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Phenol-Crotonaldehyde Resins. II. Effect of Crotonaldehyde Purity on Resin Properties*

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ABSTRACT

Acid-catalyzed polycondensation of phenol and crotonaldehyde results in soluble thermoplastic resins over a broad range of compositions. The thermal and curing behavior of the resins are found to vary markedly with the phenol to crotonaldehyde mole ratio and the purity of crotonaldehyde. Infrared analysis of the resins and their fractions separated by column chromatography indicates that all the resins are structurally similar. The number-average molecular weights of the resins fall in the range of 400 to 600. The resins from distilled crotonaldehyde exhibit higher molecular weights than those from crude crotonaldehyde. The thermal properties of the resins are comparable to the Novolak-type phenol-formaldehyde resins. The thermoplastic nature is retained even at higher fraction of crotonaldehyde, unlike for the conventional Novolak resins.

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INTRODUCTION

Phenol-aldehyde polycondensation reactions have been investigated extensively for the past 80 years [1]. Over the years a large variety of phenolic resins have been synthesized that vary widely in their properties. The parameters investigated in these studies include the type of phenol and aldehyde, catalyst type, and the relative mole ratio of phenol to aldehyde. Recent efforts in the field have been directed toward the development of novel thermoplastic and thermoset compositions for specific applications [2-7].

We have investigated the polycondensation of phenol with crotonaldehyde. Commercially, crotonaldehyde has been condensed with alkylphenol [8, 9] and polyhydric phenols [10-12] to form resins useful as tanning agents and as tackifiers. The kinetics of the phenol-crotonaldehyde (PC) polycondensation reaction has been investigated previously [13]. We have communicated the synthesis and preliminary characterization of molding grade resins by acid-catalyzed polycondensation of phenol and crotonaldehyde [14]. In this communication the dependence of the composition and properties of the resins on the purity of the crotonaldehyde is described. The effect of the temperature and amount of hexamethylenetetramine (hexa) on the curing behavior of the resins is also reported.

EXPERIMENTAL

Phenol (L.R. Grade) was obtained from S. D. Chemicals, India. TLC showed the presence of two components. Gas chromatographic analysis showed the phenol purity to be greater than 99.5%. It was used without further purification.

Crude crotonaldehyde was obtained from Deccan Sugar Institute, India. For the preparation of PC resins from crude crotonaldehyde (Set 1), the crotonaldehyde obtained was dried repeatedly over calcium chloride till free from water and then used. The water content was checked by gas chromatography using a thermal conductivity detector. GC analysis showed the purity of crotonaldehyde to be about 95%. The impurities included two low-boiling and two high-boiling fractions. For the preparation of Set 2, the dried crude crotonaldehyde was distilled. The middle fraction of crotonaldehyde representing the constant boiling fraction (102°C) was collected, redistilled, analyzed, and used. GC analysis showed its purity to be greater than 99.5%. TLC of the crude crotonaldehyde showed five components whereas that of the distilled crotonaldehyde showed one major component and a very slight impurity.

Sulfuric acid (A.R. grade) was obtained from Ranbaxy Labs. Pvt. Ltd., India, and used as received.

The polycondensation of phenol with crotonaldehyde was conducted in a 1-L kettle at 84°C for 4.5 h. The catalyst, sulfuric acid (1 wt%

in relation to phenol), was used as a 9.4 wt% aqueous solution. After completion of the reaction, unreacted monomers and water of condensation were distilled out quantitatively under reduced pressure. The distillates were analyzed for unreacted phenol and crotonaldehyde using a Nucon (Model 5500) gas chromatograph with a SE-30 column and thermal conductivity detector.

Silica gel was used as a stationary phase for TLC and column chromatography. The resins were fractionated by column chromatography. To separate different chemical constituents in the resins, a column of 50 cm length and 1 cm diameter was used at a 30:1 loading ratio. Various mixed solvent systems were used in the order of increasing polarity. The eluents were checked by TLC, and fractions with similar R_f values were pooled. The solvents were distilled off to collect the various resin fractions.

The IR spectra of the resins and resin fractions were recorded in Nujol or on KBr salt plates with a Pye Unicam (Model SP3-300) infrared spectrometer.

A Knauer vapor-pressure osmometer was used to evaluate the number-average molecular weight (\bar{M}_n) of the resins at 50°C. Ethyl acetate and benzil were used as the solvent and the standard, respectively.

The softening temperature range was determined as follows: Finely powdered resin was placed in a glass capillary sealed at one end, and the temperatures at which the opaque particles cleared into mobile liquid were recorded as the softening temperature range.

An empirical but proven parameter, the flow length, was used to study the relative curing behavior of the resins. The method consists of mixing powdered resin with a predetermined quantity of hexa (4 or 8 wt%). Exactly 0.5 g of the mixture was pelletized at room temperature using a 1.2-cm diameter die at 3.5 tons force. The pellet was placed on the horizontal plate of the flow length apparatus, kept in an air circulating oven at either 140 or 160°C. After 5 min the plate was tilted 30° toward the vertical and the molten resin was allowed to flow under gravity for 10 min. The length of the flow in millimeters was recorded as the flow length.

