

Resin II: Thermal Degradation Studies of Terpolymer Resins Derived from 2,2'-Dihydroxybiphenyl, Urea, and Formaldehyde

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ABSTRACT: The terpolymer resins have been synthesized by the condensation of 2,2'-dihydroxybiphenyl with urea and formaldehyde in the presence of 2M HCl as a catalyst and with varying molar proportions of reactants. Elemental analysis, IR, NMR and UV-Visible spectral study, and TGA-DTA analysis characterized the resins. The number average molecular weight was determined by nonaqueous conductometric titrations. Thermal studies of the resins have been carried out to determine their mode of decomposition, activation energy, order of reaction,

frequency factor, entropy change, free energy, and apparent entropy change. Freeman-Carroll and Sharp-Wentworth methods have been applied for the calculation of kinetic parameters, while the data from Freeman-Carroll method have been used to determine various thermodynamic parameters. The order of thermal stabilities of terpolymers has been determined using TGA. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 227–232, 2006

Key words: synthesis; terpolymer; degradation; BPhUF

INTRODUCTION

Aromatic polymers were introduced during the 1960s to match the thermal stability requirements of aerospace industry, automotive industry, resistance to harsh environment, nonlinear optical devices, and so forth. The aromatic and heterocyclic rings offer conjugated rigid structure with high glass transition temperature and strong linkages, allowing good resistance in harsh environment. The automotive industry needs organic material with improved thermomechanical properties upto 200–220°C. The development of new products with moderate thermooxidative properties could be achieved by increasing T_g of aliphatic condensation polymer with aromatic moieties. It can be achieved by copolycondensation by reactive process.¹ Hence, our interest is to develop new aromatic polymers that would be having aforementioned properties. Various phenol- and urea-containing polymers were studied by many earlier workers. Patel and Patel have synthesized 2-hydroxy-4-methoxy acetophenone oxime-urea-formaldehyde resin.² Chemical structure and acid catalyzed curing reaction of furan-urea-formaldehyde resin have been studied by Li et al.³ Thermogravimetric analysis of 8-hydroxyquinoline-melamine-formaldehyde resin has been studied.⁴

Thermal and ion exchange properties of Salicylic acid/2-hydroxy-4-methoxypropiofenone-urea-formaldehyde have been reported in literature.^{5–7} Thermogravimetric analysis of urea formaldehyde polycondensate were carried out by Zeman and Tokorova.⁸ Thermal, ion exchange, and electrical properties of terpolymer derived from 2,4-dihydroxyacetophenone/2,4-dihydroxyoxime-urea-formaldehyde resin have been reported by Patel et al.^{9,10} The effect of annealing on structural changes in liquid crystal of 6-hydroxy-2-naphthoic acid, *p*-hydroxybenzoic acid-terephthalic acid-4,4'-biphenol copolymer was investigated recently by Huang and coworkers.¹¹ Oxyethylene copolymer with phenyl and 4,4'-biphenyl have been reported.¹² In continuation of our earlier work on synthesis, characterization, thermal and chelating ion exchange properties of terpolymers,^{4,13,14} this communication reports thermogravimetric analysis of 2,2'-dihydroxybiphenyl-urea-formaldehyde resins.

EXPERIMENTAL

Materials

All chemicals used were of AR or chemically pure grade.

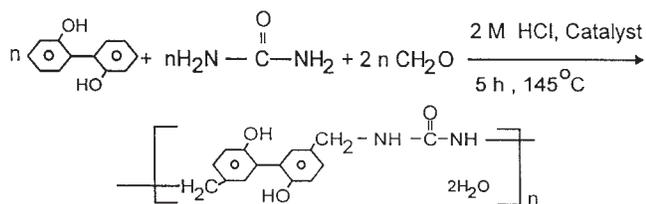
Synthesis of 2,2'-dihydroxybiphenyl (BPh)-urea (U)-formaldehyde (F) polymer (BPhUF-1)

A mixture of 2,2'-dihydroxybiphenyl (9.5 g, 0.05 mol), urea (3.1 g, 0.05 mol), and formaldehyde (8.6 mL of

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35% solution, 0.1 mol) in presence of 2M HCl (100 mL) as a catalyst was heated in an oil bath at $145^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 5 h with occasional shaking.^{15,16} The separated resinous product [BPhUF-1] was washed with hot water to remove unreacted monomers. The resin was purified by dissolution in 8% NaOH and reprecipitated by dropwise addition of 1:1 (v/v) HCl, with constant stirring. The precipitated resin product was filtered off, washed with hot water until it was free from chloride ions, dried and powdered.

