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Grafting on Some Phenolic Copolymer Chains

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ABSTRACT

A phenolic copolymer has been prepared by copolymerization of p-chlorophenol, p-cresol, and formaldehyde in the presence of acid catalyst. The copolymer was partially and completely dehalogenated by a standard method. The dehalogenated copolymer chain had a random distribution of reactive positions which were originally occupied by Cl atoms. Some substituted monomers, oligomers of known structure and molecular weight, and basic polymer chains have been grafted at these reactive positions. The halogen percentage of the grafted copolymers could be calculated on the assumption that all the available reactive positions are attached to the respective units. Reasonably good agreement has been found between the calculated and observed amount of halogen percentage in the grafted copolymers.

Phenolic polymers are extensively used in the paint, adhesive, and Bakelite industries [1]. It is well known that by grafting a chemically different chain on a main polymer chain, the properties of the polymer can be modified according to specific needs. Keeping this fact in view, it was considered of interest to see whether it would be possible to graft some polymer chains on a phenolic copolymer. In order to see the feasibility of such grafting on phenolic copolymers, it was considered necessary to do preliminary grafting with some substituted phenolic monomers, oligomers of known structure and molecular weight, and low molecular weight p-bromoaniline-formaldehyde polymer chains. In the present investigation a linear copolymer, p-chlorophenol-p-cresol-formaldehyde, was chosen as the main polymer chain. It was preferred over a homopolymer because, on dehalogenation, the copolymer is likely to have random distribution of reactive positions in the copolymer chain. Efforts have been made to graft hydroxymethyl derivatives of substituted phenolic monomers, oligomers, and basic polymer chains at these reactive positions. One can calculate the halogen percentage of grafted copolymer on the assumption that grafting of these units takes place at all the available reactive positions. Reasonably good agreement (within experimental error) has been found between observed and calculated amounts of halogen in the grafted copolymers. This simple observation may open up new possibilities of grafting different types of polymer chains on a phenolic copolymer.

EXPERIMENTAL

Preparation of Copolymer

p-Chlorophenol-p-cresol-formaldehyde copolymer (1) was prepared by refluxing the components in a definite molecular proportion with 2 mL of 10 N HCl as catalyst, for $2\frac{1}{2}$ h. The halogen content of the copolymer was estimated by a standard method [2].

Dehalogenation of Copolymer

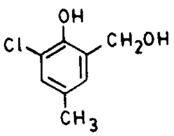
The copolymer was dehalogenated completely by refluxing it with excess metallic sodium in a monoethanol amine-dioxane mixture for $\frac{1}{2}$ h at 120°C, and finally the solution was neutralized with 5% acetic acid. The dehalogenated copolymer (2) was separated as a light yellow powder. It was filtered, washed, and dried. Partial dehalogenation of the copolymer could also be done by adding less than a stoichiometric quantity of metallic sodium.

Preparation of Substituted Monomers and Oligomers

The following substituted monomers and oligomers were grafted on the phenolic copolymer chain (2).

Chlorination [3] of p-cresol with a stoichiometric quantity of sulphuryl chloride and subsequent hydroxymethylation gives Compound (3).

Compound (4) was prepared by hydroxymethylation of 2,4-dichlorophenol [4].



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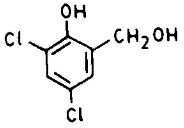

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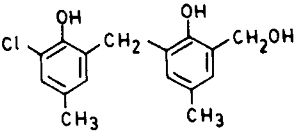

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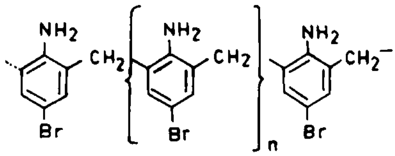


(6)

For the preparation of (5), Compound (2) was condensed with p-cresol and the resultant dinuclear compound was hydroxymethylated with formaldehyde [4].

