Synthetic, Structural, and Thermal Degradation of a Tercopolymer Derived from Salicylic Acid, Guanidine, and Formaldehyde

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ABSTRACT: A salicylic acid–guanadine–formaldehyde (SGF) tercopolymer was synthesized by the condensation of salicylic acid with guanidine carbonate and formaldehyde in 1 : 1 : 2 molar proportions in the presence of 2*M* HCl as a catalyst. The SGF tercopolymer was characterized on the basis of elemental analysis and ultraviolet–visible, IR, and NMR spectral studies. The Freeman–Carroll and Sharp–Wentworth methods were used to calculate the activation energy and thermal stability of the tercopolymer. Kinetic parameters such as activation energy, entropy change, free-energy change, frequency factor, apparent entropy change, and order of reaction were calculated with the Freeman–Carroll method. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2278–2283, 2004

Key words: synthesis; thermal properties; degradation

INTRODUCTION

For polymers having a large number of practical applications, it is necessary to investigate the effect of heat on these polymers to establish their thermal stabilities. 8-Hydroxyquinoline or phenol derivatives, such as *o*-aminophenol and resorcinol condensed with formaldehyde, have been reported in the literature.[1,2] Copolymers of hydroxybenzoic acid and formaldehyde have been investigated for their use as ion exchangers.[3,4] Resins prepared from *o/p*-hydroxybenzoic acid, urea, and formaldehyde in the presence of an acid catalyst were also studied by Joshi, Patel and colleagues.[5–7] Manavalan and Patel[8–10] synthesized copolymers of salicylic acid, urea, and formaldehyde. Lingala et al.[11] prepared and studied the thermal degradation of an 8-hydroxyquinoline, oxamide, and formaldehyde tercopolymer. Tercopolymers of salicylic acid, thiourea, and trioxane and *p*-hydroxybenzoic acid, thiourea, and trioxane have also been reported in the literature.[12–15] Extensive studies on the thermal degradation and ion-exchange properties of a tercopolymer of hydroxybenzoic acid, diamide, melamine, and formaldehyde and some coordination polymers were done in our laboratory.[16–21] This article describes the synthetic, structural, and thermal degradation of a new tercopolymer synthesized from salicylic acid, guanidine carbonate, and formaldehyde. The Sharp–Wenthworth[22] and Freeman–Carroll[23] methods were used to calculate various kinetic parameters for this tercopolymer.

The method for the estimation of kinetic parameters from dynamic thermogravimetric studies suffers because the two parameters, temperature and time, cannot be continuously changed. This problem is eliminated by the Freeman–Carroll method, where the parameters of temperature and time can be varied. Methods for the estimation of kinetic parameters from thermogravimetric studies[24–27] are mostly based on the assumption that the Arrhenius equations is valid and that the thermal and diffusion barriers are negligible.

Theoretical considerations

Freeman–Carroll method

The advantage of the Freeman–Carroll method is that the parameters of time and temperature can be varied, and at the same time, one can obtain the order of reaction (*n*) and the activation energy (E_a) in a single experiment.

In the Freeman–Carroll method, the following expression is used to evaluate various kinetic parameters:

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

where dw/dt is the rate of change of weight with time; $W_r = W_c - W$, where W_c is the weight loss at the

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completion of reaction or at a 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, a plot of $\Delta \log(dw/dt)/\Delta \log W_r$ versus $\Delta(1/T)/\Delta \log W_r$ should give an intercept on the y axis at $x = 0$ equal to the value of n and a slope of $m = -E_a/2.303R$.

Sharp–Wenthworth method

The following expression is used to evaluate E_a with the Sharp–Wenthworth method:

$$\frac{\log(dc/dt)}{1 - C} \times \log\left(\frac{A}{\beta}\right) \frac{-E_a}{2.303} \frac{1}{T}$$

where dc/dt is the fraction of mass loss with time t, $\beta = dT/dt$, A = pre-exponential factor of frequency, and C = concentration of mole fraction or amount of reactant.

EXPERIMENTAL

Chemicals

The chemical used were all analytical reagent (AR) grade.

