

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Chemical Modification: Instrument for Research on PVC Structure

A. Caraculacu^a

^a C. Poni Institute of Macromolecular Chemistry, Jassy, Romania

To cite this Article Caraculacu, A.(1978) 'Chemical Modification: Instrument for Research on PVC Structure', Journal of Macromolecular Science, Part A, 12: 2, 307 – 313

To link to this Article: DOI: 10.1080/00222337808061378

URL: <http://dx.doi.org/10.1080/00222337808061378>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Chemical Modification: Instrument for Research on PVC Structure

A. CARACULACU

C. Poni Institute of Macromolecular Chemistry
Jassy, Romania

ABSTRACT

The use of chemical modifications on PVC for the study of abnormal structures from polymer is presented. To determine labile chlorine, the reaction of the polymer with phenol and the selective isotopic exchange of the chlorine with radioactive thionyl chloride have been used. The methods of determination of labile chlorine from PVC based on the chemical modifications give results which are in good agreement with those obtained by direct NMR measurements.

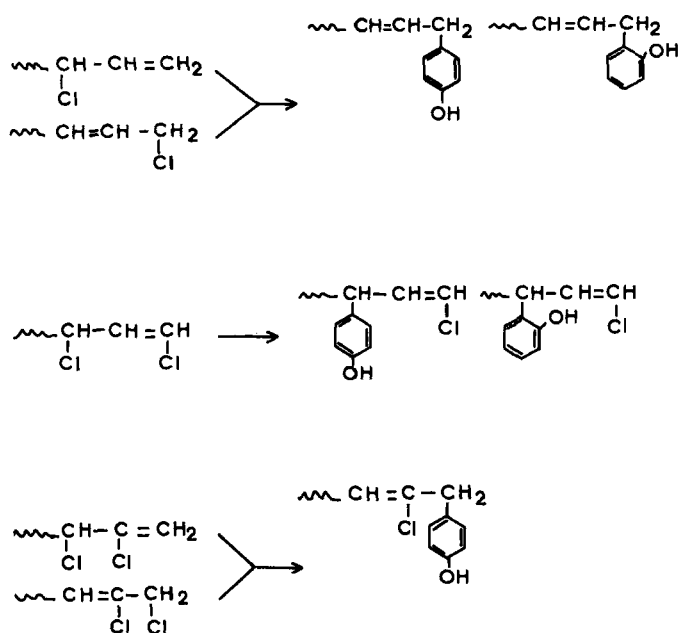
Chemical modification has long been used to help in the study of the structure of poly(vinyl chloride). Reduction, oxidation, chlorination, acylation, and so on are examples of the processes used for this purpose. Basically, the method of modification is based on the differences in the chemical behavior associated with specific structures.

Our group's work was aimed at determining the structural defects of PVC, especially those which can lead to the appearance of labile chlorine which may initiate the dehydrochlorination process and ageing reaction.

Some years ago we found that tertiary chlorine selectively solvolyzed with phenol, leading to the alkylation of the phenol without the addition of catalyst. The reaction is extremely specific. After quantitative verification with macromodels, this reaction was applied to PVC to determine the structure of the branching in PVC by means

of infrared analysis. Tertiary chlorine was not found to be present at the branching site.

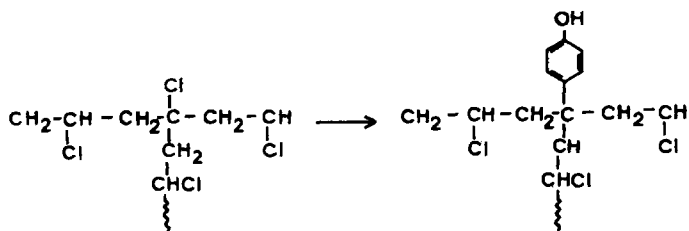
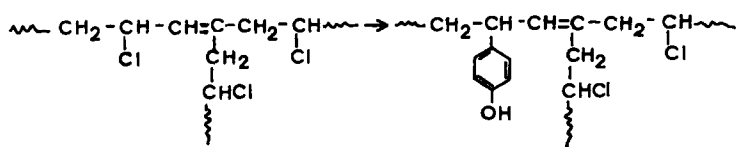
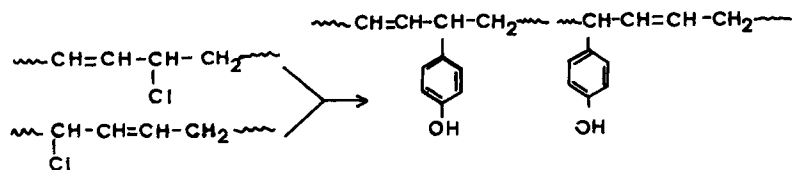
Later, we also found that phenol can react with all the types of labile chlorines which we used, including those of the allylic type, leading to the different structures shown in Schemes 1 and 2.