The reaction taking place in the synthesis of BPhUF-1 terpolymer is as follows:



Different resin samples of BPhUF namely, BPhUF-2 (1:2:4), BPhUF-3 (1:3:5), and BPhUF-4 (1:4:6) were prepared using different molar ratios of reactants.

Thermogravimetric analysis

The nonisothermal (dynamic) thermogravimetric measurements of all terpolymer resins prepared have been carried out by simultaneous TGA-DTA, Mettler Toledo, Switzerland computer controlled thermogravimetric Analyzer, Model SDTGA, at Regional Sophisticated Instrumentation Centre. The observations were recorded in temperature range from room temperature to 900°C , at a linear heating rate of $15^{\circ}\text{C}/\text{min}$ in air atmosphere.

The use of thermogravimetric data to evaluate kinetic parameters of solid state reactions involving weight loss has been investigated by number of workers.¹⁷⁻¹⁹ We have used two different methods to evaluate the kinetic parameters of solid state reactions, namely (1) Freeman-Carroll method¹⁷ and (2) Sharp-Wentworth method²⁰

In the Freeman-Carroll method, the following expression [eq. (1)] is used.

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

Hence, a plot of $\Delta \log(dw/dt)/\Delta \log W_r$ versus $\Delta(1/T)/\Delta \log W_r$ should give a straight line with an intercept on the y-axis equal to the value of n , (n = order of reaction) and a slope (m) = $-E_a/2.303R$. In eq. (1), $W_r = W_c - W$, W_c is the weight loss at the completion of the reaction, W is the total weight loss upto the time t ,

T is the temperature in Kelvin, and R is the gas constant.

Using the Sharp-Wentworth method, eq. (2) is used to evaluate the activation energy.

$$\log \left[\frac{dc/dt}{1-C} \right] = \log \left[\frac{A}{\beta} \right] - \frac{E_a}{2.303R} \frac{1}{T} \quad (2)$$

where dc/dt is the rate of change of mass loss with time t , C is the fraction of mass loss at time t , T is the temperature, and $\beta = dT/dt$ (linear heating rate).

Thus, a linear plot of $\log[(dc/dt)/(1-c)]$ versus $1/T$ is obtained whose slope gives the value of E_a , and A may be evaluated from the intercept. The linear relationship confirmed that the assumed order ($n = 1$) is correct.

RESULTS AND DISCUSSION

The four terpolymer resins used in the present study have been characterized on the basis of elemental analysis, viscosity measurements, molecular weight determinations, UV-visible, infrared, and NMR spectral studies, as described elsewhere.²¹

The thermogravimetric analysis of all the four terpolymers prepared has been carried out but, for reasons of economy of space, the thermal data and kinetic plots for only one representative case are given in Figures 1-5. The calculations of thermogravimetric analysis were done after devising two computer programs so as to reduce the individual errors.

Details of thermoanalytical data and kinetic parameters of thermal degradation of terpolymer samples have been evaluated from thermograms using Sharp-Wentworth (SW) and Freeman-Carroll (FC) methods have been incorporated in Tables I and II.