RESULTS AND DISCUSSION

Synthesis

The polycondensation of phenol and crotonaldehyde was investigated under strongly acidic conditions, with sulfuric acid as the catalyst. Two sets of polycondensation reactions were conducted using dry crude crotonaldehyde (Set 1) and dry distilled crotonaldehyde (Set 2). In each set, six different resins were synthesized by varying the mole fraction of crotonaldehyde in the reaction mixture between 0.27 and 0.57. The molar compositions of the resins (Table 1) were computed from the moles of unreacted phenol and crotonaldehyde present at the completion

TABLE 1. Resin Compositions

No.	Crotonaldehyde mole fraction			
	Set 1 ^a		Set 2 ^b	
	Feed	Polymer	Feed	Polymer
1	0.27	0.29	0.27	0.32
2	0.36	0.39	0.36	0.38
3	0.43	0.40	0.43	0.47
4	0.48	0.43	0.48	0.48
5	0.53	0.47	0.53	0.55
6	0.57	0.50	0.57	0.58

^aSet 1: Resins from crude crotonaldehyde.

^bSet 2: Resins from distilled crotonaldehyde.

of the reaction (4.5 h). The resins were all thermoplastic solids, soluble in common organic solvents, such as acetone, methanol, ethanol, ethyl acetate, and tetrahydrofuran.

In both sets, the mole fraction of crotonaldehyde in the resin increased linearly, but not proportionally, with its mole fraction in the feed (Fig. 1), indicating that the incorporation of crotonaldehyde in the condensation product is governed not only by kinetic effects of the feed composition but also by reactivity. At lower feed mole fractions, crotonaldehyde adds to phenol to a marginally greater extent. At higher mole fractions, crotonaldehyde encounters a greater concentration of less reactive, more sterically hindered substituted phenols. This, perhaps, accounts for the decreased incorporation of crotonaldehyde at higher feed mole fractions.

At any feed composition, a greater fraction of crotonaldehyde was incorporated when distilled crotonaldehyde was used. The apparent decreased reactivity of crude crotonaldehyde is probably due to such impurities ($\approx 5\%$) as ethanol, acetaldehyde, acetic acid, acetaldol, dimer, and trimer of crotonaldehyde present in it. It is known that acetaldehyde reacts more rapidly with phenol [15-17], thereby leaving fewer reactive sites for crotonaldehyde.

In comparison, under highly acidic conditions, phenol-formaldehyde polycondensations result in thermoplastic, solid resins termed Novolaks. The polycondensation rates are much higher [18]. However, the thermoplasticity is retained only over a narrow range of formaldehyde mole fraction, 0.29-0.45. Below 0.29 the resins are liquids and above 0.45 the resins are infusible [19]. PC resins, on the other

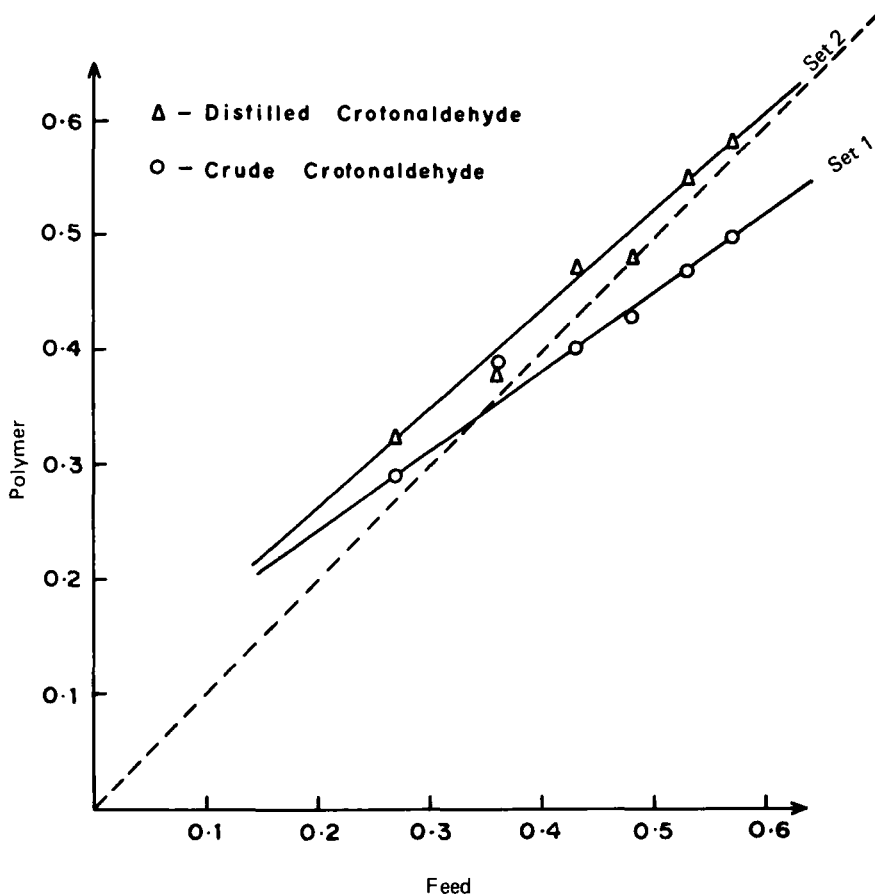


FIG. 1. Mole fraction of crotonaldehyde in the resin as a function of that in the feed.

