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CHEMICAL MODIFICATION OF PVC WITH PHENOLIC GROUPS

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ABSTRACT

The reaction of poly(vinyl chloride) with phenol was studied without catalysts at temperatures between 60 and 182°C. The reaction products were analyzed by NMR, IR and UV spectroscopy, elemental analysis, viscometry, osmometry, and OH groups determinations. The content of phenolic groups bound to polymer chain increased with the reaction temperature. At the same time, some scissions of macromolecular chains can occur.

INTRODUCTION

Poly(vinyl chloride) provides tremendous opportunities for chemical modifications due to its polyhalogenated molecular structure. In order to improve the specific properties of the polymer, various reactions have been carried out which lead to a larger number of applications [1–3].

Reactions for the displacement of chlorine atoms from poly(vinyl chloride) with phenolic compounds (*m*-aminophenol, bisphenol A, and phenolphthalein) were described in some recent papers [4–7]. In this way, sulfonic and phosphoric cation-exchange resins have been obtained.

The synthesis of so-called “spaced phenols,” which have extensive practical use, is accomplished by using the high temperature reaction of a mixture of chlorinated hydrocarbons with a hydroxyaromatic compound [8]. This reaction is performed with Friedel–Crafts catalysts [8] or in the presence of a raw silicium aluminum clay, such as bentonite, diatomite, and montmorillonite [9], without previous

activation. Also, chlorinated aliphatic hydrocarbons, partially dehydrochlorinated with KOH to unsaturated compounds, have been used as alkylation agents for phenol [10] at 120–185°C in the presence of H₂SO₄.

In previous papers [11–14] we showed that PVC can react with phenol without catalysts by substitution of allylic or tertiary chlorine structures. If this reaction is carried out at 60°C for 98 hours, quantitative amounts of the labile structures from the polymer are obtained. Generally, in the conditions specified above, reaction products with a *p*-substituted phenolic structure have been obtained. Small quantities of *o*-substituted phenols or etheric compounds were also formed according to some studies on low molecular models [15]. Compounds with polyphenolic structure were obtained in this way, but due to the low content of labile chlorine in poly(vinyl chloride), only 1–2 phenolic groups per 1000 monomer units can be introduced into the polymer [13].

The purpose of the present paper was to increase the phenolic group number on the polymer chain by using the chloroallylic structures appearing by thermal degradation of poly(vinyl chloride).

EXPERIMENTAL

Reaction of PVC with Phenol

PVC samples were polymers synthesized by suspension (PVC I) or bulk polymerization (PVC II). Some of their characteristics are presented in Table 1.

For chemical modification, 2 g PVC and 20 g phenol were reacted in closed vessels at temperatures from 60 to 160°C for 24 hours (Table 2). The reaction mixture was poured in methanol, and successively washed with this solvent. Then three precipitations were carried out in dichloroethane–methanol and tetrahydrofuran–water systems. The polymers were filtered and dried in air at 60°C.

To react PVC at the boiling temperature of phenol, 10 g polymer and 100 g phenol were mixed and heated for 24 hours. The reaction mixture appeared as a black homogeneous fluid. Excess phenol was removed by vacuum distillation. The residue was diluted with acetone and precipitated in water. The polymer, obtained as a brown-gray powder, was filtered and dried.

TABLE 1. Characteristics of PVC Samples before Reaction with Phenol

Sample	Cl, %	Cl _L ^a	T _i , °C ^b
PVC I	55.47	1.01	150
PVC II	55.62	1.49	147

^aCl_L = labile chlorine content, atoms/1000 monomer units.

^bT_i = temperature of initiation of dehydrochlorination.

