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Synthesis and Study of Tercopolymers

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ABSTRACT

Tercopolymers have been prepared by condensing a mixture of salicylic acid, thiourea, and any one of such comonomers as o-cresol, p-cresol, o-chlorophenol, and p-chlorophenol with trioxane in the presence of 2 M HCl as catalyst. The tercopolymers were characterized by elemental analyses. Their $\overline{M}_n$ was determined by nonaqueous conductometric titration both against standard sodium methoxide and tetra-n-butyl ammonium hydroxide and also by the VPO method. Also made were an IR spectral study, a viscometric study in dimethylformamide (DMF), and a thermal study based on TGA. Chelation ion-exchanging properties of selected tercopolymer samples were also studied by employing the batch equilibration method.

INTRODUCTION

Copolymers from a mixture of salicylic acid and a phenolic or amino derivative and formaldehyde have been reported to have several interesting applications [1-3]. Some of the copolymers synthesized from a mixture of resorcinol, formaldehyde, and either salicylic acid

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[4], β-resorcylic acid [5], or p-aminosalicylic acid [6] have been proven to be specific ion exchangers. Moreover, copolymers obtained from a mixture of salicylic acid, thiourea, and trioxane in the presence of 2 M HCl have also been proven to be ion exchangers [7]. The present paper deals with the synthesis, characterization, and chelation ion-exchange properties of tercopolymers. Among the three comonomers condensed jointly with trioxane (T), two are salicylic acid (S) and thiourea (T) and the other comonomer is either o-cresol (OC), p-cresol (PC), o-chlorophenol (OCP) or p-chlorophenol (PCP). The number-average molecular weight ($\overline{M}_n$) of the tercopolymers has been determined by vapor pressure osmometry (vpo) and conductometric titration methods. The IR spectral properties and the thermal behavior of these polymers have been studied. The batch equilibration method was adopted for the study of the chelation ion-exchanging properties of the tercopolymer samples. The effect of various electrolytes on the absorption of Cu(II) metal ions by tercopolymers at a constant pH, the rates of the uptake of metal ion under specified conditions, and the distribution of Cu(II) ions between the polymeric ligand and the liquid phase have been studied.

EXPERIMENTAL

Preparation of Tercopolymers

For the sake of convenience the names of the tercopolymer samples have been abbreviated and the significance of the abbreviation used is indicated in Table 1. Thus a tercopolymer designated as S.T. PCP. T-1 is salicylic acid-thiourea-p-chlorophenol-trioxane tercopolymer.

Condensation of a mixture of salicylic acid, thiourea, and a comonomer (p-chlorophenol, o-chlorophenol, o-cresol, or p-cresol) with trioxane was carried out in the presence of 2 M HCl as catalyst. In the synthesis of tercopolymers both salicylic acid and thiourea have been considered as parent monomers and are polymerized either with chlorophenol (o- and p-) or cresol (o- and p-) monomers with trioxane to yield tercopolymers. Four series of tercopolymers prepared with the above phenolic compounds in varying molar ratios are indicated in Table 1.

Copolymerization of Salicylic Acid (S), Thiourea (T), and p-Chlorophenol (PCP) with Trioxane (T) in the Presence of 2 M HCl

A mixture of salicylic acid (12.5 g, 0.9 mol), thiourea (7.6 g, 1.0 mol), p-chlorophenol (1.2 g, 0.1 mol), and trioxane (6.0 g, 2 mol) was refluxed with stirring at 130°C in an oil bath for 4 h. During this time the solid product which separated out was filtered off, washed with hot water, and finally with benzene to remove unreacted monomers. This was followed by steam distillation to remove the last traces of unreacted monomers. The yellow-colored tercopolymer thus obtained was purified by dissolving in 10% NaOH and reprecipitating by dropwise addition of 1:1 HCl. The tercopolymer was washed with boiling water and dried. The tercopolymer did not melt up to 160°C. The sample was designated as S.T. PCP. T-1, yield 3.5 g.

Apparatus and Methods of Characterization

Elemental Analysis. Halogen and sulfur content in all the tercopolymer samples were estimated by the Carius method and nitrogen by the Kjeldahl method.

The number-average molecular weight ($\overline{M}_n$) of the tercopolymer samples in pyridine against a 0.01 M solution of tetra-n-butyl ammonium hydroxide (TBAH) was estimated by the method reported for p-hydroxybenzoic acid-formaldehyde polymers [8]. A Metrohm Herisau Konductoskop E 365, Switzerland, was used for the conductometric titrations. The tercopolymer solution in the titration vessel (conductance cell EA645, England) was stirred with a magnetic stirrer. Titrations of a solution of tercopolymer samples in pyridine were also carried out against a 0.01 M solution of sodium methoxide (NaOMe). The $\overline{DP}$ of the tercopolymer samples was estimated from the results of conductometric titrations. A Hewlett-Packard model 302 B vapor pressure osmometer (vpo) was used to calculate the $\overline{M}_n$ of the tercopolymer samples.