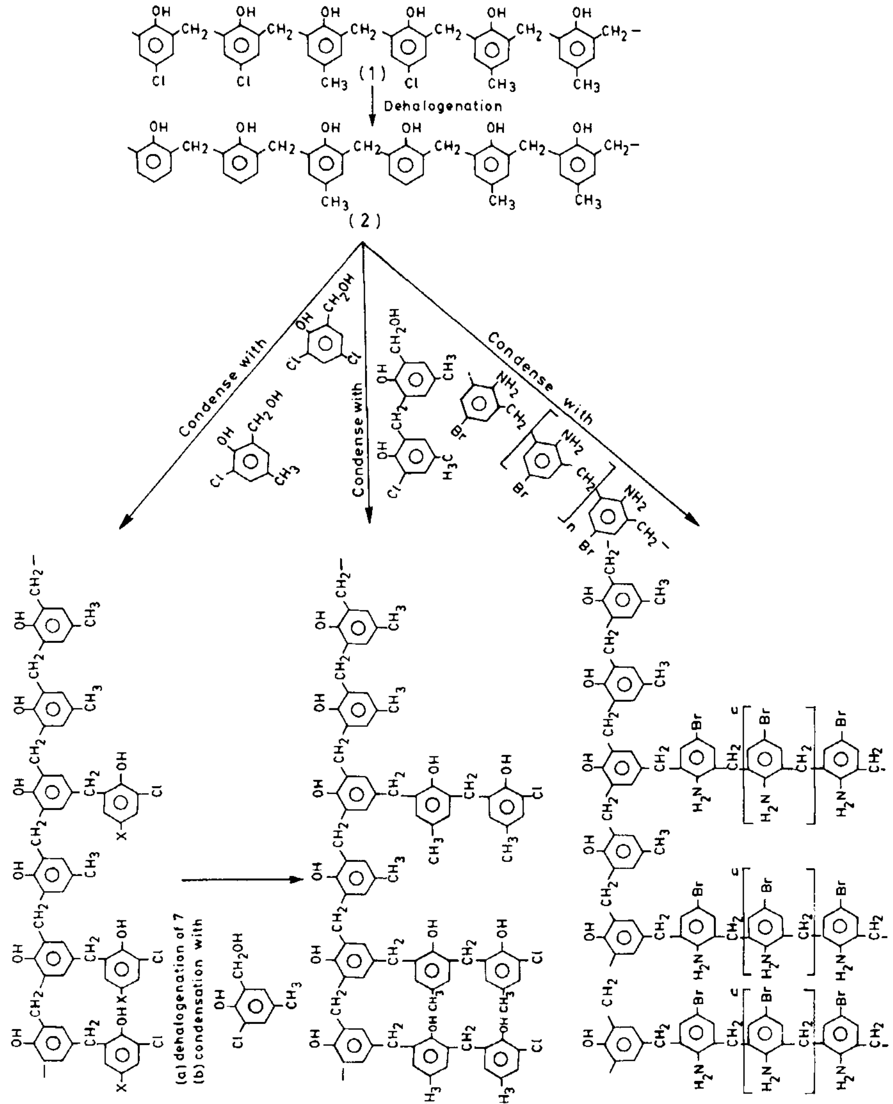
p-Bromoaniline-formaldehyde linear polymer of low molecular weight was prepared by mixing stoichiometric quantities of p-bromoaniline and formaldehyde at room temperature (30° C) for 30 min in the presence of 1 mL of 10 N HCl. The precipitated solid Product (6) was then separated by centrifugation. The average DP of the Homopolymer (6) was determined by electrometric titration techniques in nonaqueous solvent [5] and found to be around five.

Grafting on the Main Copolymer Chain

Grafting on the dehalogenated Copolymer (2) was done by refluxing with stoichiometric quantities of the Components (3), (4), and (5), respectively, in the presence of 2 mL of 10 N HCl as catalyst for 2 h. The resultant product was poured in ice-cold water and washed several times with water and methanol to remove the unreacted soluble monomers and dimers. The linear basic Homopolymer (6) was grafted by refluxing with the dehalogenated Copolymer (2) in the presence of 2 mL of 10 N HCl as catalyst for 2 h. Since the basic Homopolymer (6) was soluble in water, the grafted copolymer could be freed from the homopolymer by washing several times with water.

RESULTS AND DISCUSSION

p-Chlorophenol-p-cresol-formaldehyde copolymer (1) has a random distribution of the two monomeric units (e.g., p-chlorophenol and p-cresol) in the chain. Halogen estimation of the copolymer gives the probable proportion of p-chlorophenol units in the chain. On complete dehalogenation the copolymer is expected to have reactive



Copolymer (7) $X = CH_3$
Copolymer (8) $X = Cl$

Copolymer (10)

Copolymer (9)

TABLE 1. Calculated and Observed Halogen Content in Different Grafted Copolymers

	Halogen (%)	
Copolymer	Observed	Calculated
1	7.42	-
7	6.27	6.12
8	11.20	11.80
9	29.38	31.33
10[a]	5.77	5.07
10[b]	5.41	5.07

[a] Obtained by condensation of (2) with (5).

[b] Obtained by condensation of dehalogenated (7) with (3).

positions which were originally occupied by Cl atoms. At these reactive positions some hydroxymethyl derivatives of substituted phenolic Monomers (3) and (4) and Oligomers (5) and (6) have been grafted. The grafted Copolymer (7) was again dehalogenated and then condensed with Monomer (3). The resultant product was found to have almost the same percentage of halogen as in Copolymer (10) which was obtained by condensation of Copolymer (2) with the Oligomer (5). A schematic representation of the different stages of the reaction is given on the preceding page.

As mentioned earlier, by assuming that all available reactive positions in the Copolymer chain (2) have been occupied by Components (3), (4), (5), and (6), one can calculate the percentage of halogen expected to be present in each of the grafted copolymers (e.g., 7, 8, 9, and 10). The halogen content of each of these grafted copolymers has been estimated and a comparison of calculated and observed values is shown in Table 1. It can be seen from the table that the calculated and observed amounts of halogen content in the grafted copolymers tally reasonably well within experimental error. Fairly good agreement has also been observed between the calculated and observed halogen percentage in the case of grafted copolymers obtained from partially dehalogenated Copolymer (1). This obviously indicates that linear phenolic copolymers can be prepared by blocking the reactive positions with halogen and subsequently dehalogenating the copolymer to give rise to reactive positions where suitable monomers, oligomers, and basic polymer chains can be attached.

We conclude that by grafting phenolic copolymers with different polymer chains, products which are likely to find wider application in industry may be obtained.

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