4		
2.12	2.11	2.13	2.13	Methyl proton Ar--CH_3 group	2.00 to 3.00
2.33	2.25	2.25	2.24	Methylenic proton of Ar--CH_2 moiety	2.00 to 3.00
3.33	3.26	3.20	3.30	Methylenic proton of $\text{Ar--CH}_2\text{--N}$ -moiety	3.00 to 3.5
5.19	5.19	5.19	5.18	Proton of --NH bridge	5.00 to 8.00
6.75	6.54	6.69	6.65	Aromatic proton (Ar--H)	6.20 to 8.5
7.91	7.73	7.74	7.76	Proton of phenolic --OH involved intramolecular hydrogen bonding	8.00 to 12.00

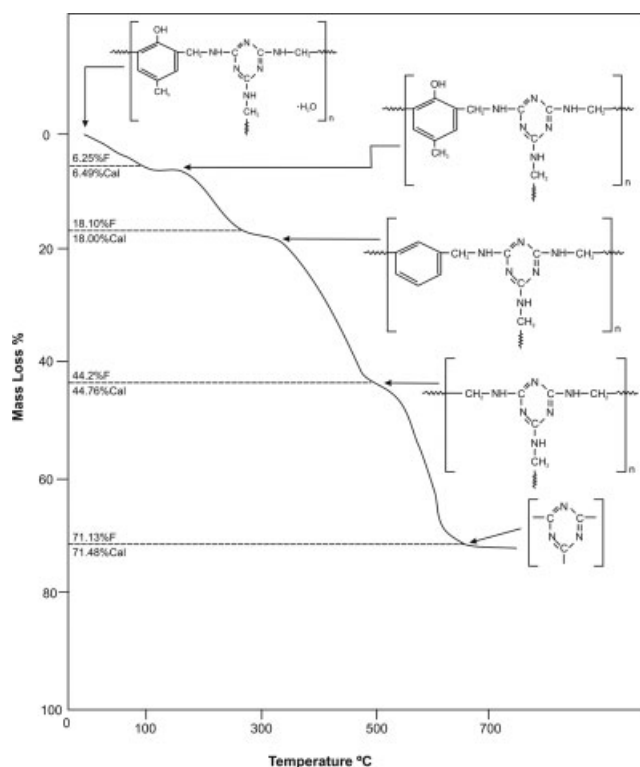


Figure 6 Thermogravimetric curve and decomposition pattern of representative copolymer resin *p*-CMF-I.

clearly the intramolecular hydrogen bonding of —OH group.³⁶

Thermogravimetry of all *p*-CMF copolymer resins has been carried out using Perkin–Elmer thermogravimetric analyzer. A brief account of thermal behavior of these copolymers is given below. But for reason of economy of space the thermal data and ki-

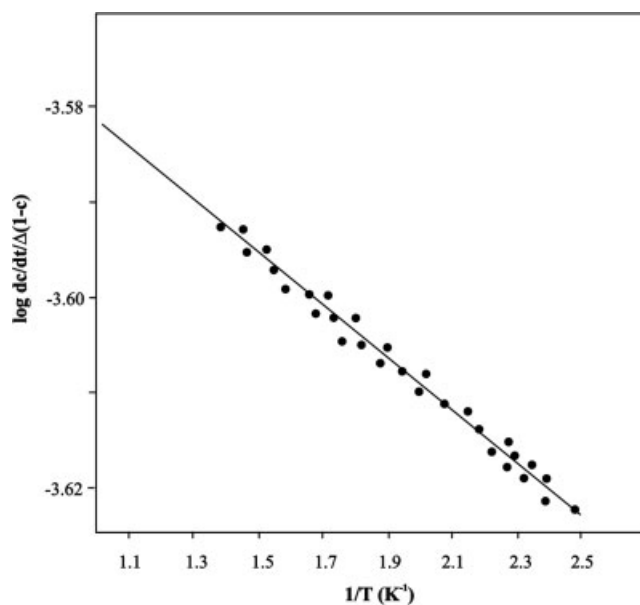


Figure 7 Sharp-Wentworth plot of *p*-CMF-I copolymer resin.

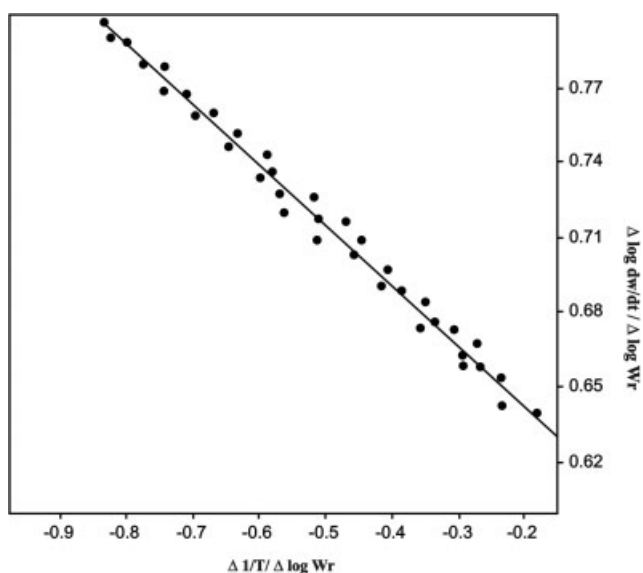


Figure 8 Freeman-Carroll activation energy plot of *p*-CMF-I copolymer.

netic plots for only one representative case have been given in Figure 6–9.