The solution viscosity in DMF of the tercopolymer samples was measured at 35 ± 0.1°C with an Ubbelohde-type dilution viscometer (made of Pyrex glass). The solvent and solution were passed through a sintered glass crucible (G-4) to free them of any dust particles. The intrinsic viscosity $[\eta]$ measured from a linear plot of η_{sp}/c vs concentration (Table 1).

The IR spectra were taken in KBr on a UR-10 spectrophotometer. Thermogravimetric analysis (TGA) of all the tercopolymer samples was carried out at a heating rate of 10°C/min.

Ion-Exchange Properties

To ascertain the effectiveness of particular moiety present in a given polymeric chain in the metal uptake, ion-exchange studies of all the tercopolymer samples with Cu^{2+} ions was carried out by using the batch equilibration method [9]. Tercopolymer samples (S.T. PCP. T-1 and S.T. PCP. T-2), described earlier, were ground to pass through a 300-mesh size and swollen under the conditions of study. They were used in all experiments described for batch equilibration in an ion-exchange study.

TABLE 1. Percent Yield, Molecular Weight, and Intrinsic Viscosities of Tercopolymers

No.	Tercopolymer	Molar ratio of monomers	Mole ratio of (conductometry) x y z^a
1	S.T. PCP. T-1	0.9:1.0:0.1:2.0	0.24:0.21:0.38
2	S.T. PCP. T-2	0.8:1.0:0.2:2.0	0.34:0.15:0.32
3	S.T. PCP. T-3	0.6:1.0:0.4:2.0	0.35:0.09:0.31
4	S.T. OCP. T-4	0.9:1.0:0.1:2.0	0.19:0.24:0.42
5	S.T. OCP. T-5	0.8:1.0:0.2:2.0	0.32:0.17:0.32
6	S.T. OCP. T-6	0.6:1.0:0.4:2.0	0.32:0.11:0.39
7	S.T. OC. T-7	0.9:1.0:0.1:2.0	0.23:0.22:0.43
8	S.T. OC. T-8	0.8:1.0:0.2:2.0	0.24:0.22:0.40
9	S.T. OC. T-9	0.6:1.0:0.4:2.0	0.24:0.24:0.41
10	S.T. PC. T-10	0.9:1.0:0.1:2.0	0.23:0.22:0.44
11	S.T. PC. T-11	0.8:1.0:0.2:2.0	0.24:0.26:0.35
12	S.T. PC. T-12	0.6:1.0:0.4:2.0	0.24:0.21:0.43

[a] x = (o- or p-) cresol or (o- or p-) chlorophenol, y = thiourea, z = salicylic acid.

TABLE 1 (continued)

No.	Percent yield	$\overline{M}_n$, conductometry		VPO	$[\eta] \times 10^2$ (dL/g)	K' + K''
		TBAH	NaOMe			
1	75.5	516	563	500	4.92	0.46
2	73.0	688	660	461	4.95	0.47
3	72.5	551	585	440	4.75	0.45
4	74.2	511	571	587	5.36	0.49
5	71.5	598	661	524	5.11	0.48
6	70.4	570	608	485	4.85	0.45
7	80.0	658	609	550	5.24	0.46
8	75.4	636	632	515	4.91	0.46
9	73.0	533	623	490	4.97	0.41
10	76.0	658	705	535	5.19	0.48
11	71.0	571	605	529	5.05	0.47
12	70.6	498	530	484	4.74	0.50

Study of the Effect of Various Electrolytes on the Metal Ion Uptake under Equilibrium Conditions at a Fixed pH

The S.T. PCP. T-1 tercopolymer sample (25 mg) was stirred in a solution of a given electrolyte (25 mL) of known concentration and the pH was adjusted to the required value using either 0.1 M HNO_3 or 0.1 M NaOH. The mixture was stirred for 24 h at 25°C. To this suspension 2 mL of a 0.1 M solution of Cu(II) metal ion was added and the pH was adjusted to the required value (in the present case 4.5). Stirring was continued at 25°C for 24 h. The filtrate and the washings were collected, mixed, and titrated against standard EDTA to estimate the metal ion [10]. A blank experiment was also carried out in the same manner and for the same time period without adding the tercopolymer sample. The difference in the metal ion concentrations in the blank and in the actual experiment was used to calculate the amount of metal ion taken up by the tercopolymer under the given conditions of the experiment. The experiment was repeated in the presence of several other electrolytes and also with S.T. PCP. T-2 tercopolymer. The results are reported in Table 4.