Examination of thermograms and TG data of BPhUF terpolymers showed that these polymers have resistance to elevated temperatures. Thermogram of all BPhUF terpolymers exhibited two stages of decomposition except BPhUF-1 terpolymer, which exhibits three stages of decomposition. In case of BPhUF-1 terpolymer sample, weight loss 11.61% when temperature was raised from 190 to 300°C . This initial weight loss may be due to loss of water of crystallization associated with terpolymer sample.^{15,22,23} In DTA curve, the loss of water of crystallization is shown by a broad endotherm.^{24,25}

Second decomposition stage in BPhUF-1 terpolymer represents degradation of both phenolic hydroxyl groups, side chain attached to aromatic nucleus, and partial decomposition of aromatic nucleus, while first decomposition stage in the case of BPhUF-2, BPhUF-3, and BPhUF-4 represents degradation of side chain attached to aromatic nucleus.

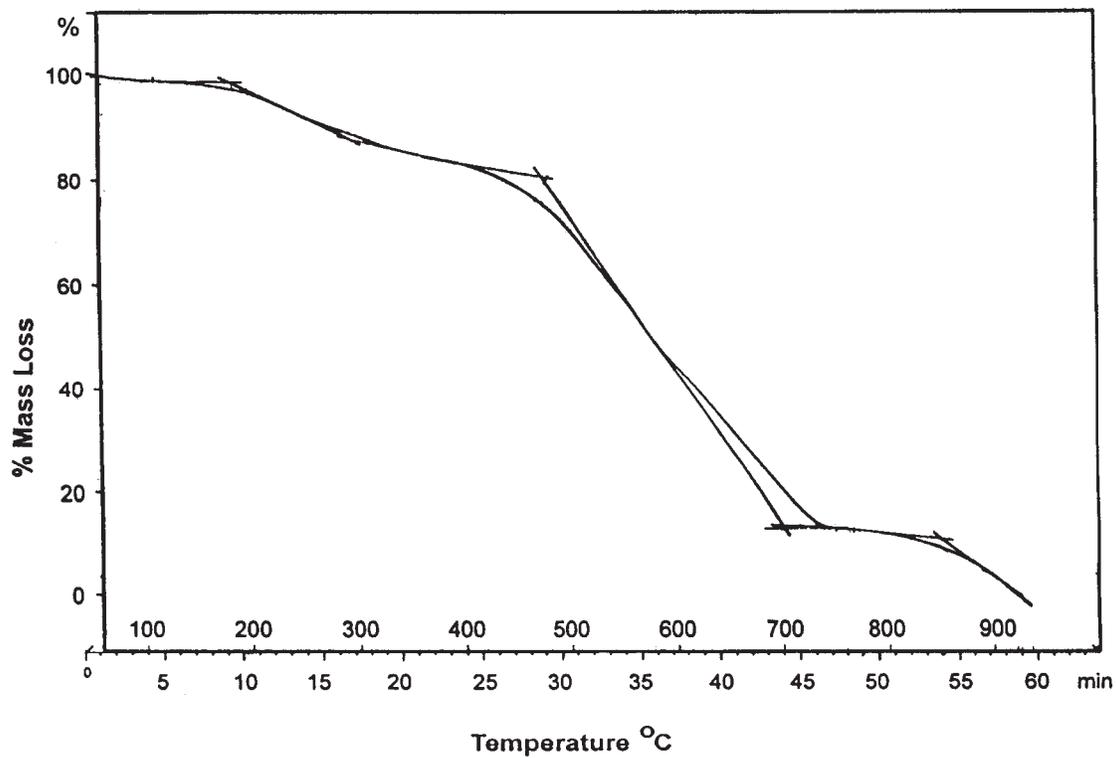


Figure 1 Thermogram of BPhUF-1 polymer.