TABLE 2. Composition of PVC Samples Modified with Phenol

Sample	Reaction temperature, °C	Content of hydroxyaromatic groups/1000 monomer units	Cl, %	
			Calculated	Found
PVC I ^a	60	0.60	55.21	55.04
	80	1.69	55.07	55.79
	100	3.33	54.85	55.08
	120	6.30	54.23	53.41
	140	12.20	53.69	54.80
	160	60.26	47.27	47.72
PVC I ^b	60	0.67		
	80	1.58		
	100	2.28		
	120	6.00		
	140	14.96		
	160	41.95		
PVC II ^a	60	1.10	54.91	55.51
	80	2.21	54.76	54.30
	100	4.30	54.49	55.31
	120	6.59	54.19	55.28
	140	14.13	53.20	51.70
	160	61.08	47.21	47.50
PVC II ^b	160	47.87		

^{a,b}Independent reactions carried out on the same PVC sample.

Measurements

The phenolic group content of polymers was determined by UV in solution. Purified and UV-verified tetrahydrofuran was used as the solvent. The measurements were performed using the method presented for labile chlorine determination [13] by means of a calibration curve constructed for low molecular phenolic models. UV absorbance at 250–300 nm was measured, and the corresponding value of hydroxyaromatic group content was calculated with the aid of the calibration curve.

The starting dehydrochlorination temperature of PVC samples (T_i), as a measure of thermal stability, was estimated by a conductometric method [16]. The degradation of the samples and the detection of evolved hydrogen chloride were performed with an apparatus described by Braun [17]. The thermal degradation was made in an inert atmosphere (argon) using a 0.2-g sample. The heating rate was 4.5°C/min, and it was obtained by means of a linear temperature programmer. The variation of conductivity with time was followed with a recorder by using the output of a radiometer conductometer of the CDM type.

IR spectra were registered in KBr using an SP-100 spectrophotometer.

$^1\text{H-NMR}$ measurements were performed on a Jeol NMC-60HL instrument in a mixture of acetone- d_6/CS_2 .

The viscosities were determined in cyclohexanone at 25°C with a modified Ubbelohde viscometer.

The osmometric measurements were carried out by means of a Mechrolab Model 502 membrane osmometer with tetrahydrofuran solutions at 25°C .

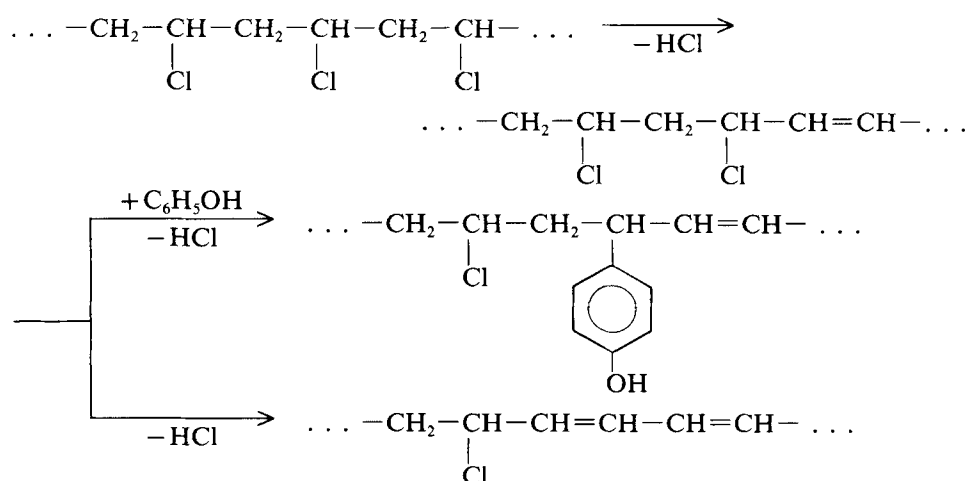
Determination of OH groups was made by reaction with acetic anhydride in excess and then titration of the reactant excess.