hand, retain their thermoplasticity over a much wider range of crotonaldehyde mole fraction. Phenol and crotonaldehyde are known to be trifunctional in these polycondensations [20, 21]. Interestingly, the resin formed with a crotonaldehyde mole fraction of 0.48 was still thermoplastic. The trifunctionality is perhaps only partially utilized due to the steric factors associated with such a reaction.

Characterization

The resins were Soxhlet extracted for 24 h with distilled water to remove the final traces of phenol and crotonaldehyde. The dried resins were used for characterization.

TABLE 2. Microanalysis and Molecular Weight Data

Set-serial no. of resin	Microanalysis data				\bar{M}_n^a
	C	H	O	S	
1-1	76.07	7.03	16.05	0.50	380
1-2	77.38	6.98	14.71	0.93	285
1-3	75.37	7.17	17.21	0.34	285
1-4	76.38	7.24	15.08	0.85	380
1-5	72.89	7.17	18.84	1.10	370
1-6	78.07	7.18	14.21	0.54	531
2-1	78.79	7.07	13.89	0.55	570
2-2	77.28	6.95	14.83	0.94	557
2-3	78.37	6.94	14.21	0.58	425
2-4	78.64	7.33	13.04	0.99	629
2-5	77.68	7.54	13.26	1.52	519
2-6	75.43	7.03	17.06	0.48	562

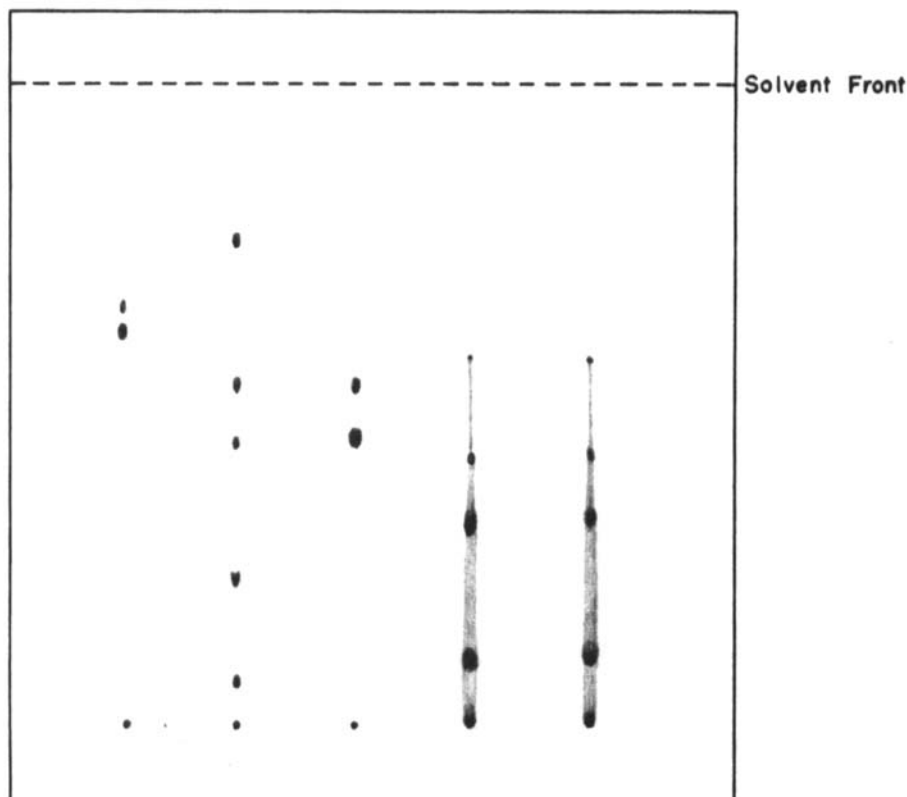
^aBy vapor-pressure osmometry.

Elemental analysis of purified resins (Table 2) indicates the presence of sulfur in the resins, in an amount corresponding almost quantitatively to that added. Thus, the role of sulfuric acid in the reaction is not exclusively as a catalyst. It may be incorporated in the polymer structure either as sulfate or by addition across the double bond of crotonaldehyde.

The TLC of the resins from Set 1 and Set 2 are very similar. Extensive tailing was observed, indicating the presence of structurally similar species differing in molecular weight (Fig. 2).