Evaluation of the Rate of Metal Ion Uptake

In order to estimate the time required to reach the equilibrium state under given experimental conditions, a series of experiments of the type described above have been carried out in which the metal ion taken up by the tercopolymer sample was estimated from time to time at 25°C in the presence of 25 mL of 1 M $NaNO_3$ solution at pH 3. The time interval of the experiment was varied from 0.5 h to a time beyond which there was no change in the amount of metal ion absorbed. It is assumed that under the given experimental conditions the equilibrium state is established in 24 h. The amount of metal ion taken up by the same amount of polymer is expressed as % attainment at the equilibrium state by using the formula

$$\frac{\text{Amount of metal ion absorbed} \times 100}{\text{Amount of metal ion absorbed at equilibrium}}$$

The results of this study are presented in Table 5.

Evaluation of Distribution of Metal Ions at Different pH Values

The distribution of Cu(II) metal ions between the tercopolymer phase and the aqueous phase was estimated in the presence of 1 M $NaNO_3$ solution at 25°C. The experiments were carried out as described earlier at different pH values ranging from 1 to 7. The distribution ratio D, is defined by

$$D = \frac{\text{mg of metal ions taken up by 1 g of tercopolymer}}{\text{mg of metal ions present in 1 mL of solution}}$$

The results are presented in Table 5.

RESULTS AND DISCUSSION

The tercopolymer samples were yellow amorphous powder having a melting point of ~160°C. They were soluble in pyridine and DMF and developed a violet color with aqueous ferric chloride solution. Elemental analyses values are presented in Table 2. From this, the tercopolymer composition has been calculated.

The number-average molecular weight ($\overline{M}_n$) and the average degree of polymerization ($\overline{DP}$) of the tercopolymers as estimated by nonaqueous conductometric titrations are shown in Tables 1 and 2. The ($\overline{M}_n$) of the tercopolymer samples estimated by the VPO method, as given in Table 1, varies from 400 to 550 g/mol. The ($\overline{M}_n$) of the tercopolymers estimated from conductometric titration and VPO methods is comparable. It has been observed that tercopolymers containing cresol (o- and p-) showed higher molecular weights than those of tercopolymers containing chlorophenol (o- and p-). This may be due to the lower reactivity of chlorophenols compared to cresols toward their reaction with formaldehyde.

On the basis of elemental analyses, tercopolymer composition has been calculated. Thus, the total number of moles of chlorophenol repeating unit (x) in 100 g of chlorine-containing tercopolymers is given by

$$\text{Moles of chlorophenol } (x) = \frac{\text{percentage of chlorine}}{35.5}$$

Hence, the weight percentage of chlorophenol (o- and p-) repeating unit in the tercopolymer is x × 140.5%. Similarly, y, the percentage of sulfur and hence the percentage of thiourea repeating unit, can be calculated.

Therefore, the weight percentage of salicylic acid (comonomer) repeating unit is

$$\{100 - [(x \times 140.5) + (y \times 88)]\}\%$$

TABLE 2. Characterization of Tercopolymers[a]

No.	Tercopolymer sample	Elemental analysis			Tercopolymer composition (elemental analysis)
		N (%)	S (%)	Cl (%)	x y z
1	S.T. PCP. T-1	8.12	12.21	7.79	0.24:0.22:0.41
2	S.T. PCP. T-2	7.02	10.69	5.15	0.31:0.21:0.4
3	S.T. PCP. T-3	6.92	12.60	6.12	0.30:0.10:0.42
4	S.T. OCP. T-4	6.88	13.69	8.66	0.22:0.19:0.43
5	S.T. OCP. T-5	6.75	10.35	6.42	0.29:0.23:0.45
6	S.T. OCP. T-6	7.11	12.60	7.14	0.32:0.11:0.45
7	S.T. OC. T-7	10.82	13.97	-	- - -
8	S.T. OC. T-8	10.71	13.74	-	- - -
9	S.T. OC. T-9	10.64	10.83	-	- - -
10	S.T. PC. T-10	10.87	12.95	-	- - -
11	S.T. PC. T-11	10.56	11.53	-	- - -
12	S.T. PC. T-12	10.34	13.64	-	- - -

TABLE 2 (continued)

No.	Conductometric titration (in pyridine against TBAH) mmol of base added at first break of titration	mmol of base added at final break of titration	Degree of polymerization, $\overline{DP} = y/x$	C=O cm^{-1}	C=S cm^{-1}
	curve X	curve Y			
1	85	185	3.0	1650 (s)	860 (s)
2	60	175	3.0	1648 (s)	850 (s)
3	85	200	2.5	1645 (s)	855 (s)
4	95	205	2.5	1650 (b)	860 (s)
5	75	190	2.5	1648 (b)	855 (b)
6	80	195	2.5	1648 (s)	845 (b)
7	70	195	3.0	1650 (b)	850 (s)
8	70	190	3.0	1655 (s)	860 (b)
9	80	185	2.5	1650 (b)	855 (b)
10	70	195	3.0	1648 (s)	856 (s)
11	80	195	2.5	1648 (s)	858 (b)
12	95	205	2.5	1650 (s)	860 (s)

[a] x = (o- or p-) chlorophenol, y = thiourea, z = salicylic acid, s = sharp, b = broad.