RESULTS AND DISCUSSION

Reaction of PVC with Phenol

PVC was transformed with phenol, without catalyst, at temperatures between 60°C and the boiling temperature of phenol, and a reaction time of 24 hours. After this time the appearance of the reaction mixture changed, the change depending on the transformation temperature. At lower temperatures the polymer can be easily distinguished in the melting phenol, whereas at 160° a homogeneous violet mixture was obtained. The color of the purified and dried polymers varied from white (reaction temperature 60°C) to yellowish (reaction temperature 80°C) to beige-gray (reaction temperature 160°C). A blank PVC sample became completely brown after 24 hours heating without phenol.

As is known, poly(vinyl chloride) evolves hydrochloric acid with heating, and double bonds are formed in the chain. After elimination of the first HCl molecule, dehydrochlorination occurs by allylic activation, and polymer becomes colored due to the polyene sequences. It is expected that by heating the poly(vinyl chloride) in phenol, the polymer will react with newly formed chloroallylic structures. In this way, dehydrochlorination propagation is interrupted and polyphenolic compounds are obtained:



The extent of reaction was quantified by determining the content of phenolic groups in the purified polymer by UV spectroscopy [13]. The results are presented in Table 2.

TABLE 3. Influence of Reaction Time on Degree of Transformation

Sample	Reaction temperature, °C	Reaction time, h	Hydroxyaromatic groups/1000 monomer units
PVC I	80	24	1.69
	80	48	2.18
	80	72	2.69

It is evident from Table 2 that the content of phenolic groups in the polymer increases with the reaction temperature. About such 60 groups/1000 monomer units (m.u.) were introduced at 160°C. This increase occurs progressively until 140°C, with a jump observed above this temperature. There was satisfactory reproducibility except for the reactions performed at 160°C. The rapid increase of substitution and the loss of reproducibility can be explained by the fact that the reaction temperature is higher than the temperature of the beginning of dehydrochlorination for unmodified PVC samples (Table 1). The degree of dehydrochlorination was determined by a conductometric method [16].

An attempt was made to introduce more phenolic groups and to avoid advanced degradation by lowering the reaction temperature and increasing the reaction time. These new conditions did not lead to the expected important increase of phenolic structures content (Table 3).

Finally, the reaction of PVC with phenol was carried out at the boiling temperature of phenol (182°C). The resulted polymer (PVC-PhT) was a brown-gray powder. The highest degree of substitution has obtained in this case as evidenced by the very high concentration of phenolic groups (Table 4).

Characterization of Reaction Products

After treatment with phenol, the polymers were soluble in such common solvents for PVC as cyclohexanone, tetrahydrofuran, and 1,2-dichloroethane, thus proving the absence of crosslinks. The phenolic groups don't alter the solubility, perhaps due to their low concentration.

TABLE 4. Characteristics of Polymer Obtained by Boiling PVC in Phenol

Sample	Cl, %	Hydroxyaromatic groups/1000 monomer units	C _{OH} ^a	OH, %
PVC-PhT	8.87	650	205.8	6.23

^aC_{OH} = OH number, mg KOH/g.

TABLE 5. Variation of the Molecular Weights with the Concentration of Phenolic Groups

Sample	Phenolic groups/ 1000 monomer units	η_{sp}/c , ^a dL/g	\bar{M}_n
PVC II	0.00	0.97	37,500
	14.13	0.77	30,000
	61.08	0.40	12,000

^ac = 0.6 g/dL.

Elemental analysis of the products obtained shows a decrease in chlorine content, especially for the reactions carried out at higher temperatures (Table 2). The theoretical values for chlorine content were calculated by taking into account that two chlorine atoms are eliminated for each hydroxyaromatic group introduced into the polymer. Good agreement was found between the theoretical and found values, which is proof of dehydrochlorination followed by labile chlorine substitution with phenolic groups.

The polymer viscosity decreases with an increase in the phenolic groups content (Table 5), very probably due to a lowering of the degree of polymerization. Osmometry was used to verify this. An increase in the number of phenolic groups bound to the polymer was accompanied by a decrease of molecular weight. This observation leads to the conclusion that some scissions of the macromolecular chain take place.