The resins were fractionated by column chromatography into chemical moieties that showed single spots on TLC. The IR spectra of the fractions were almost identical, indicating that the various resin fractions are structurally quite similar.

The prominent IR frequencies of phenol, crotonaldehyde (crude and distilled), and representative resins from Set 1 and Set 2 (1-3 and 2-3) are presented in Table 3. Crotonaldehyde absorbs at frequencies corresponding to the trans C=C double bond and C=O groups. The resins and their fractions do not absorb at these frequencies. Therefore, the



1 Phenol

2 Crude Crotonaldehyde

3 Distilled Crotonaldehyde

4 Resin from crude crotonaldehyde (1-3)

5 Resin from distilled crotonaldehyde (2-3)

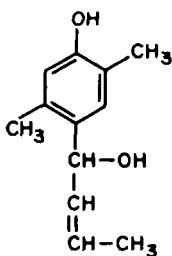
Solvent system : 70% Pet. Ether + 30% Ethyl acetate. (V/V)

FIG. 2. TLC of phenol, crotonaldehyde, and resins.

TABLE 3. Prominent Infrared Frequencies

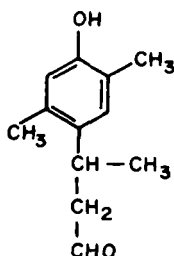
Frequency, cm^{-1}		Resins ^b			Remarks
Crotonaldehyde ^a		1-3	2-3		
Phenol ^a	Crude	Distilled	1-3	2-3	
3 400-3 300	-	-	3 400-3 200	3 400-3 200	-OH, stretching frequency
-	2 740	2 740	-	-	-CH, stretching frequency of aldehydes
-	1 680	1 680	-	-	-C=O, stretching frequency of α, β unsaturated aldehydes
1 600, 1 500, 1 480	-	-	1 600, 1 500, 1 460	1 600, 1 500, 1 460	Aromatic C-C in plane skeleton vibrations
-	1 640, 1 310, 970	1 640, 1 310, 970	-	-	C=C (trans) double bond vibrations
-	-	-	1 250	1 250	=C-O-C, aryl-alkyl ether vibrations
760, 690	-	-	-	-	Aromatic ring substitution (mono) vibrations
-	-	-	830, 750, 695	830, 750, 695	Aromatic ring substitution at O; O, O'; O, O', P position on the phenyl ring

^aSpectrum obtained neat on KBr salt plates.^bSpectrum obtained in Nujol.



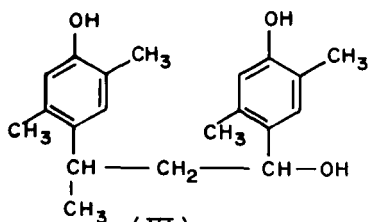
(I)

(Molecular weight-192)



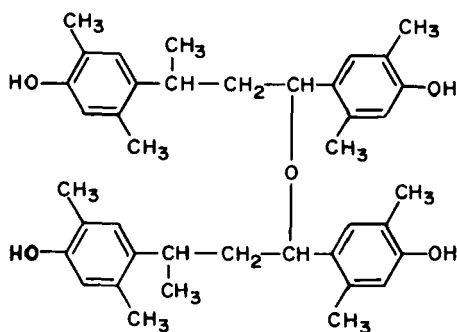
(II)

(Molecular weight-192)



(III)

(Molecular weight-311)



(IV)

(Molecular weight-610)

FIG. 3. Structures of acid-catalyzed polycondensates of alkylphenol and crotonaldehyde.

polycondensation reaction probably proceeds by addition across the C=C double bond and condensation across the aldehyde group.

The occurrence of such reactions in acid-catalyzed polycondensation of alkyl phenols with crotonaldehyde has recently been demonstrated by ¹³C-NMR studies [20, 21]. The various structures proposed for the reaction products are shown in Fig. 3. Interestingly, the molecular weights of the proposed structures, in particular III and IV, fall in the range observed in the present study. However, the exact sequence of events in the reaction leading to such structures is still not clear.

The number-average molecular weights of the resins (Table 2) indicate that the resins are essentially oligomers, consistent with other reports on acid-catalyzed phenol-aldehyde reactions [19]. For any given phenol-to-crotonaldehyde ratio, the resins synthesized with distilled crotonaldehyde exhibit a higher molecular weight than those prepared with crude crotonaldehyde. Phenol is perhaps involved in non-polymeric side reactions with impurities present in crude crotonaldehyde, such as dimer and trimer. Also, crotonaldehyde can form acetal with the alcoholic impurities under the reaction conditions [22]. Such low molecular weight side products would decrease the molecular weight of the resins.