Instruments used

C, H, and N were analyzed on a Carlo Erber elemental analyzer. Fourier transform infrared spectra in the region $400–4000$ cm^{-1} were recorded on a PerkinElmer instrument (USA) with KBr pellets. The electronic spectrum of the tercopolymer was recorded in dimethylformamide (DMF) at room temperature with a UV-240 Shimadzu double-beam spectrophotometer. The NMR spectrum was scanned at 300 MHz with deuterated dimethyl sulfoxide (DMSO) solvent at the Regional Sophisticated Instrumentation Centre (RSIC), Chandigarh. The nonisothermal thermogravimetric measurement of
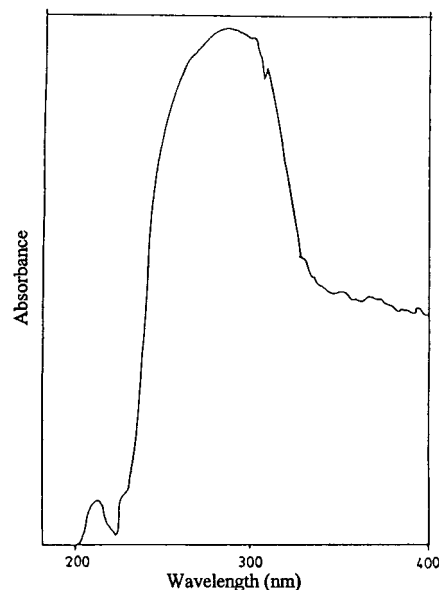

Figure 1 UV-vis spectrum of the SGF tercopolymer.

the tercopolymer was done at RSIC, Nagpur, with Pt–Pt Rh thermocoupled from $20–600°C$ at a linear heating rate of $15°C/min$ in air.

Synthesis of the salicylic acid–guanadine–formaldehyde (SGF) tercopolymer

A mixture of salicylic acid (0.1 mol) with guanidine carbonate (0.1 mol), and formaldehyde (0.2 mol) at the ratio of 1 : 1 : 2 was refluxed in the presence of 100 ml, of 2N hydrochloric acid in an oil bath at $132°C$ for 5 h. The reaction took place as follows:

The separated light pink product was washed with hot water. The resin was purified by dissolution in NaOH and reprecipitated by the dropwise addition of 1 : 1 (v/v) HCl. The reprecipitated product was fil-

TABLE I
IR Spectrum Data of the SGF Tercopolymer

| Assignment	Observed band frequency (cm^{-1})	Expected band frequency (cm^{-1})	References
Phenolic —OH stretching	3300–3150	3500–3000	30–32
—N—H stretch (imide)	2950	3320–3140	33 and 34
>C=O stretching			
(aldehyde/imide)	1670	1690–1650	33–36
Phenolic C—O stretching	1410–1300	1410–1310	35 and 37
Aromatic ring vibration	1600–1480	1600–1450	35
Methylene bridge (—CH2) modes			
Bend	1450	1460	31 and 37
Rock	760	775	31 and 37
Wagging	1300–1200	1300–1200	31 and 37
1,2,3,5-substituted benzene ring	1200–800	>800	31 and 32
N—H bend wagging	800–650	800–666	31, 32, and 36
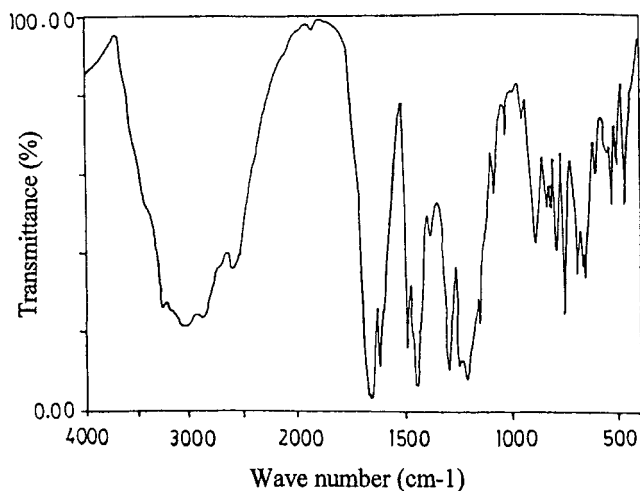
Figure 2 IR spectrum of the SGF tercopolymer.