From this it follows that

$$\{100 - [(x \times 140.5) + (y \times 88)]\}/\text{molecular mass of comonomer repeating unit}$$

will be equal to the number of moles (z) of comonomer repeating unit per 100 g of the tercopolymer. Thus, tercopolymer composition will be given by

o-chlorophenol repeating unit:thiourea repeating unit:
salicylic acid repeating unit = x:y:z (Table 1)

Titration against standard sodium methoxide in pyridine furnished information about the total number of moles of both COOH and phenolic OH groups. Titration against standard TBAH would furnish information about COOH groups only [8]. It can be shown that if the amount of 1 <u>M</u> TBAH required for 1 g of tercopolymer is equal to "a" mL and the amount of 1 <u>M</u> NaoMe required for 1 g of tercopolymer is equal to "b" mL, then the ratio a:(b - 2a) = salicylic acid repeating unit: phenolic comonomer repeating unit. It was found that the tercopolymer composition calculated by the conductometric titration method is nearly equal to the composition estimated on the basis of elemental analysis. The results are presented in Tables 1, 2, and 3.

Reduced viscosities of solutions of tercopolymers in DMF were obtained from viscosity measurements. The intrinsic viscosity $[\eta]$ of the tercopolymers obtained from a linear plot of η_{sp}/c vs concentration is shown in Table 1. It has been found that those tercopolymers having higher molecular weight showed higher intrinsic viscosities. The values of $[\eta]$ calculated by the application of Huggins' relation

$$\eta_{sp}/c = [\eta] + K'[\eta]^2 C$$

and Kraemer's relation

$$\eta_{inh} = \ln \eta_r/c = [\eta] + K''[\eta]^2 C$$

are found to be nearly the same. The sum of Huggins' constant (K') and Kraemer's constant (K") is found to lie between 0.46 and 0.50, which is very close to the expected value of 0.50 [11]. The values are shown in Table 1.

IR spectra of the tercopolymer samples are shown in Fig. 1. The spectra of all the tercopolymers are found to be similar in all aspects. The broad band in the spectra extending from 2500-3600 cm^{-1} has inflections at ~2900 and 2800 cm^{-1} which may be due to intermolecular H bonding. The inflections at ~2900 and ~2800 cm^{-1}, a comparatively broader band at ~1455 cm^{-1}, and a small but sharp band at ~800 cm^{-1} are all characteristic vibrations of C–H of the $-CH_2$ bridges [12].