The softening temperature ranges of the resins are presented in Table 4 and are plotted in Fig. 4 as a function of the crotonaldehyde mole fraction. Differential thermal analysis of representative resin samples (Resins 1-3 and 2-3), shown in Fig. 5, indicate the occurrence of a second-order transition in the same temperature range. The resins made from distilled crotonaldehyde manifested a higher softening temperature range than those prepared from crude crotonaldehyde, in part due to their higher molecular weights. The oligomeric side products present in the resins based on crude crotonaldehyde could also lower their softening temperature by acting as plasticizers. The plasticizing effect may also be due to the formation of resins with inferior thermal properties by the polycondensation between phenol and dimer and/or trimer of crotonaldehyde. The softening temperature range of the resin mixture with 4 and 8 wt% hexa was only marginally higher (5-9°C) than that of pure resins (Table 4, Figs. 6 and 7). As a general trend, the softening temperature range of the resins and their mixtures with hexa increased with an increase in the crotonaldehyde mole fraction.

Flow length data at 140 and 160°C are presented in Table 4. Generally, for a fixed composition, shorter flow lengths are indicative of a faster rate of curing. The resins prepared from distilled crotonaldehyde cure faster than resins prepared from crude crotonaldehyde. Similarly, resins cure faster at 160°C than at 140°C. As expected, the curing rate increases with increasing temperature and amount of crosslinking agent.

It is interesting to note that, even after curing at elevated temperature, the resins remained thermoplastic as indicated by fusibility and solubility in common organic solvents such as acetone, ethanol, methanol, and ethyl acetate. With the exceptions of Resins 2-1 and 2-2 cured with 8% hexa at 160°C, all the cured resins were soluble and fusible. However, the softening points of the cured resins were considerably higher as indicated by the ΔT values in Table 5. This indicates that the resins react with hexa to form only linear linkages. Thus, the resins remain soluble and fusible (thermoplastic) after curing for short times (15 min) with low amounts of hexa (4-8%) at 140-160°C. This unusual behavior offers interesting processing possibilities. It may be possible to process the PC resins containing 8-12% hexa on thermoplastic injection molding equipment into intricate

TABLE 4. Thermal and Curing Behavior of the Resins

Set-serial no. of resin	Mole fraction of crotonaldehyde in polymer	Softening temperature range, °C	Softening temperature range with hexa, °C				Flow length with hexa, mm			
			4%		8%		At 140°C		At 160°C	
			4%	8%	4%	8%	4%	8%	4%	8%
1-1	0.29	69 ± 2	78 ± 2	82 ± 2	38	35	24	20		
1-2	0.39	92 ± 2	98 ± 2	101 ± 2	26	21	16	13		
1-3	0.40	82 ± 2	92 ± 2	95 ± 2	42	38	26	22		
1-4	0.43	86 ± 2	90 ± 2	93 ± 2	42	39	27	22		
1-5	0.47	90 ± 2	95 ± 2	97 ± 2	43	39	28	24		
1-6	0.50	132 ± 2	138 ± 2	140 ± 2	-	-	20	18		
2-1	0.32	96 ± 2	99 ± 2	104 ± 2	31	27	22	17		
2-2	0.38	97 ± 2	101 ± 2	106 ± 2	29	25	21	18		
2-3	0.47	102 ± 2	107 ± 2	111 ± 2	28	25	25	22		
2-4	0.48	110 ± 2	114 ± 2	118 ± 2	21	17	19	16		
2-5	0.55	102 ± 2	107 ± 2	111 ± 2	26	24	20	18		
2-6	0.58	107 ± 2	112 ± 2	118 ± 2	22	18	19	16		