UV spectroscopy was used to prove the presence of phenolic groups in the polymers [13]. All the reaction products showed absorption bands at 250–300 nm, and the extent of chemical modification was quantified in this way (Tables 2 and 4).

IR and proton NMR spectra of the reaction products with low degrees of substitution resemble that of PVC (Figs. 1a and 2a). IR spectra of samples reacted at 160°C show both PVC bands and absorption bands at 1500 and 1580–1600 cm^{-1} due to the aromatic structures (Fig. 1b). A strong absorption band at 3520 cm^{-1} can also be seen; it is attributed to OH phenolic groups.

¹H-NMR spectra of highly substituted products show the characteristic signals for aromatic protons between 6.3 and 7.1 ppm (Fig. 2b). In the NMR spectrum of

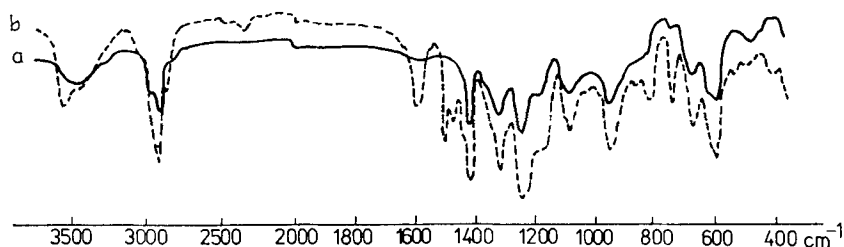


FIG. 1. IR spectra of polymers after reaction with phenol: (a) 120°C; (b) 160°C.

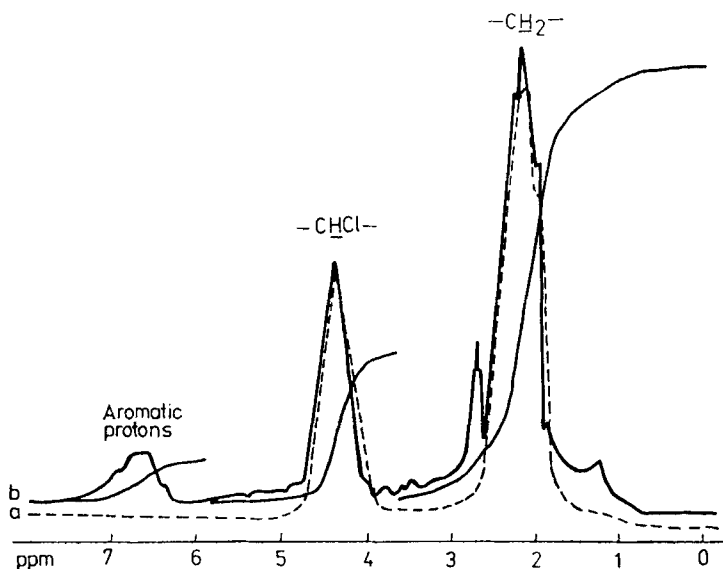


FIG. 2. NMR spectra of polymers after reaction with phenol: (a) 120°C; (b) 160°C.

the polymer synthesized at 182°C (PVC-PhT), a notable increase of the signal from 6.3 to 7.3 ppm, belonging to aromatic protons, can be clearly observed, while that from 4.2 to 4.8 ppm, characteristic of $-\text{CHCl}-$ protons, decreases (Fig. 3). The signal at 3.18 ppm is attributed to benzylic protons. The spectral region of $-\text{CH}_2-$ protons from PVC has been wholly modified. There is a solvent signal (acetone- d_6 /CS₂) at 2.07 ppm. In neither the IR nor NMR spectra can the presence of olefinic structures be observed, even at advanced degrees of substitution and as the results