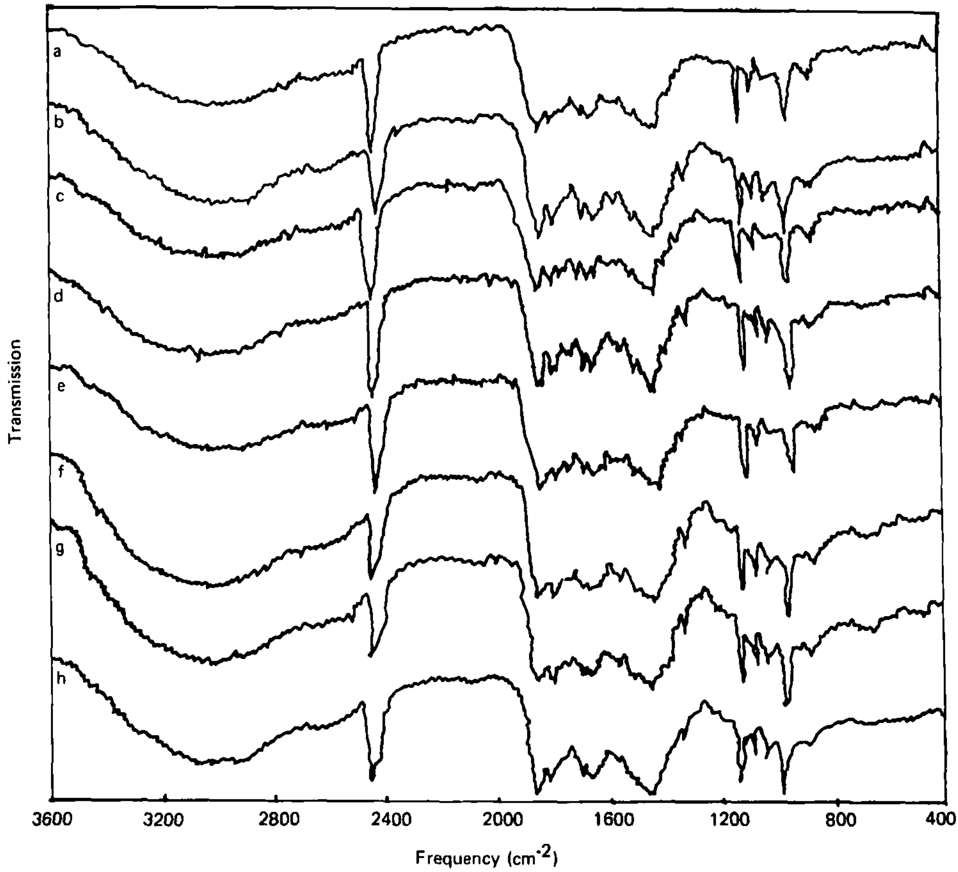


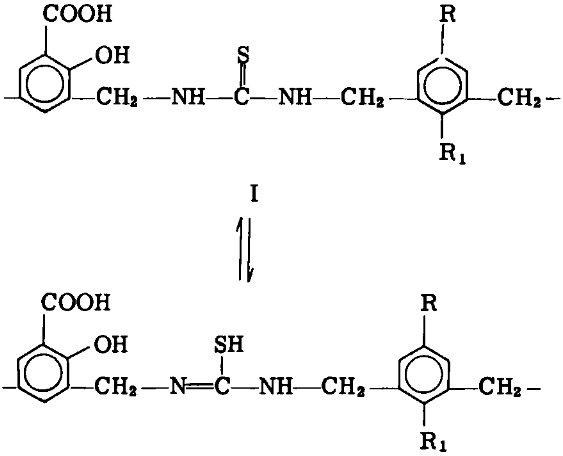
FIG. 1. IR spectra of tercopolymers of (a) S.T. PCP. T-1, (b) S.T. PCP. T-2, (c) S.T. OCP. T-4, (d) S.T. OCP. T-5, (e) S.T. OCP. T-6, (f) S.T. OC. T-7, (g) S.T. OC. T-8, and (h) S.T. PC. T-10.

This affords clear evidence for the existence of methylene bridges in the tercopolymers. This is further confirmed by the bands appearing in the 1180-1300 cm^{-1} range due to methylene bending (twisting and wagging) modes [12]. The sharp band at ~1670 cm^{-1} is assigned to the C=O stretching vibrations of the COOH group of salicylic acid. The IR spectra also show strong absorptions in the 2900-3300 cm^{-1} region due to νNH and the 1600-1610 cm^{-1} region due to νC=N [13]. Absorption bands in the 850-860 cm^{-1} region, attributed to the C=S group, have also been observed [14]. The weak band observed in the 2380-2400 cm^{-1} region may be due to the presence of the SH group

TABLE 3. Thermogravimetric Analysis of Tercopolymers

No.	Tercopolymers	Molar ratio of monomers	Percentage weight loss at temperature °C (T)						Temperature range for decomposition °C (T)		Energy of activation (kJ/mol)
			100	200	300	400	500	600	First step	Second step	
1	S.T. PCP. T-1	0.8:1.0:0.2:2	2.0	5.5	20.5	37.0	50.0	80.0	200-300	300-650	17.56
2	S.T. PCP. T-2	0.6:1.0:0.4:2	1.0	4.5	25.0	47.0	58.0	81.0	200-300	300-625	15.75
3	S.T. OCP. T-3	0.8:1.0:0.2:2	2.0	5.5	25.0	48.5	60.0	85.0	225-280	280-660	17.89
4	S.T. OCP. T-4	0.6:1.0:0.4:2	2.0	4.0	23.0	48.0	55.0	85.5	200-290	290-650	14.41
5	S.T. OC. T-5	0.9:1.0:0.1:2	3.0	6.0	24.0	45.0	55.0	85.0	275-310	310-640	21.04
6	S.T. PC. T-6	0.6:1.0:0.4:2	2.0	5.0	24.5	45.5	54.5	87.5	225-325	325-620	17.72

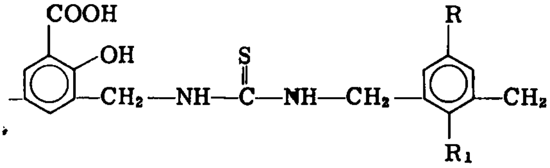
which indicates that the tercopolymers exist in equilibrium in the keto I and enol II tautomeric forms as indicated below [15].


I

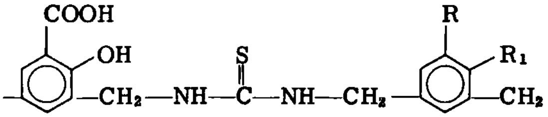
II

where R = CH_3 or Cl, and R_1 = OH.