TG of *p*-CMF-(1) copolymer

Thermogram of the copolymer is shown in Figure 6 and depicts three step decomposition in temperature range 30–800°C, after loss of water molecule (6.25% found and 6.49% calculated). First step decomposition starts from 120 to 320°C which represents the degradation of side chain attached to aromatic nucleus and hydroxyl group (18% found and 18.05% calculated). Second step decomposition starts from

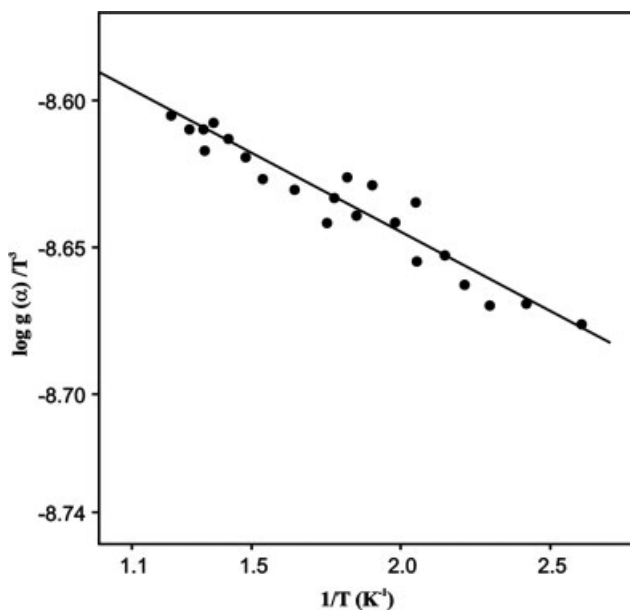


Figure 9 Freeman-Carroll plot of *p*-CMF-I copolymer.

TABLE IV
Results of Thermogravimetric Analysis of *p*-CMF Copolymers Resins

Copolymer	Half decomposition temperature (K)	Activation energy (J/mol)		Entropy change ΔS (J)	Free energy change ΔF (kJ)	Frequency factor Z (s^{-1})	Apparent entropy change S^* (J)	Order of reaction n
		E.C.	S.W.					
<i>p</i> -CMF-1	633	283.56	268.05	157.80	71.19	590	-19.23	0.63
<i>p</i> -CMF-2	653	319.11	320.03	158.60	71.52	650	-19.16	0.74
<i>p</i> -CMF-3	663	359.00	348.12	159.83	72.04	690	-19.12	0.85
<i>p</i> -CMF-4	673	382.94	386.66	161.01	72.55	720	-19.09	0.86

F.C., Freeman-Carroll; S.W., Sharp-Wentworth.

320 to 480°C, corresponding to 44.2% loss of aromatic nucleus against calculated 44.76%. Third step decomposition starts from 480 to 680°C which corresponds to removal of side chain of triazine polymer (71.13% found and 71.48% calculated). Consequently, residue may be assigned at 1,3,5 triazine (28.87% found and 28.52% calculated).

TG of *p*-CMF-(2) copolymer

Thermogram of this copolymer depicts three step decomposition in the temperature range 30–800°C, after loss of water molecule (4.12% found and 4.33% calculated). First step decomposition starts from 140 to 350°C which represents the degradation of side chain attached to aromatic nucleus and hydroxyl group (20.21% found and 20.65% calculated). Second step decomposition starts from 350 to 570°C corresponding to complete loss of aromatic nucleus (59–14% found and 59.44% calculated). Third step decomposition starts from 570 to 800°C representing the removal of side chain of triazine (81.89% found and 81.36% calculated). Consequently, residue may be assigned as 1, 3, 5 triazine (18% found and 18.64% calculated).

TG of *p*-CMF-(3) copolymer

Thermogram of this copolymer depicts three step decomposition in the temperature range 30–800°C, after loss of water molecule (3.3% found and 3.5% calculated). First step decomposition starts from 160 to 360°C which represents the degradation of side chain attached to aromatic nucleus and hydroxyl group (21.96% found and 22.61% calculated). Second step decomposition starts from 360 to 600°C corresponding to loss of aromatic nucleus (67.89% found and 67.26% calculated). Third step decomposition starts from 600 to 800°C representing the removal of side chain of triazine polymer (84% found and 84.52% calculated). Consequently, residue may be assigned as 1, 3, 5 triazine (16.12% found and 15.48% calculated).