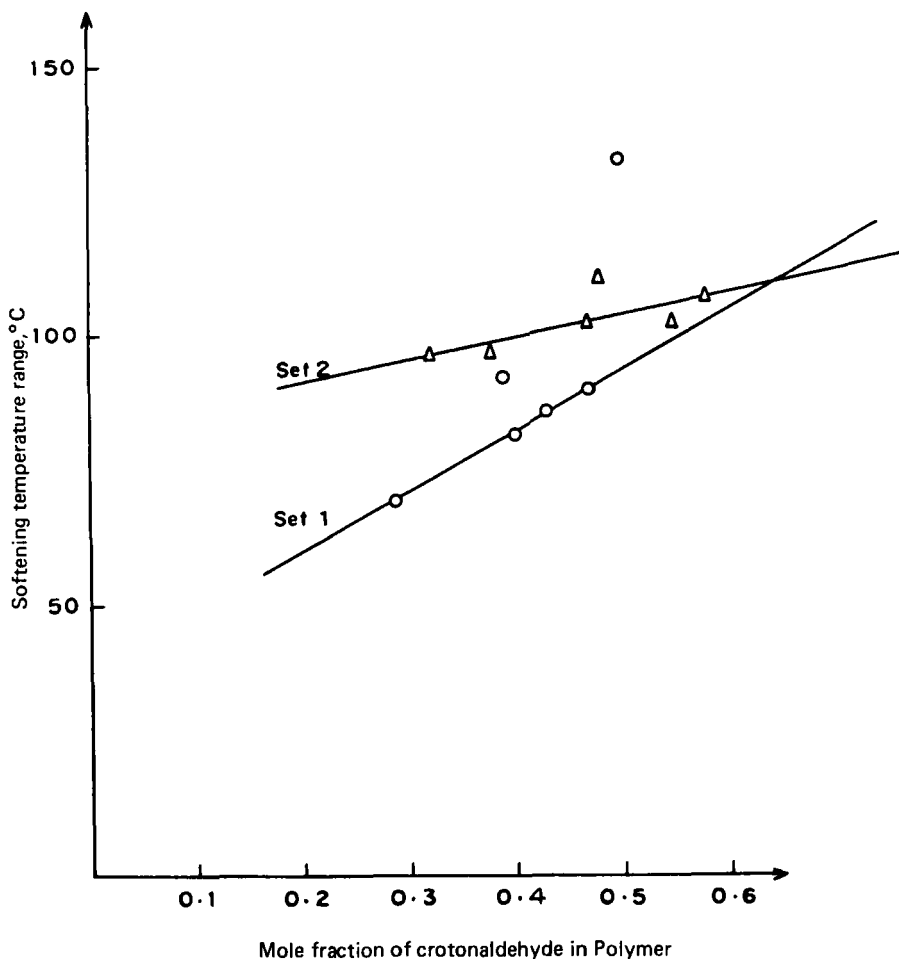


FIG. 4. Effect of crotonaldehyde mole fraction on softening temperature range of the resins.

product shapes, since the molding times would be short. The thermo-plastic molded parts may be further postcured in ovens to impart the desired thermoset characteristics to them.

The enhancement in softening temperature, ΔT , increases with increasing hexa and curing temperature. Resins cured at 160°C with 8% hexa showed the highest ΔT values. It is interesting to note that the cured resins of Set 2 with lower crotonaldehyde fraction (Resins 2-1 and 2-2) were insoluble and did not soften up to 250°C . Also, the mole

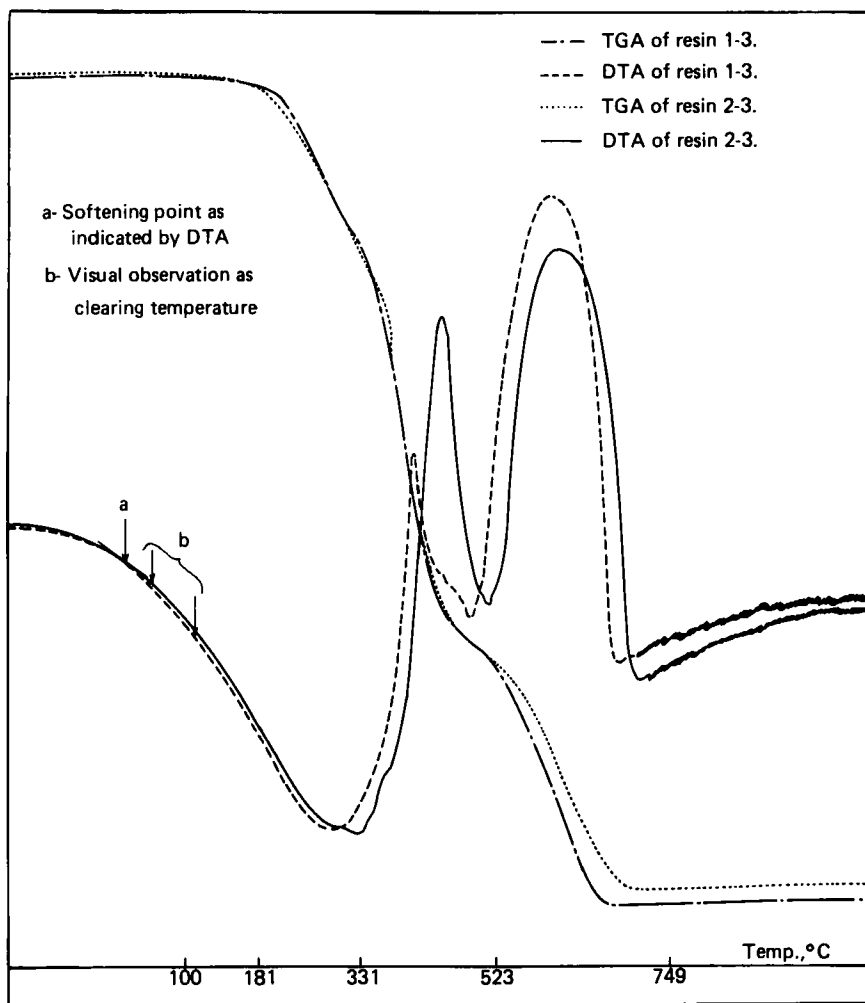


FIG. 5. TGA and DTA scans of Resins 1-3 and 2-3.

fraction of crotonaldehyde in the resin appears to exert an influence on the increase in the softening temperature, mainly in the case of resins made from distilled crotonaldehyde (Set 2). Thus, there is a decreasing trend in ΔT with increasing mole fraction of crotonaldehyde, except for the cure at 140°C with 4% hexa. As such, the resins with low mole fraction of crotonaldehyde cured at 160°C with 8% hexa are infusible up to 250°C.