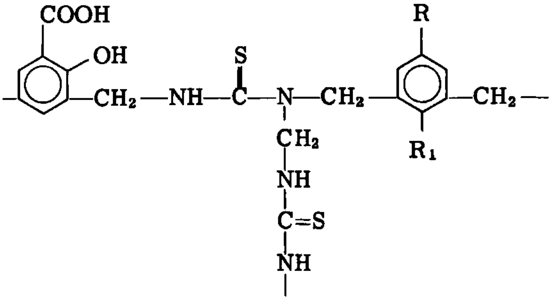
The polymers under study are tercopolymers and hence it is very difficult to assign the exact, correct structures to them. By considering the structure of salicylic acid-formaldehyde polymers [16] and also the cross-linked structure of urea or thiourea-formaldehyde homopolymers, p-hydroxybenzoic acid-formaldehyde 8, and p-cresol-formaldehyde polymers [17], the most favorable structures suggested for the tercopolymers are


III

where R = Cl or CH_3, and R_1 = OH.

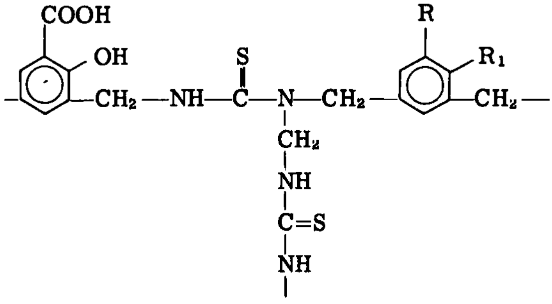

IV

where R = Cl or CH_3, and R_1 = OH.



V

where R = Cl or CH_3, and R_1 = OH.



VI

where R = Cl or CH_3, and R_1 = OH.

The thermograms of selected tercopolymers samples are shown in Fig. 2. Examination of the TG analysis results reported in Table 3 reveals that each tercopolymer sample undergoes degradation in two steps. The samples lose nearly 8% weight when decomposition commences around 200°C. Beyond this temperature the rate of weight loss increases rapidly. The rate of loss in weight becomes much higher around 500°C. Decomposition is complete around 660°C when 70-90% mass loss has been observed. The first step in degradation of the tercopolymers, which appears from 200-325°C as reported in Table 3, may be due to decarboxylation of the "salicylic acid units" present in the tercopolymer chain [16, 18], and the further degradation in the second step which appears from 300-660°C may be a random degradation reaction affording simpler degradation products [19]. The energy of activation calculated from the thermograms is presented in Table 3 [20]. The results of the kinetic parameter indicate that all these tercopolymers follow nearly the same mechanism of degradation. The energy of activation ranges from 14.41 to 21.04 kJ/mol. Degradation

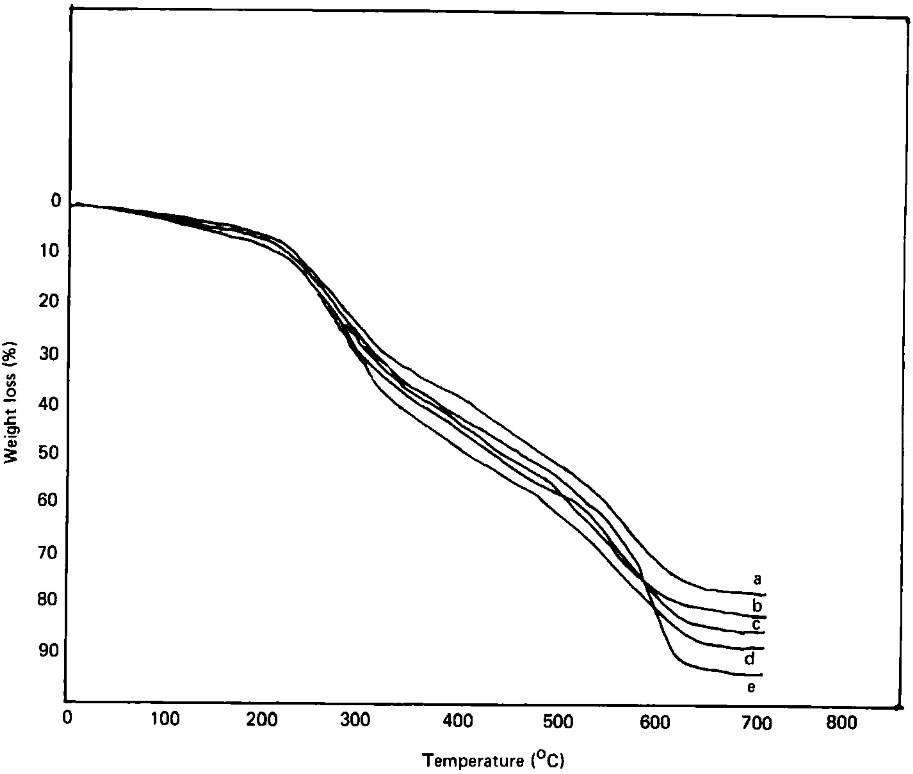


FIG. 2. Thermogravimetry of tercopolymers (a) S.T. PCP. T-1, (b) S.T. PCP. T-3, (c) S.T. OCP. T-5, (d) S.T. OC. T-6, and (e) S.T. PC. T-9.