TG of *p*-CMF-(4) copolymer

Thermogram of this copolymer depicts three step decomposition in the temperature range 30–800°C, after loss of water molecule (2.80% found and 2.40% calculated). First step decomposition starts from 180 to 360°C which may be due to degradation of side chain attached to aromatic nucleus and hydroxyl group (34.10% found and 33.92% calculated). Second step decomposition starts from 360 to 640°C corresponding to loss of aromatic nucleus (78.12% found and 77.55% calculated). Third step decomposition starts from 680 to 800°C corresponding to removal of side chain of triazine polymer (88.98% found and 89.29% calculated). Consequently 1, 3, 5 triazine may be suggested as residue (11.02% found and 10.71% calculated).

DISCUSSION

A plot of percentage mass loss versus temperature is shown in Figure 6 for representative *p*-CMF-(1) copolymer. From the TG curves, the thermoanalytical and the decomposition temperature were determined (Table IV) to obtain the relative thermal stabilities of the various polymers. The method described by Sharp-Wentworth²⁵ was adopted. On the basis of the initial decomposition temperature, the thermal stabilities of the copolymers, have also been used here to define their relative thermal stabilities, neglecting the degree of decomposition (Table IV).

Using thermal decomposition data and then applying the Sharp-Wentworth method (a representative Sharp-Wentworth plot of *p*-CMF-(1) copolymer is shown in Fig. 7) activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method.²⁶ A representative thermal activation energy plot (Fig. 6) and Freeman-Carroll plot (Figs. 8 and 9) for the polymer have been shown. Thermodynamic parameters such as entropy change (ΔS), free energy change (ΔF), frequency factor (Z), and Apparent entropy change (S^*) calculated on the basis of thermal activation energy are given in Table IV, using equations are given below.

i. Entropy change

$$\text{Intercept} = \log \frac{KR}{h\Phi E} + \frac{\Delta S}{2.303R}$$

where, $K = 1.3806 \times 10^{-16}$ erg/deg/mol, $R = 1.987$ cal/deg/mol, $h = 6.625 \times 10^{-27}$ erg sec, $\Phi = 0.166$, ΔS = change in entropy, E = activation energy from graph.

ii. $\Delta F = \Delta H - T\Delta S$

where, ΔH = Enthalpy change = Activation energy, T = Temperature in K, ΔS = Entropy change {from (i) used}.

iii. Frequency factor

$$B_{2/3} = \frac{\log ZE_a}{R\Phi} \quad [1]$$

$$B_{2/3} = \log 3 + \log[1 - 3\sqrt{1 - \alpha}] - \log p(x) \quad [2]$$

where, Z = Frequency factor, B = Calculated from eq. [2], $\log p(x)$ = Calculated from Doyle table corresponding to activation energy.

iv. Apparent entropy change

$$S^* = 2.303R \log \frac{Zh}{RT^*} \quad [3]$$

where, Z = from relation [1], T^* = Temperature at which half of the compound is decomposed from its total loss.

The *p*-CMF copolymers prepared from higher molar ratio of *p*-cresol exhibited a lower rate of decomposition. Hence, the sequence of thermal stability is suggested to be *p*-CMF-(1) < *p*-CMF-(2) < *p*-CMF-(3) < *p*-CMF-(4). The sequence of thermal stability of the copolymers predicted on the basis of the initial as well as half decomposition temperatures is in harmony with that predicted from the activation energy values. This fact is further supported by the increasing order of melting points from *p*-CMF-1 to *p*-CMF-4. This order of stability may be due to the possibility of an almost linear structure of the copolymer having higher molar ratio of *p*-cresol which may give rise to a stable structure to the copolymer chain.^{5,6} In the present study, in case of *p*-CMF-(1) copolymer the removal of water from the polymer is completed around 120°C, which may be due to solvent or moisture probably crystal water entrapped in the copolymer samples.

The analysis of the thermograms indicate that the decomposition of the copolymers is three stage process after a loss of water molecule at 80–160°C. In the first step side chain attached to aromatic nucleus and hydroxyl groups decompose. In the second step, aromatic nucleus decompose while in the third step side chain attached to triazine polymer is degraded and finally the residue remained may be ascribed as

1, 3, 5 triazine. Decomposition is completed at about 800°C in all copolymer resins.

By using the data of the Freeman-Carroll method, various thermodynamics parameters have been calculated (Table IV). The values of these thermodynamic parameters for all copolymers are about the same. The similarity of the values indicates a common reaction mode.²⁶ From the abnormally low values of frequency factor, it may be concluded that the decomposition reaction of *p*-CMF copolymers can be classed as a 'slow' reaction. There is no other obvious reason.^{27–29}

Fairly good straight line plots are obtained using the two methods. This is expected since the decomposition of copolymer is known not to obey first order kinetics perfectly.^{27–29}

CONCLUSIONS

1. A copolymer, *p*-CMF, based on the condensation reaction of *p*-cresol and melamine with formaldehyde in the presence of acid catalyst, was prepared.
2. In TGA the kinetic parameters evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be similar, indicating the common reaction mode. However, it is difficult to draw any unique conclusion regarding the decomposition mechanism.

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