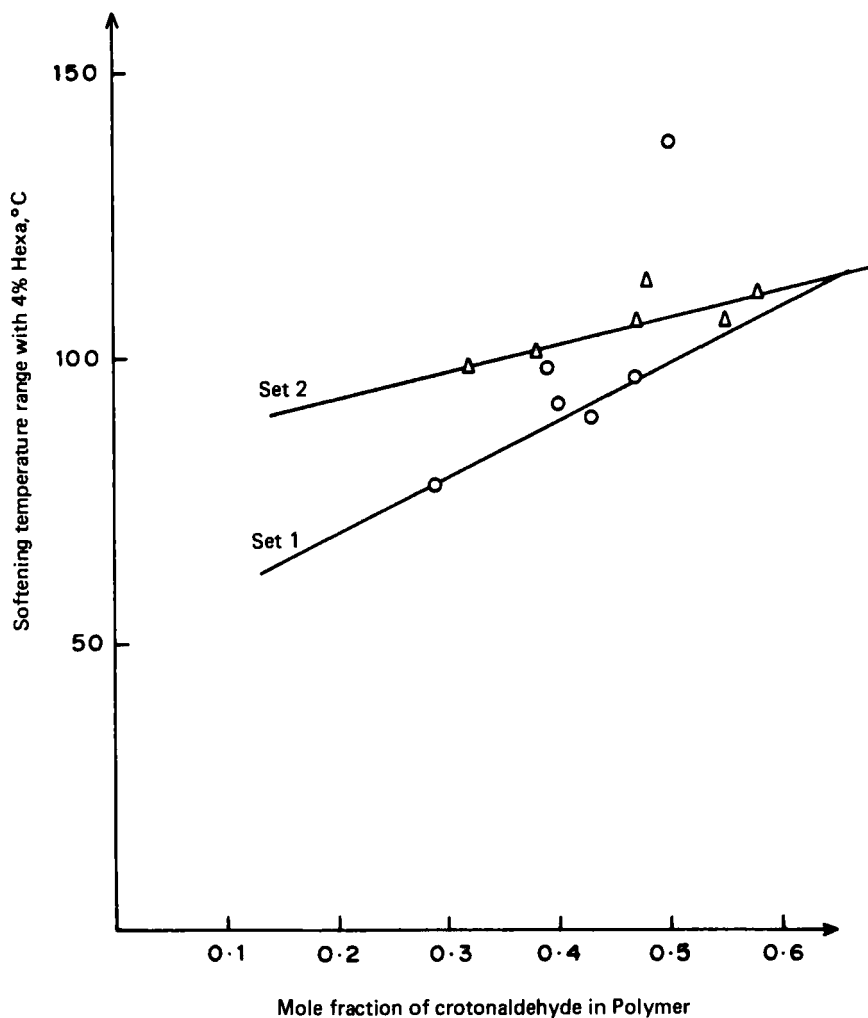


FIG. 6. Effect of crotonaldehyde mole fraction on softening temperature range of resins with 4% hexa.