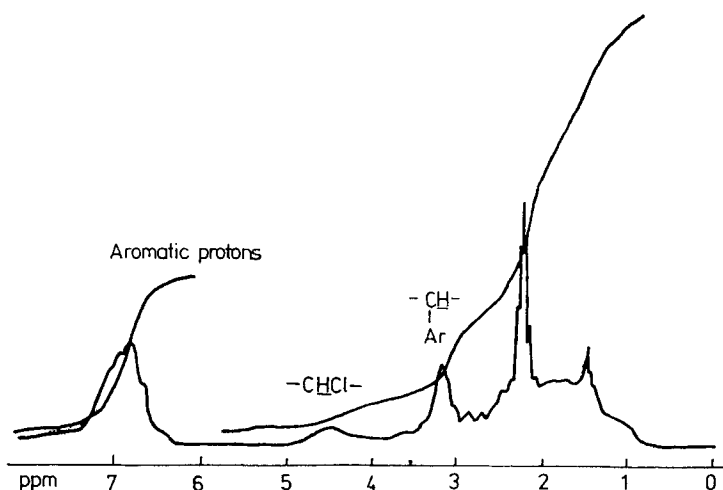


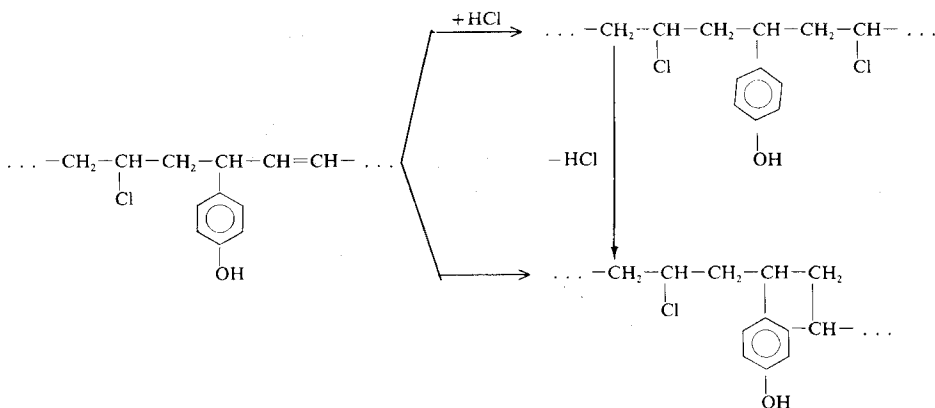
FIG. 3. NMR spectrum of polymer treated with phenol at 182°C (PVC-PhT).

of elemental analysis would suggest. The presence of a signal at 1.22 ppm in spectrum of PVC-PhT indicates the appearance of some polymethylene sequences.

For the polymer prepared at 182°C, which has a higher content of aromatic structures, we tried to measure quantitatively the phenolic hydroxyl group content by acetylation. The values of C_{OH} and OH% are presented in Table 4. To provide evidence of OH groups in samples with lower degrees of substitution, some specific methods for OH analysis in polymers, such as potentiometric ones, should be tried [19-21].

CONCLUSION

Our data present some new suggestions regarding the development of the PVC reaction with phenol. Thus, the correlation of the absence of olefinic structure signals from spectra with lowering of the chlorine content suggests the formation of some cyclic structures. Hydrochloric acid evolved in the reaction might lead to the double bonds [15, 22], simultaneously producing a secondary intramolecular cyclization to an aromatic ring:



Such structures appearing in Friedel-Crafts reactions with aromatic hydrocarbons have been proposed [23, 24]. The simultaneous production of hydrogenation reactions by the reductive action of phenol appears to be supported by NMR spectra, and some polymethylene sequences could be formed.

In conclusion, heating of PVC in phenol, without catalysts, gives a simple and advantageous way to modify the chemical structure of poly(vinyl chloride) by displacement of some chlorine atoms by phenolic groups. Up to 650 such groups per 1000 monomer units were introduced, opening new perspectives for some second modifications of this polymer.

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