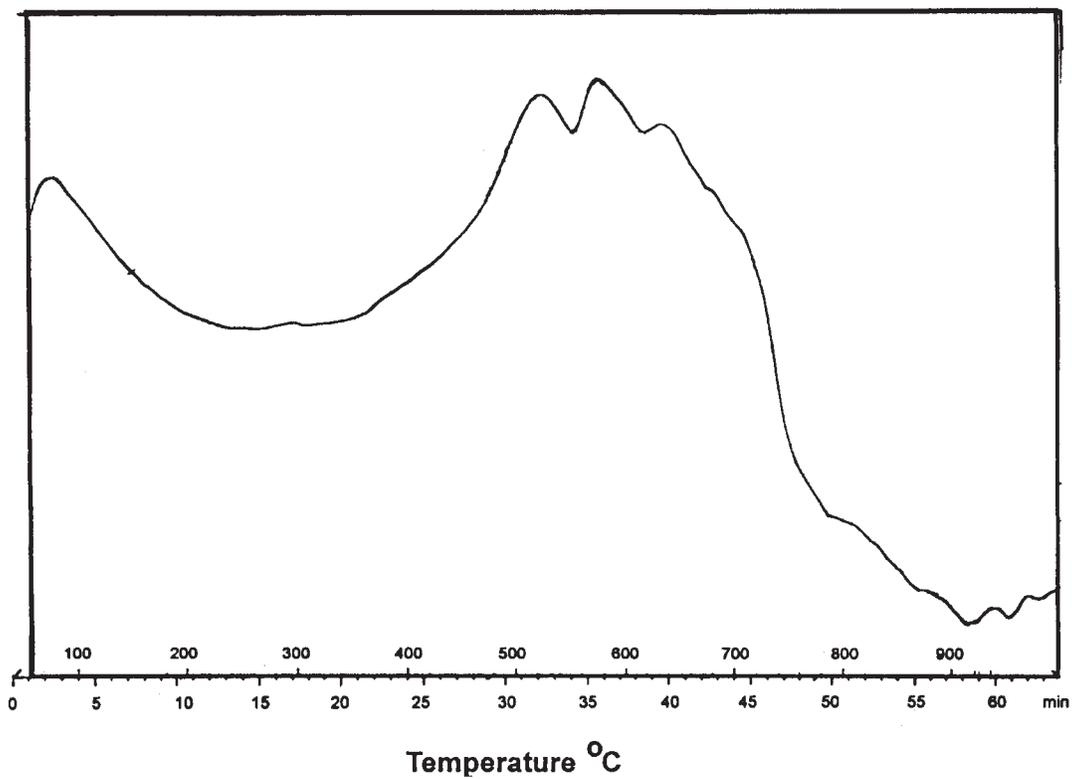


Figure 2 DTA curve of BPhUF-1 polymer.

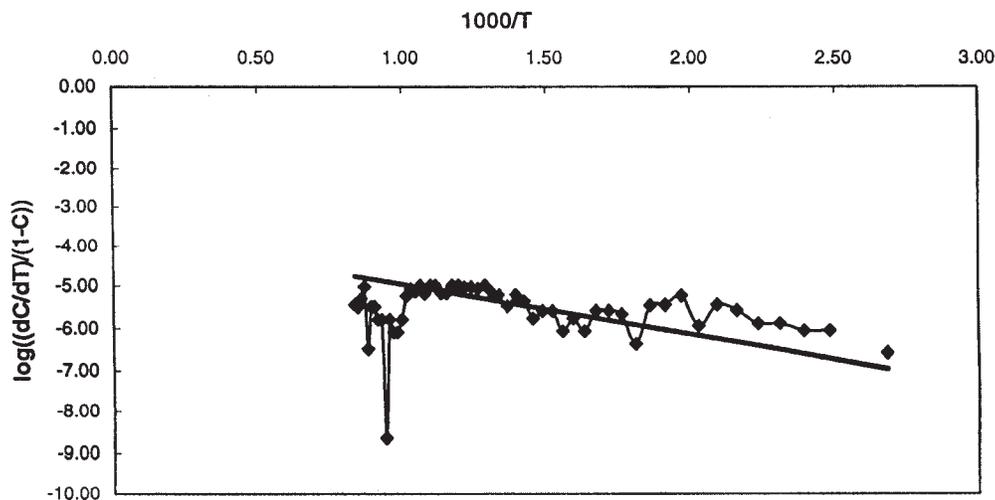


Figure 3 Sharp-Wentworth plot of BPhUF-1 terpolymer.