of tercopolymers appears to be almost entirely due to the breaking of methylene bridges [21]. It is extremely difficult to draw any conclusions from the magnitude of thermal activation energy because the decomposition mechanism is expected to be complicated [22].

Ion-Exchange Properties of S.T. PCP. T-1 and S.T. PCP. T-2 Tercopolymers

The results of the experiments carried out for batch equilibration in the ion-exchange study of tercopolymer samples S.T. PCP. T-1 and S.T. PCP. T-2 are presented in Tables 4 and 5.

TABLE 4. Evaluation of the Influence of Different Electrolytes on the Uptake of Cu(II) Metal Ions: $[Cu(NO_3)_2] = 0.1$ mol/L[a]

Electrolyte (mol/L)	Weight (in mg) of the metal ion taken up in the presence of			
	$NaClO_4$	NaCl	$NaNO_3$	Na_2SO_4
0.01	1.2[b] (1.07)[c]	0.35 (0.29)	1.20 (1.10)	2.63 (2.42)
0.05	2.01 (1.85)	0.92 (0.89)	1.78 (1.55)	1.40 (1.21)
0.10	2.14 (2.03)	2.01 (1.54)	2.05 (1.96)	1.05 (1.02)
0.50	2.89 (2.50)	2.62 (2.12)	2.48 (2.12)	0.98 (0.91)
1.00	3.45 (3.02)	3.20 (2.78)	2.81 (2.52)	0.52 (0.3)

[a] Volume of electrolyte solution, 25 mL; volume of metal ion solution, 2 mL; pH, 4.5; time, 24 h; 25°C.
[b] S.T. PCP. T-1 tercopolymer.
[c] S.T. PCP. T-2 tercopolymer.

TABLE 5

	Rates of Metal (Mt) Cu(II) Ions Uptake			Distribution ratios, D, of Cu(II) metal ions as a function of the pH	
Time (h)	Percentage of the attainment of the state of equilibrium		pH	Distribution ratio ($D \times 10^2$ mL/g) Cu(II) metal ions (±5%)	
0.5	45.55[a]	(38.2)[b]	2.0	-	-
1	50.1	(40.5)	2.5	-	-
2	59.6	(50.6)	3.0	1.80	(125.5)
3	65.5	(55.8)	4.0	2.05	(19.52)
4	76.4	(66.4)	5.0	3.05	(2.58)
5	87.5	(77.5)	6.0	9.04	(8.50)
6	95.6	(97.3)	7.0	9.98	(9.21)

[a] S.T. PCP. T-1 tercopolymer.
[b] S.T. PCP. T-2 tercopolymer.

Influence of Electrolytes on the Cu(II) Metal Ion Uptake

The data presented in Table 4 reveal that the amount of metal ions taken up for a given amount of tercopolymer sample depends on the nature and concentration of the electrolyte present in the solution. At an electrolyte concentrations below 0.05 M, not enough anions are present to complex Cu(II) completely. At an electrolyte concentration of 0.05 M, an excess of anions is present. From here on the Cu(II) ions uptake by the tercopolymers increases with an increase in the concentration of Cl^-, NO_3^-, and ClO_4^-, but decreases with an increase in the concentration of SO_4^{2-}. This can be explained in terms of stability constants of the complexes which Cu(II) forms with these ligands [23, 24]. Sulfate forms rather strong complexes with Cu(II) {(SO_4^{2-}: K_1 ~2.36 at $\mu = 0$) [25] while Cl^-, NO_3^-, and ClO_4^- form weak complexes (Cl^-: K_1 ~0.14 to 0.05 at $\mu = 1$ to $\mu = 0$ [26], NO_3^-: K_1 ~-0.49 at $\mu = 0$ [27], and ClO_4^-: K_1 ~0.72 at $\mu = 0$ [28])}. Therefore, Cl^-, NO_3^- and ClO_4^- cannot be expected to influence the position of the Cu(II)-salicylate equilibrium as much as SO_4^{2-}. The amount of metal ions taken up by S.T. PCP. T-1 tercopolymer, which is slightly more than that of S.T. PCP. T-2, may be due to the greater salicylic acid content in the former.

