Thermal Characterization of Some Products Obtained by Chemically Modified Poly(vinyl chloride) with Phenol

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SYNOPSIS

The chemical modification of poly(vinyl chloride) (PVC) in reaction with phenol, in the absence of a catalyst and at temperatures within the range of 60°C and the boiling temperature of phenol (180°C), led to the reaction products with the general structure of a vinyl chloride–vinyl phenol copolymer. The synthesized polyphenols were thermally characterized using the following experimental techniques: thermo–optical analysis (TOA), thermogravimetry (TG), derivative thermogravimetry (DTG), and pyrolysis in combination with gas chromatography (P–GC). The PVC samples modified with phenol show a thermal stability lower than the original PVC sample. The glass transition temperatures (T_gs) increase with increased degree of chlorine substitution. The main pyrolysis products of the modified PVC samples are hydrocarbons with low boiling points (C_1–C_4), benzene, toluene, naphthalene, indan, and phenol. The semiquantitative estimation of the pyrolysis products of the synthesized samples led to the conclusion that the following structural element types can be present, statistically distributed along the chain: vinyl chloride and vinyl phenol units, acetylenic and ethylenic units, and indan type structures. © 1995 © John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) has a polyhalogenated molecular structure and by substitution,[1] elimination,[2] and solvolise[3] reactions leads to new polymer derivates. Recently Biswas and Moitra[4,5] described the preparation and characterization of sulfonic acid cation exchange resins from PVC chemically modified through Cl displacement reaction with meta-aminophenol, bisphenol A, and phenolphthalein.

In our laboratory the reaction of PVC with phenol under a variety of conditions[6,7] was carried out with the object of placing into evidence the differences present in the reactivity of the groups with secondary, allylic, and tertiary chlorine and to measure the labile structures existing in polymer. A more recent study[8] reports the synthesis and characterization of the products obtained by chemically modified PVC with phenol, in the ab-

sence of a catalyst and at temperatures placed in the range within 60°C and 180°C. The reaction products were examined by ¹H-NMR, IR and UV spectroscopy, elemental analysis, viscometry, osmometry, and OH-groups determination. The products have a parasubstituted phenolic structure, which appeared as a result of the phenol alkylation with PVC. The preliminary structure of these products was proposed to be preponderantly a vinyl chloride (VC)–vinyl phenol (VPh) copolymer. Some unsolved aspects regarding the structure of the chemically modified PVC led us to conduct new investigations in this direction.

The present paper reports some data referring to the thermal behavior of the products obtained by chemically modified PVC with phenol. The experimental techniques used, namely, thermooptical analysis (TOA), thermogravimetry (TG), derivative thermogravimetry (DTG), and pyrolysis in combination with gas chromatography (P–GC) bring new evidence concerning the thermal stability and the structure of the synthesized polyphenols.

EXPERIMENTAL

Polymer Synthesis

The synthesis of VC–VPh copolymers was carried out under conditions similar to those previously reported.[8] The raw materials were PVC and phenol, used as supplied. The PVC was a commercial product (Oltchim, Vâlcea, Romania), obtained by suspension polymerization. The original PVC sample had a total chlorine content of 55.62% and a labile chlorine content of 1.49 atoms/1000 monomer units, determined as described elsewhere.[6] The method is based on reaction of the labile atoms with phenol. Briefly, the PVC original sample was reacted for 96 h with phenol at 60°C, then the unreacted phenol was removed by decantation and distillation at reduced pressure. The obtained polymer was washed several times with methanol and reprecipitated in a THF–methanol system. The product was analyzed on models and verified on copolymers with known labile chlorine content.

Samples of VC–VPh copolymer were prepared by heating the PVC sample in phenol (Merck, Darmstadt, Germany) in a molar ratio of 1 : 10 w/w, for a reaction duration of 24 h and at various reaction temperatures. The reactions were performed in the absence of a catalyst. After the excess phenol was removed, the obtained polyphenols were purified as presented above.

Characterization Tests

The synthesized polymers, together with the elemental analysis data and the reaction temperatures, are listed in Table I.

The content of hydroxyaromatic groups given in Table I were determined by phenolysis reaction with the aid of the method reported before.[6] The measurements were carried out on solutions in THF, using the calibration curve obtained for low molecular phenolic models on a UNICAM SP-800 Spectrofotometer.