Third decomposition step in the case of BPhUF-1 terpolymer shows the complete degradation of left aromatic nucleus, while in the case BPhUF-2, BPhUF-3, and BPhUF-4 second decomposition stage correspond to loss of two phenolic hydroxyl group, degradation of side chain attached to aromatic nucleus, and partial decomposition of aromatic nucleus except in BPhUF-2 that shows a complete decomposition of polymer.

First and second decomposition of BPhUF-2, BPhUF-3, and BPhUF-4 terpolymer shows endothermic decomposition in DTA curve, while in the case of BPhUF-1 terpolymer, second decomposition stage shows exothermic peak and third stage depicts endothermic. The exotherm in the case of BPhUF-1 polymer may be due to oxidation reaction.

CONCLUSIONS

All the terpolymers are cream in color and partly soluble in DMF, DMSO, and insoluble in commonly used organic solvents and concentrated acids.

Thermograms of all these terpolymer resins depict two stage decomposition, except for BPhUF-1 which shows a three step decomposition. The BPhUF-1 resin has 2 mol of water associated with each repeat unit of polymer. The observed weight loss is little higher than the calculated. This may be due to the degradation of side chains or some other chain involved in the pyrolysis of terpolymers.^{15,26,27}

To obtain the relative thermal stability of various polymers the method described by SW²⁰ was adopted. The thermal stability of terpolymers, based on initial decomposition temperatures, has also

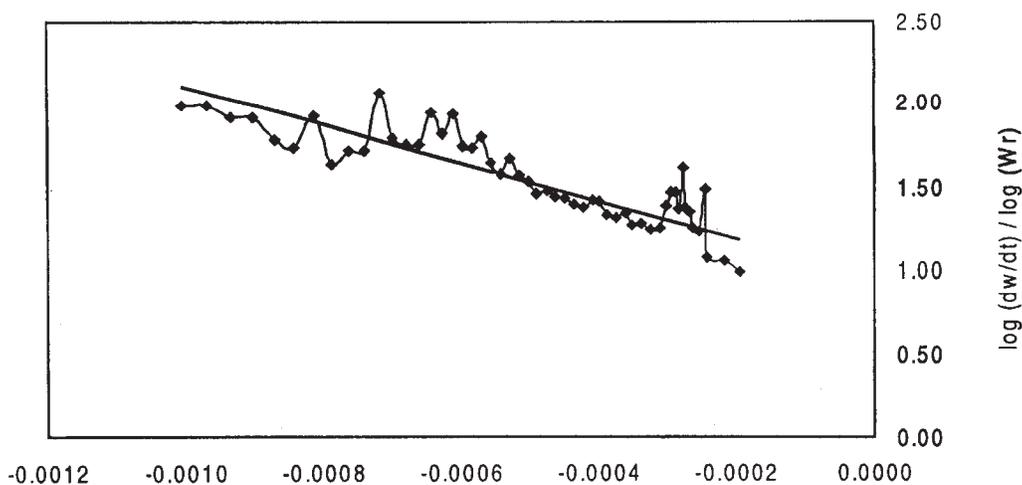


Figure 4 Thermal activation energy plot of BPhUF-1 terpolymer.

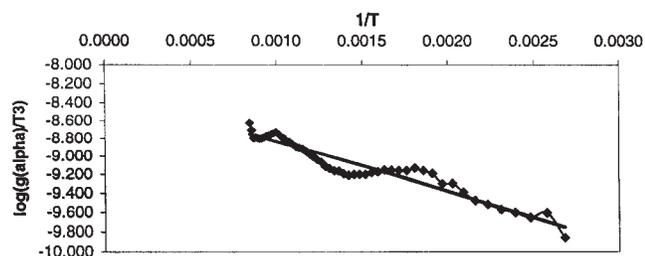


Figure 5 Freeman-Carroll plot of BPhUF-1 terpolymer.

been used here to define their relative thermal stabilities, neglecting the degree of decomposition (Table II).

By using thermal decomposition data and then applying the SW method (a representative plot is shown in Fig. 3) activation energy is calculated which is in agreement with the activation energy calculated by the FC method¹⁷ (Table II). A representative thermal activation energy plot (Fig. 4) and FC plot (Fig. 5) for the polymer are shown. The thermodynamic parameters have been calculated on the basis of thermal activation energy. These values are incorporated in Table II.