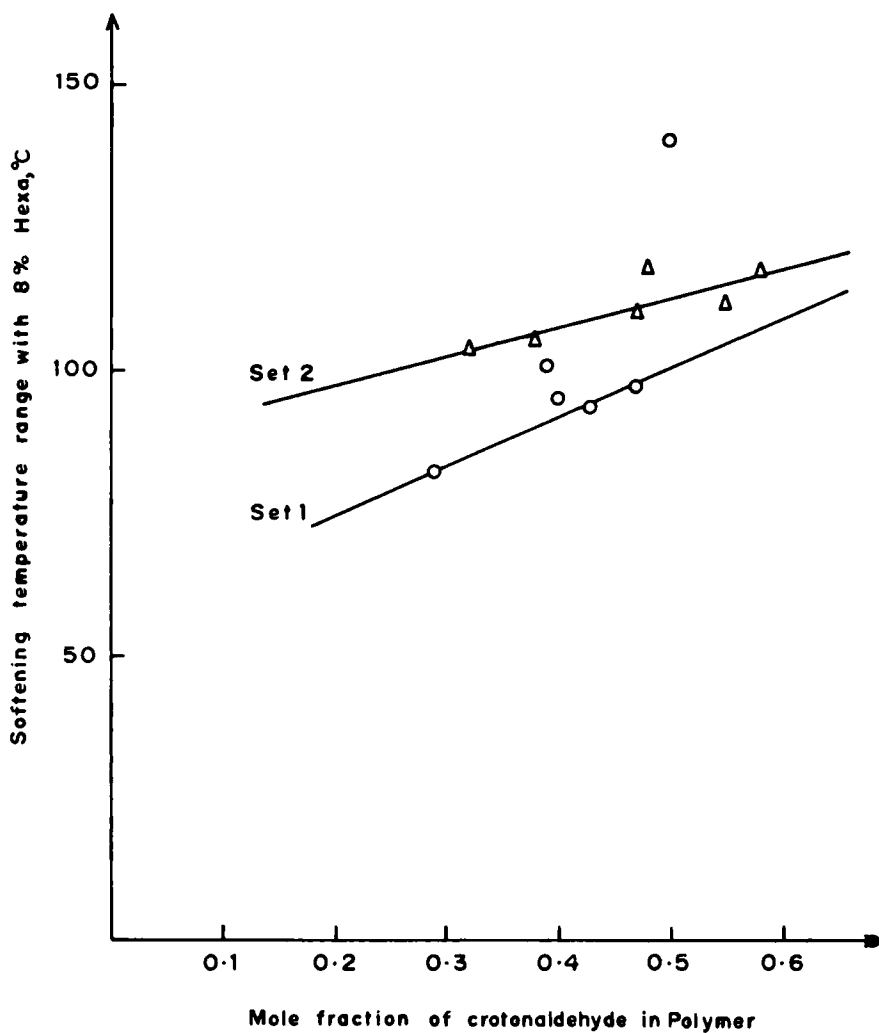


FIG. 7. Effect of crotonaldehyde mole fraction on softening temperature range of resins with 8% hexa.

TABLE 5. Thermal Behavior of the Cured Resins

Set-serial no. of resin	Mole fraction of crotonaldehyde in polymer	Softening temperature range before curing, °C						Softening temperature range after curing								
		4%			8%			140°C/15 min			160°C/15 min					
		Hexa	8%	Hexa	4%	Hexa	ΔT	4%	Hexa	ΔT	4%	Hexa	ΔT	4%	Hexa	ΔT
1-1	0.29	78 ± 2	82 ± 2	113 ± 2	35 ± 2	123 ± 2	41 ± 2	132 ± 2	54 ± 2	161 ± 2	80 ± 2					
1-2	0.39	98 ± 2	101 ± 2	133 ± 2	35 ± 2	142 ± 2	41 ± 2	175 ± 2	77 ± 2	190 ± 2	91 ± 2					
1-3	0.40	92 ± 2	95 ± 2	130 ± 2	38 ± 2	140 ± 2	45 ± 2	165 ± 2	73 ± 2	222 ± 2	127 ± 2					
1-4	0.43	90 ± 2	93 ± 2	121 ± 2	31 ± 2	131 ± 2	34 ± 2	155 ± 2	65 ± 2	171 ± 2	78 ± 2					
1-5	0.47	95 ± 2	97 ± 2	134 ± 2	39 ± 2	144 ± 2	47 ± 2	165 ± 2	70 ± 2	176 ± 2	79 ± 2					
1-6	0.50	138 ± 2	140 ± 2	-	-	-	-	178 ± 2	40 ± 2	191 ± 2	51 ± 2					
2-1	0.32	99 ± 2	104 ± 2	123 ± 2	24 ± 2	153 ± 2	49 ± 2	178 ± 2	79 ± 2	a	-					
2-2	0.38	101 ± 2	106 ± 2	127 ± 2	26 ± 2	161 ± 2	56 ± 2	184 ± 2	83 ± 2	a	-					
2-3	0.47	107 ± 2	111 ± 2	137 ± 2	30 ± 2	151 ± 2	40 ± 2	180 ± 2	73 ± 2	230 ± 2	119 ± 2					
2-4	0.48	114 ± 2	118 ± 2	132 ± 2	18 ± 2	142 ± 2	24 ± 2	168 ± 2	59 ± 2	201 ± 2	83 ± 2					
2-5	0.55	107 ± 2	111 ± 2	126 ± 2	19 ± 2	137 ± 2	25 ± 2	173 ± 2	66 ± 2	194 ± 2	84 ± 2					
2-6	0.58	112 ± 2	118 ± 2	135 ± 3	23 ± 2	145 ± 2	27 ± 2	153 ± 2	41 ± 2	172 ± 2	54 ± 2					

^aDoes not melt up to 250°C.

CONCLUSIONS

Thermoplastic solid resins can be prepared by acid-catalyzed reaction of phenol and crotonaldehyde over a range of mole fraction of crotonaldehyde (0.27-0.58). In comparison, conventional phenolic powder resins exhibit thermoplasticity over a narrower range of formaldehyde mole fraction (0.28-0.45). The resins were oligomeric with number-average molecular weights ranging from 400 to 600. The purity of crotonaldehyde influences the extent of conversion of crotonaldehyde at a fixed ratio of reactants in the feed. It also has a significant effect on the molecular weight, as well as thermal and curing behavior of the resins. In general, resins from distilled crotonaldehyde were higher in molecular weight and exhibited improved thermal and curing properties than resins from crude crotonaldehyde.

The resins were found to be similar in their chemical structure, independent of the purity of crotonaldehyde and its mole fraction. The retention of thermoplasticity and concurrent increase in softening temperature after short-time curing offers considerable scope for combining the processability of thermoplastics and the desirable thermal and dimensional stability of thermosets.

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