Figure 3 NMR spectrum of the SGF tercopolymer.
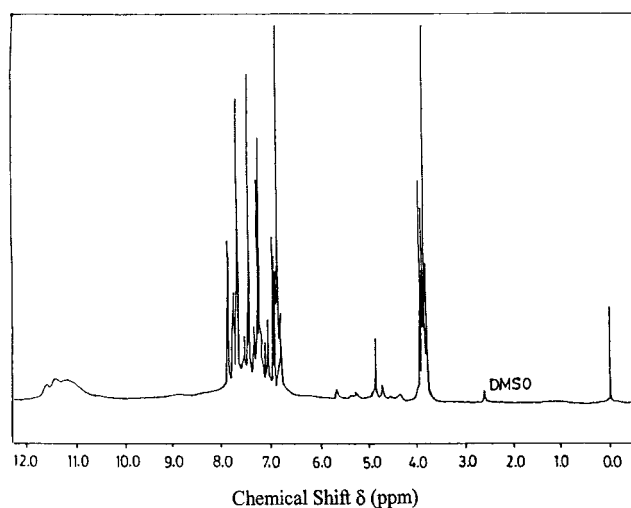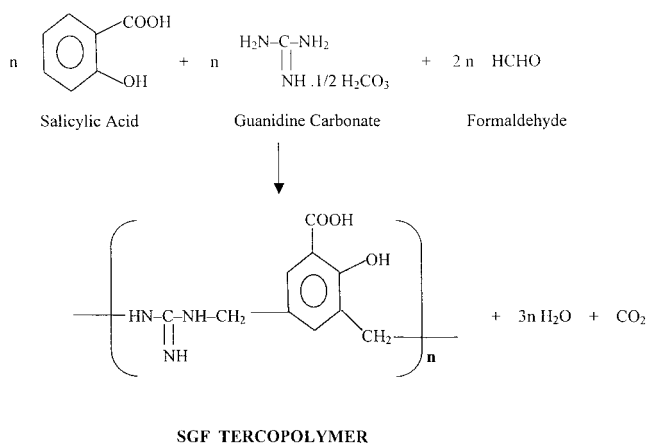

SGF TERCOPOLYMER

tered, washed with hot water, and dried (yield = 9.84 g; mp = 129°C).

ANAL: Calcd for $C_{10}H_{11}N_3O_3$: C, 51.34%; H, 1.93%; N, 16.6%. Found: C, 53.34%; H, 4.93%; N, 18.6%.

RESULTS AND DISCUSSION

The tercopolymer was soluble in DMF and DMSO; however it is insoluble in common organic solvents. The composition of the polymeric unit was assigned on the basis of a detailed study of the elemental anal-

ysis of the polymer, ultraviolet–visible (UV–Vis), IR, and NMR spectral studies and thermogravimetric analysis (TGA). The tercopolymer was analyzed for its elemental composition to determine the composition of polymeric units.

UV–vis studies

The electronic spectrum of the SGF tercopolymer is shown in Figure 1. The spectrum depicted two characteristic bands in the region of 200–220 and 240–320 nm. The band at 200–220 nm indicated the presence of a carbonyl ($>C=O$) group containing a carbon–oxygen double bond in conjugation with an aromatic nucleus and was characteristic of a $\pi \rightarrow \pi^*$ transition.[28] The absorption band between 240 and 320 nm indicated the presence of $>C=N$ of the guanidine molecule, which was in conjugation with the aromatic nucleus and was assigned to the $n \rightarrow \pi^*$ transition.[29]

IR spectral studies

The IR spectrum data is tabulated in Table I, and the spectrum is shown in Figure 2. The IR spectrum recorded in a KBr matrix for the SGF tercopolymer showed a peak in the range 3300–3150 cm^{-1},[30–35]

TABLE II
NMR Spectrum Data of the SGF Tercopolymer

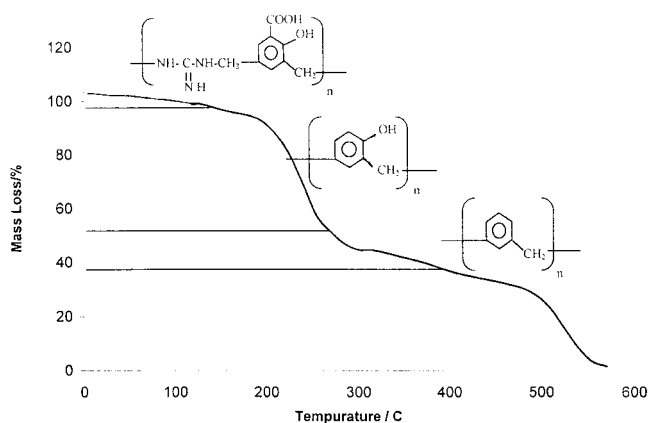| Chemical shift (δ) of the tercopolymer (ppm)	Nature of proton assigned in the NMR spectrum	Expected chemical shift (δ ppm)	References
7.4–7.7	Aromatic (Ar—H)	7.3–8.8	31, 32, and 37
7.8	Phenolic (Ar—OH)	7.5–12	31, 32, and 37
7.41	Carboxylic (Ar—COOH)	7.41	31 and 33
6.9	—NH bridging	5.0–4.5	32 and 37
3.5–4.10	Ar—CH₂—N moiety	2.5–4.5	31, 32, 38, and 39