The glass transition temperatures $(T_g s)$ were evaluated by TOA, with the aid of an apparatus made in laboratory[9] on the basis of technical construction and operation elements described elsewhere.[10,11] The heating rate was 7°C/min and T_g was considered as the initial temperature on changes in the light intensity transmitted through the sample from the basis line.

Both TG and DTG experiments were carried out with the aid of a derivatograph (MOM, Budapest, Hungary) under the following conditions: sample weight 50 mg, heating rate 12°C/min, decomposition in air (28 ml/min), and reference material α-Al_2O_3.

The pyrolysis of VC–VPh copolymer samples was accomplished by means of a filament type pyrolysis unit described elsewhere.[12] The analysis and the separation of the thermal degradation products were carried out with a Siemens L-400 gas chromatograph provided with a flame ionization detector and a chromatographic column from stainless steel (2 × 3 mm i.d.) packed with Chromosorb W (60–80 mesh), acid-washed, and coated with 5% w/w Carbowax 20M. The column temperature was programmed from 60°C to 200°C at a rate of 7°C/min and then operated isothermally at 200°C. The carrier was argon with a rate of 26 ml/min.

RESULTS AND DISCUSSION

Glass Transition Temperatures

The T_g values of the synthesized samples are listed in Table II, together with the T_g value of the original PVC.

The displacement of chlorine in PVC with voluminous phenolic groups influences the T_g values.

Table I Some Characteristics of the Synthesized VC–VPh Copolymers

Sample	Reaction Temperature (°C)	Hydroxyaromatic Groups/1000 m.u.*	Elemental Analysis		
			Cl (%)	C (%)	H (%)
A	60	1.10	55.51	38.20	5.13
B	80	2.21	54.30	39.30	5.36
C	100	4.30	55.31	39.96	5.13
D	120	6.59	55.28	40.42	5.42
E	140	14.13	51.70	40.65	5.38
F	160	61.08	47.50	45.38	5.70

* m.u. = monomer units.

Table II T_g **Evaluated for PVC and Chemically Modified PVC Samples with Phenol**

| Sample	T_g (°C)
Unmodified PVC	78
A	81
B	81
C	84
D	86
E	89
F	85

This can be explained by the stiffness effects of the molecular chain[13] and the appearance of some intermolecular interactions in the case of the new structures (due to the phenolic groups, especially). Generally, as can be seen in Table II, the T_g values increase with increases in the substitution degree of chlorine in the main chain of PVC. At the same time, the sample F shows a lower T_g value than the samples D and E. This suggests the hypothesis that the high reaction temperature used in synthesizing sample F (160°C) creates the important modifications in the polymer structure.

Thermogravimetric Measurements

Figure 1 shows TG and DTG curves recorded for the original PVC sample and for some chemically modified PVC samples with phenol.

The TG and DTG analyses show important changes in some experimental parameters which characterize the thermal decomposition of PVC samples modified with phenol. The samples analyzed by TG and DTG show three decomposition stages. The most important is the first stage, in which the weight loss of the samples was very great. The temperatures which characterize the first stage of decomposition—respectively, the initial temperature (T_i), the temperature corresponding to the maximum rate of decomposition (T_m), and the final temperature (T_f)—together with the weight loss (W) were estimated and some evaluated for the original PVC sample and for samples A, C, E, and F; results are listed in Table III.