Rate of Metal Uptake

The rates of metal adsorption by the tercopolymers were measured for Cu(II) ions in the presence of 1 M $NaNO_3$ to determine the time required to reach the equilibrium stage. Table 5 shows the dependence of the rate of Cu(II) metal ions uptake on the nature of the metal. Examination of the results of the tercopolymers S.T. PCP. T-1 and S.T. PCP. T-2 indicates that Cu(II) ions required about 6 h for the establishment of equilibrium. Comparison of the rate of uptake of Cu(II) metal ions by S.T. PCP. T-1 and S.T. PCP. T-2 made on the basis of the data presented in Table 5 reveals that the rate of metal uptake by the former is, on the whole, greater than that of the latter. This may be due to the higher salicylic acid content present in the S.T. PCP. T-1 tercopolymer.

Distribution Ratios of Metal Ions at Different pH Values

The results of the effect of pH on the amount of metal ions distributed between two phases are presented in Table 5. This data indicate that the amount of Cu(II) ions taken up by S.T. PCP. T-1 and S.T. PCP. T-2 increases with an increase in the pH of the medium. This study was carried out up to pH 7.0 in order to prevent the hydrolysis of metal ions at higher pH values. The distribution ratio becomes 5 times greater as the pH is varied from 1 to 7. Comparison of the distribution coefficients of Cu(II) ions for these tercopolymers reveals that there is not much difference in the values.

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REFERENCES

[1] A. A. Rozhanovskaya and A. A. Zasova, Chem. Abstr., 70, 20530W (1969).

[2] K. Shuji and K. Musabiro, Ibid., 77, 76561 (1972).

[3] N. V. Vlasyuk and M. E. Natanson, Ukr. Khim. Zh., 42, 473 (1976); Chem. Abstr., 85, 79743f (1976).

[4] W. Christopher, J. Morgan, C. Alfred, and R. Raul, Ibid., 83, 142526p (1975).

[5] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, Ind. Eng. Chem., Process Des. Dev., 2, 43 (1963).

[6] M. M. Dyaltova, V. Ya. Temkina, E. S. Kllesnik, G. F. Yaroshenko, and R. P. Lastovskii, Tr. Vses. Nauchno-Issled. Inst. Khim. Reakt., 25, 91 (1964); Chem. Abstr., 61, 777 (1964).

[7] R. Manavalan and M. M. Patel, Makromol. Chem., Accepted for Publication.

[8] S. K. Chatterjee, J. Polym. Sci., Part A-1, 8(5), 1299 (1970).

[9] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, Anal. Chem., 34, 845 (1962).

[10] A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, 2nd ed., Longmans, London, 1960.

[11] O. F. Solomon and B. S. Gottesman, Makromol. Chem., 127, 153 (1969).

[12] R. M. Patel, J. C. Patel, K. C. Patel, and R. D. Patel, Angew. Chem., 106, 161 (1982).

[13] M. Z. A. Badr, M. M. Aly, Z. H. Khalil, and A. A. Attalla, Indian J. Chem., 21B, 115 (1982).

[14] M. R. Patel, M. M. Patel, A. K. Ray, and M. R. Patel, J. Inorg. Nucl. Chem., 43, 509 (1981).

[15] K. C. Satpathy and T. D. Mahana, J. Indian Chem. Soc., 56, 1173 (1979).

[16] R. C. DeGeiso, L. G. Donaruma, and E. A. Tomic, J. Org. Chem., 27, 1424 (1962).

[17] S. K. Chatterjee, *J. Polym. Sci., Part A-1*, **9**, 3225 (1971).
[18] H. S. Patel and S. R. Patel, *J. Macromol. Sci.–Chem.*, **A17**, 1383 (1982).
[19] W. M. Jackson and R. T. Conley, *J. Appl. Polym. Sci.*, **8**, 2873 (1964).
[20] A. Broido, *J. Polym. Sci.*, **7**, 1761 (1969).
[21] J. M. Barrales-Rienda and J. Gonzalez Ramos, *J. Polym. Sci., Poly. Symp.*, **42**, 1249 (1973).
[22] R. G. Charles, *J. Polym. Sci.*, **A1**, 267 (1963).
[23] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd ed., Wiley-Interscience, New York, 1972, p. 594.
[24] S. L. Davadov and N. A. Plate, *Coord. Chem. Rev.*, **16**, 195 (1975).
[25] J. Bjerrum, G. Schwarzenback, and L. G. Sillen, *Stability Constants of Metal-Ion Complexes*, Vol. II, The Chemical Society, London, 1958, p. 83.
[26] Ref. 25, p. 100.
[27] Ref. 25, p. 48.
[28] Ref. 25, p. 83.

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