Figure 4 TGA curve of the SGF tercopolymer.

attributed to the stretching vibration of the —OH group of the polymeric associated phenolic group and the intermolecular H bonding between the hydroxy group of —COOH from different acid units in the polymeric chain. The broad band observed around 2950 cm^{-1} may have been due to the stretching vibration of —N—H— (imide), and the sharp band between 800 and 650 cm^{-1} suggested a bending vibration of an N—H bent (imide) group.[31,32,36] The band around 1670 cm^{-1} may have been observed because of >C═O stretching.[31,32] A sharp peak around 1600–1480 cm^{-1} may have been due to aromatic skeletal ring breathing modes.[31,32] The bands observed between 1200 and 800 cm^{-1} may have been caused by a 1,2,3,5-tetra-substituted benzene ring.[31,32] The band at 1410–1300 cm^{-1} suggested phenolic >C—O stretching modes of vibration.[31,32] The inflections around 1450 and 760 and from 1300–1200 cm^{-1} were due to the stretch, rock, and twisting modes of —CH$_2$, which suggested the presence of methylene bridges in the tercopolymer.[31,37]

NMR studies

The NMR spectrum of the SGF tercopolymer shown in Figure 3 exhibited signals in the region of 7.4–7.7 δ (ppm), which may have been due to the proton of the aromatic ring (Ar—H), and the signal in the region 7.8 δ ppm) may have been due to the phenolic —OH proton in hydrogen bonding (Ar—OH).[31,32,37] The sig-

nal displayed at 7.41 δ (ppm) may have been due to the carboxylic proton of Ar—COOH.[31,33] The presence of a broad signal around 6.9 δ (ppm) may have been due to the presence of —NH bridges.[32–37] A methylene proton Ar—CH2—N moiety was inferred by the appearance of a weak singlet signal at 2.5–4.5 δ (ppm).[31,32,38,39] The spectral data is tabulated in Table II.

TGA

The thermal degradation curve for the SGF tercopolymer is shown in Figure 4. The thermogram of the SGF tercopolymer exhibited four-stage decomposition in the temperature range 60–600°C. The first-stage decomposition, which was slow, ranged from 123 to 157°C corresponding to loss (≈4%), which may have been due to moisture entrapped in the tercopolymer sample.[9,10] The second-stage decomposition started at 218°C and ended at 266°C, which may have been due to the loss of the side chain attached to the aromatic nucleus $\left(\begin{array}{c} \text{NH—} \quad C \text{ —HN} \\ \| \\ \text{NH} \end{array}\right)$ and the carboxyl group (—COOH; 56.8% Calcd and 55.42% Found).[16] The third-step decomposition started at 324–366°C, corresponding to a 65.96% loss, which may have been due to the degradation of hydroxyl group, calculated as 64.59%. The fourth-step decomposition started from 490–548°C, which may have been a result of the complete decomposition of the polymer ring (100% Calcd and 99.66% Found). The half-decomposition temperature of the SGF tercopolymer is also given in Table III.

Using thermal decomposition data and then applying the Sharp–Wenthworth method, we obtained a Sharp–Wenthworth plot for the tercopolymer as shown in Figure 5. E_a calculated by this method was in agreement with the E_a calculated by the Freeman–Carroll method. A thermal E_a plot and a Freeman–Carroll plot for the polymer is shown in Figures 6 and 7, respectively. The thermodynamic parameters for the polymers were calculated on the basis thermal E_a values, which are shown in Table III.

From the data in Table I, we concluded that the values of the thermodynamic parameters were com-

TABLE III
TGA Results for the SGF Tercopolymer

Tercopolymer	Half-decomposition temperature (°C)	E_a (kJ/mol)		Entropy change (J)	Free energy change (kJ)	Frequency factor (s^{-1})	Apparent entropy change (kJ)	n
		FC	SW					
SGF	267	20.35	16.31	−285.66	152.43	586.63	−23.69	0.9332