The shape of TG and DTG curves in Figure 1 and the decomposition temperatures of the samples summarized in Table III show, contrary to expectation, a decrease in the thermal stability of PVC samples modified with phenol as against the original PVC sample. The decrease in thermal stability of the modified PVC samples could be due to the fact
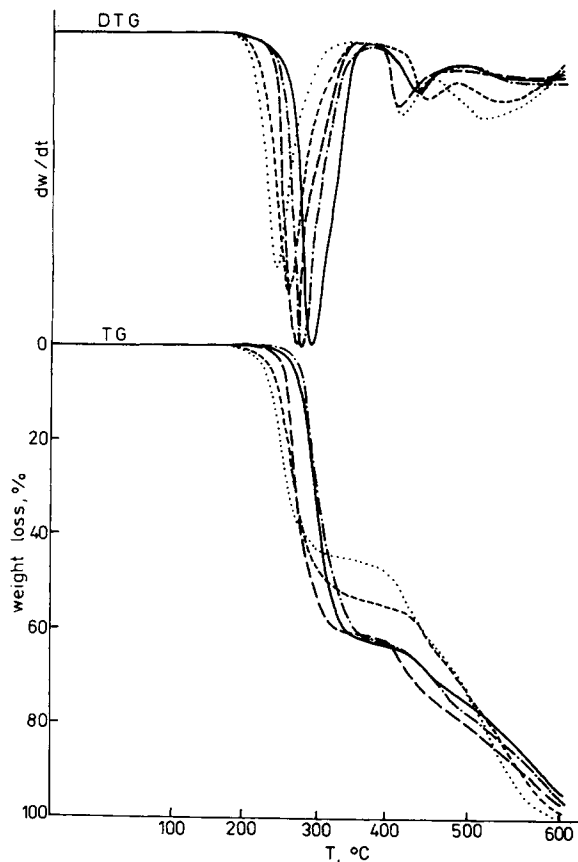
Figure 1 TG and DTG curves of PVC and chemically modified PVC samples with phenol: (– · – · –) unmodified PVC; (———) A; (– – –) C; (· · · · · ·) E and (– – – – –) F.

that the reaction between PVC and phenol takes place at high temperatures and at prolonged lengths of time. Because the decrease in thermal stability of the modified PVC samples is observed and for low temperatures in a low proportion (see sample A), we can take into consideration the presence of oxygen in the reaction medium, which could cause the appearance of some labile structures on the main macromolecular chain, oxygen-containing

Table III   Some Characteristics of the First Thermal Decomposition Stage

Sample	T_i (°C)	T_m (°C)	T_f (°C)	W (%)
Unmodified PVC	245	290	370	60.5
A	235	300	365	60.0
C	240	290	365	59.0
E	205	255	350	48.0
F	200	260	355	51.5

groups,[14,15] for example. These labile structures can be taken as degradation initiation centers at temperatures higher than 200°C.

Pyrolysis–Gas Chromatography

The P–GC technique was used in our laboratory with good results in determining the structure and studying the thermal degradation mechanism of the condensed polymers obtained by Friedel–Crafts reaction of PVC with benzene, toluene, and naphthalene.[16] In the present study, the P–GC data show that the single products which appear at decomposition of the original PVC sample are benzene and naphthalene at temperatures around 300°C. The samples of modified PVC pyrolyzed at low temperatures, in the same conditions as the original PVC sample, yield benzene, naphthalene, and phenol, the last being noticed only in the case of samples E (trace) and F. The aromatic hydrocarbons evolved at high decomposition temperatures were identified by using the retention data of variable reference substances expected to be formed from the original and modified PVC samples. Figure 2 shows a typical pyrogram recorded for the original PVC sample decomposed at 560°C, while Figure 3 reproduces a typical pyrogram recorded for sample F at the same temperature (560°C).

As Figures 2 and 3 show, the PVC samples modified with phenol yield the same pyrolysis compounds as those found on pyrolysis of the original PVC sample, with the exception of phenol. The main pyrolysis products of the analyzed samples are hydrocarbons with low boiling points (C_1–C_4), benzene, toluene, styrene, indan, naphthalene, and phenol, the last being remarked only for the samples with more than 10 phenol groups at 1000 monomer units. The composition of these decomposition products varies with the pyrolysis temperature. As a general behavior, all the samples analyzed show that the content of C_1–C_4 high-volatility hydrocarbons increases with increased temperature.

Starting from the experimental observation that the analyzed samples yield only hydrocarbons by pyrolysis in an inert medium (sample F gives and phenol, but in small amount) and taking into consideration that the response of the flame ionization detector is a function of the carbon atoms in the component, we have considered the relative weight sensitivity of each component to be regarded as a unit.[16] In this way a semiquantitative evaluation of the pyrolysis products of the modified PVC samples was carried out.