The sequence of thermal stability of the polymers has been predicted on the basis of initial decomposition temperature. The sequence of thermal stability was found to be BPhUF-1 > BPhUF-3 > BPhUF-4 > BPhUF-2.

From the above order, it can be concluded that the higher thermal stability of BPhUF-1 may be due to

the stronger intermolecular hydrogen-bonding present in polymer structure because of water of crystallization (which would be more difficult to break and hence more resistant to high temperature). The order of stability of the remaining polymers indicates that thermal degradation behavior is independent of their molecular weight. It may be due to the colinear arrangement of monomer unit in polymer chain, which allows for establishment of strong intermolecular hydrogen bonding that would be more difficult to break and therefore more resistance to high temperature.²⁵

By using the data of FC method various thermodynamic parameters have been calculated (Table II). The values of these thermodynamic parameters for terpolymer resins are comparable. The results indicate a common reaction mode of decomposition.²⁷⁻³⁰ Because of abnormally low value of frequency factor (Z), it may be concluded that the reaction of decomposition of terpolymers can be classified as a slow reaction and no other obvious reason can be given.^{27,29,31,32}

The negative values for entropy indicate that the activated polymer has more ordered structure than that of the reactants, and the reactions are slower than normal. This is further supported by a low Z value.²⁹

It is very difficult to draw any unique conclusion from the magnitude of thermal activation energy [E_a] as decomposition mechanism is expected to be complicated.^{33,34} The decomposition of terpolymers is known to obey first order kinetics but not perfectly, as

TABLE I
Thermoanalytical Data and Decomposition Temperature for BPhUF Terpolymer

S. no.	Terpolymer	Temperature range (°C)	Stage of decomposition	Species degraded	% Weight loss	
					Found	Calculated
1	BPhUF-1	190-300	First	Loss of 2H ₂ O molecule	11.61	11.76
	BPhUF-2	—	—	—	—	—
	BPhUF-3	—	—	—	—	—
	BPhUF-4	—	—	—	—	—
2	BPhUF-1	475-700	Second	Two hydroxyl group, side chains —CH ₂ —NH—CO—NH— attached to aromatic ring of biphenyl and partial decomposition of aromatic nucleus	78.93	75.66
	BPhUF-2	220-340	First	Side chain —CH ₂ —NH—CO—NH— attached to aromatic ring of biphenyl	22.14	24.29
	BPhUF-3	240-325	First	—	23.55	23.55
	BPhUF-4	235-310	First	—	26.40	28.92
3	BPhUF-1	760-920	Third	Complete decomposition left aromatic nucleus	100.00	100.00
	BPhUF-2	340-790	Second	Two hydroxyl group, side chains attached to aromatic ring of biphenyl and partial decomposition of aromatic nucleus loss two —OH group	97.50	100.00
	BPhUF-3	560-715	Second	—	87.12	87.12
	BPhUF-4	520-775	Second	—	97.02	97.00

TABLE II
Kinetic Parameters of Terpolymer Resin

Terpolymer	Decomposition temperature (°C)	Half decomposition temperature T* (°C)	Activation energy (kCal/mol)		ΔS (cal)	ΔF (kcal)	Z (s ⁻¹)	S* (cal)	Order of reaction, <i>n</i>
			FC	SW					
BPhUF-1	475	580	4.49	4.383	-73.41	59.4	60.74	-26.41	0.96
BPhUF-2	220	610	2.702	3.29	-47.43	26.08	16.90	-27.72	0.95
BPhUF-3	240	595	6.95	6.31	-71.28	43.51	988.78	-23.63	0.71
BPhUF-4	235	565	4.81	4.99	-53.41	31.94	161.25	-25.41	0.94

FC, Freeman-Carroll method; SW, Sharp-Wentworth method.

observed by Jacobs and Tompkin³⁵ and by Coats and Redfern.³⁶

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