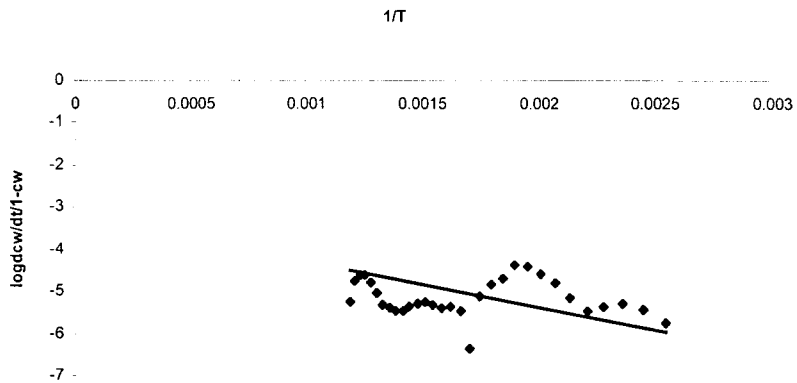FC = Freeman–Carroll; SW = Sharp–Wentworth.

Figure 5 Sharp–Wenthworth plot of the SGF tercopolymer.
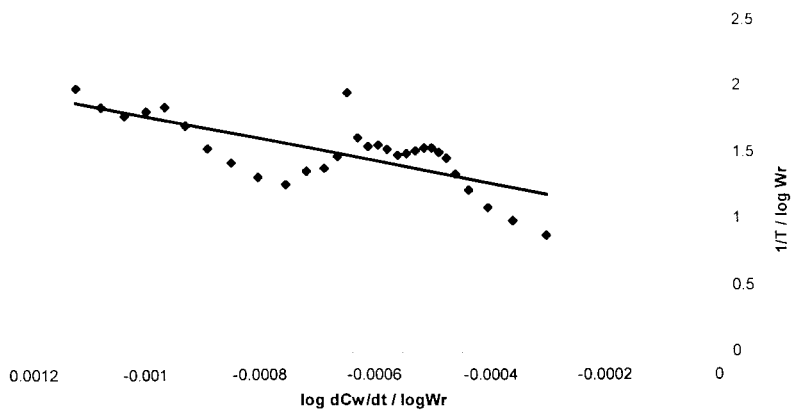
Figure 6 Thermal E_a plot of the SGF tercopolymer.
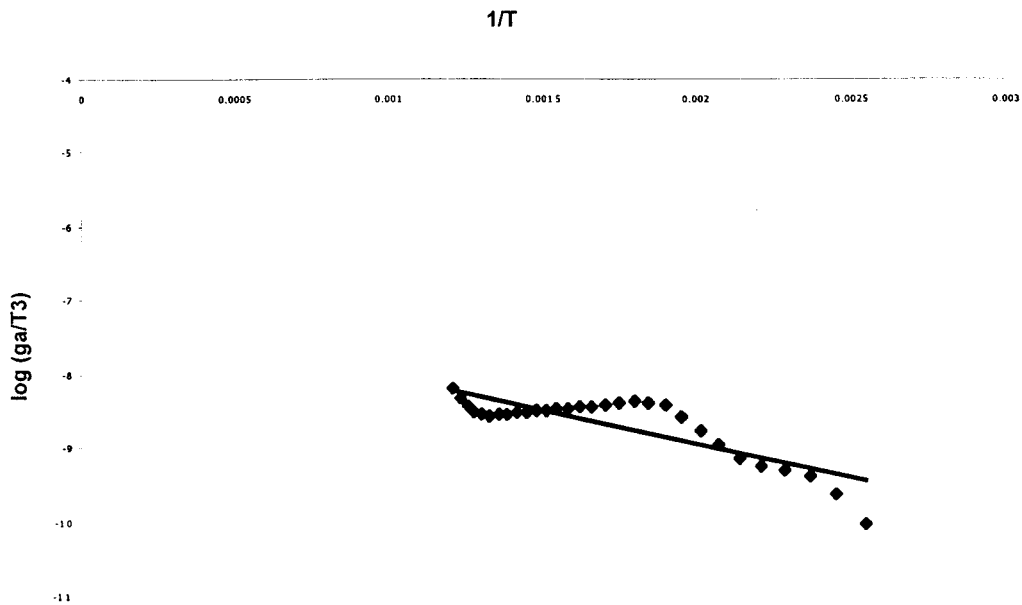
Figure 7 Freeman–Carroll plot of the SGF tercopolymer.

parable indicating a common reaction mode.[26,40,41] The abnormally low values of the frequency factor led us to conclude that the decomposition of the SGF polymer can be classified as a slow reaction for which there is no other obvious reason.[41,42] The decomposition of the tercopolymer is known to obey first-order kinetics but not perfectly, as observed by Shrivastava and Juneja.[42]

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