The influence of the nature of the sample upon the distribution of the main pyrolysis products, ob-

Figure 2 Typical pyrogram of PVC at 560°C. 1: hydrocarbons with low boiling points (C_1–C_4); 2: saturated and unsaturated aliphatic hydrocarbons (C_5–C_6); 3: benzene; 4: toluene; 5: ethylbenzene; 6: xylenes; 7: chlorbenzene; 8: styrene; 9: α-methylstyrene; 10: indan; 11: unknown; 12: naphthalene.

tained on pyrolysis of both original and modified PVC samples is shown in Table IV.

As can be remarked in Table IV, together with increase of the chlorine substitution degree in PVC, an increase of the content in hydrocarbons with low boiling points (C_1–C_4) and a decrease of the content in benzene takes place. The decrease in benzene content could be explained taking into account the mechanism already proposed[17] for the appearance of benzene on PVC degradation:

a) dehydrochlorination

$$\sim\!CHCl - CH_2 - CHCl - CH_2 - CHCl$$

$$- CH_2\!\sim \xrightarrow[-3HCl]{} \sim\!CH=CH - CH=CH$$

$$- CH=CH\!\sim$$

b) cyclization

$$\sim\!CH=CH - CH=CH$$

$$- CH=CH\!\sim \rightarrow benzene$$

The displacement of chlorine in the original PVC chain and its replacement with phenol leads to interruption of the process of polyacetylene sequences formation and to the decrease in the number of cyclizations to yield benzene. The increase in the content of hydrocarbons with low boiling points with the increase in the substitution degree of chlorine could be due to both the decreased number of cyclizations of polyacetylene sequences ($-CH=CH-CH=CH-$) and the action of the phenol as a reduction agent. The reaction between phenol and the double bonds, which are present in the main chain of PVC due to the break of the carbon–chlorine bonds in the initial step of degradation, leads to polyethylene structures ($-CH_2-CH_2-CH_2-$), with a pronounced signal in the ^{1}H-NMR spectra at 1.2 ppm as reported previously.[8]

The gentle increase of the content of indan with the increased substitution degree of chlorine in PVC, associated with the fact that the ^{1}H-NMR technique does not indicate the presence of unsaturation to be equal with hydroxyphenyl groups introduced in polymer,[8] could suggest the presence of some indan-type structures as follows:
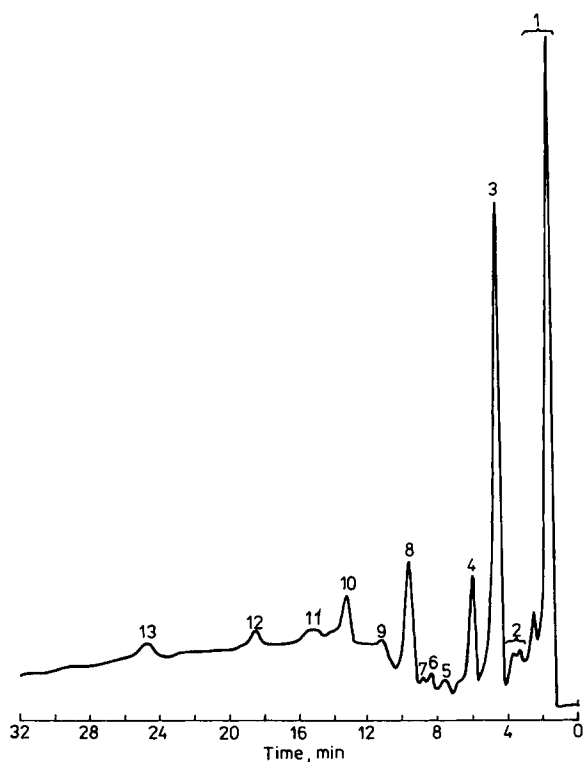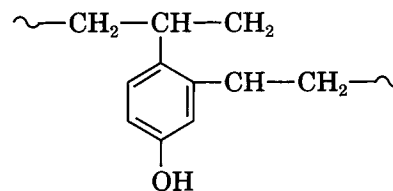
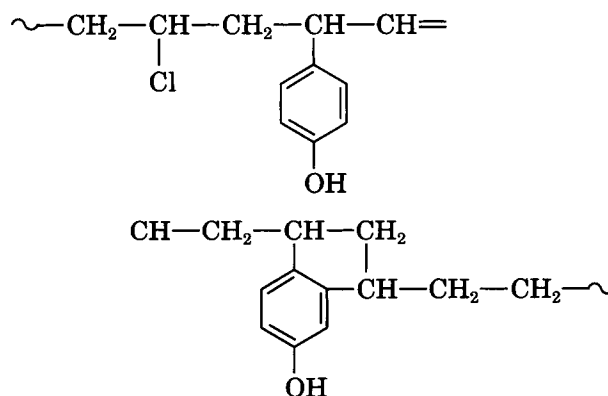**Table IV   Composition of the Pyrolysis Products of PVC and Chemically Modified PVC Samples with Phenol at 560°C**

		Sample		
	PVC	B	D	F
Products		Content (%)		
Hydrocarbons with low boiling points (C_1–C_4)	33.8	35.2	37.4	39.0
Benzene	38.8	34.6	32.2	28.2
Toluene	7.6	7.2	7.2	6.8
Styrene	5.4	7.1	7.4	8.0
Indan	4.1	4.8	5.6	6.4
Naphtalene	4.2	4.6	4.4	4.1
Phenol	—	—	Trace	3.1

Such structures, previously proposed to be present in the Friedel–Crafts reactions of PVC with aromatic hydrocarbons,[16,18,19] could appear as the result of some readdition reactions of hydrogen chloride to the double bonds (the reaction being performed in a closed system), followed by an intramolecular secondary cyclization at the aromatic ring.

Finally, on the basis of the experimental results obtained by pyrolysis of chemically modified PVC with phenol correlated with the data previously reported,[8] the following structural element types can be suggested, statistically distributed along the chain:

Figure 3   Typical pyrogram of sample F at 560°C. The semnifications of peaks 1 to 12 are as in Figure 2. Peak 13: phenol.

REFERENCES

1. M. Lambla, *J. Vinyl Technol.*, **5**, 9 (1983).
2. M. Bowley, D. Gerhard, and W. Maddams, *Makromol. Chem.*, **186**, 707 (1985).
3. T. Suzuki, *Pure and Appl. Chem.*, **49**, 539 (1977).
4. M. Biswas and S. Moitra, *J. Appl. Polym. Sci.*, **37**, 1855 (1989).
5. M. Biswas and S. Moitra, *J. Appl. Polym. Sci.*, **40**, 1703 (1990).
6. G. Robilă, E. Buruiană, and A. Caraculacu, *Europ. Polym. J.*, **13**, 21 (1977).
7. E. Buruiană, A. Airinei, G. Robilă, and A. Caraculacu, *Polym. Bull.*, **3**, 267 (1980).
8. G. Robilă, E. Buruiană, and A. Caraculacu, *J. Macromol. Sci., Pure and Appl. Chem.*, **A32**, 301 (1995).
9. C. Vasile, A. Stoleriu, M. Eşanu, and Gh. Adamescu, *Materiale Plastice (Bucharest)*, **27**, 117 (1990).
10. A. J. Kovacs and S. Y. Hobbs, *J. Appl. Polym. Sci.*, **16**, 301 (1972).
11. R. Kaneko, *Kobunshi Ronbunshu (Jap.)*, **26**, 253 (1969).
12. C. N. Caşcaval, H. Oleinek, I. Zugrăvescu, and I. A. Schneider, *Makromol. Chem.*, **169**, 129 (1973).
13. V. P. Privalko, *J. Macromol. Sci.*, **B-9**, 551 (1974).
14. J. Bauer and A. Label, *Angew. Makromol. Chem.*, **47**, 15 (1975).
15. M. H. George and A. Garton, *J. Macromol. Sci., Chem.*, **A11**, 1389 (1977).
16. C. N. Caşcaval, Ig. C. Poinescu, and I. A. Schneider, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2259 (1975).
17. S. Tsuge, T. Okumoto, and T. Takeuchi, *Makromol. Chem.*, **123**, 123 (1969).
18. Ph. Thesie and G. Smets, *J. Polym. Sci.*, A-1, **55**, 351 (1956).
19. D. Hace and M. Bravor, *J. Polym. Sci.*, A-1, **33**, 325 (1971).