Scheme 1

Schemes 1 and 2 are respectively related to end groups and internal allylic chlorines. The last reaction of Scheme 2 represents our first work on tertiary chlorine. Because it is expected that such a labile chlorine structure would be formed in very low concentrations, we have perfected a procedure involving the use of ultraviolet spectroscopy. The reaction products have characteristic UV spectra (Fig. 1). The spectra for phenol, normal PVC (which has no maximum), and PVC treated with phenol are shown here.

Since the molar extinction coefficient was approximately the same for all these compounds, we were able to develop a quantitative analytical method with sufficient accuracy, based on the standard curves which are visible. All the curves have approximately the same slope



Scheme 2

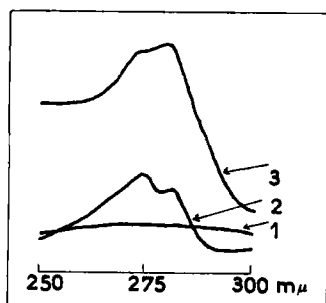


FIG. 1. UV absorption spectra of (1) PVC; (2) phenol; (3) phenolyzed PVC in THF solution.

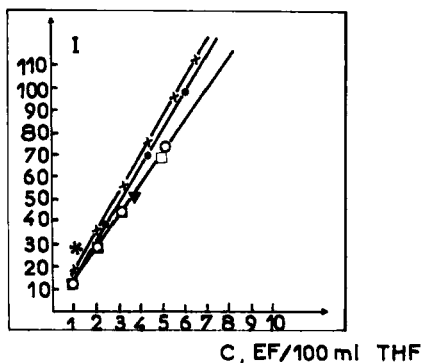


FIG. 2. Plot of UV signal intensity at 285 nm for (●) phenol, (×) 3-(p-hydroxyphenyl)pentene-1, (○) 3-(p-hydroxyphenyl)3-ethylpentane, (□) 4-(p-hydroxyphenyl)-hexene-2, (▼) copolymer Cl_A , and (*) copolymer Cl_A as a function of concentration.

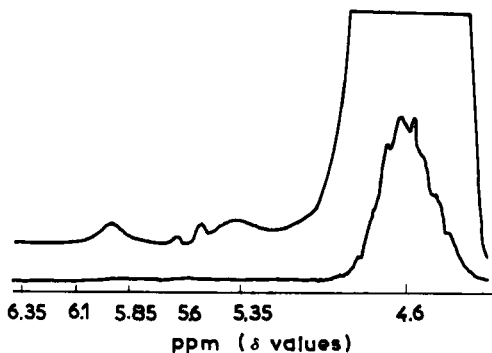


FIG. 3. -PFT-NMR spectrum of an unsaturated region of a commercial PVC sample.

(Fig. 2), enabling us to use approximately the same curve to determine the content of labile chlorine. This method was verified by using micro and macromodels especially synthesized and containing a precise quantity of different types of labile chlorine introduced by us artificially and proved by isotope analysis.

The results were comparable with those obtained by us using another method based on the selective isotope exchange of the labile chlorine with radioactive thionyl chloride. This latter method, however,

TABLE 1. PFT-NMR Technique Determination of Structure and Concentration of Unsaturated End Groups in PVC^a

Structure	Chemical shift δ (ppm central)	Cl ¹³⁵ concentration (atoms/1000 monomer units)		
		PLIOVIC-BL-90	Romanian PVC	Hostalit 3057
-CH ₂ -CH-CH=CH ₂ Cl	5.35	1.2	0.7	0.7
-CH ₂ -CH-C=CH ₂ Cl Cl				
and (or)	5.55	-	-	1.0
-CH ₂ -CH-CH=CH-CH ₂ - Cl				2.85
-CH ₂ -CH=C-CH ₂ Cl Cl				
and (or)	5.95	1.25	1.76	2.7
-CH ₂ -CH=C-CH- Cl Cl				0.6
Weak signals	5.68 5.78	0.2-0.5 0.15-0.45		0.2-0.7 0.15-0.45
Total		2.45	4.46	4.4
				5.05

^aData of Caraculacu et al. [1].

TABLE 2. Comparison of the Values Obtained by Phenolysis with Those Obtained by Other Methods^a

Polymer	CIL (%)		
	Phenolysis	NMR	Radiochemical
PVC - R - 3	0.144	0.245	-
PLIOVIC BL - 90	0.095	0.246	-
Hostalit MPV	0.19	0.44	-
PVC Turda	0.12	-	0.16
Breon	0.169	-	0.16

^aData of Cararulacu et al. [2].

results in labeling only of the allylic chlorine but not the tertiary chloride.

Two years ago we succeeded with the aid of Fourier transform accumulation spectra in obtaining evidence about the unsaturated groups in PVC. We have directly determined the type and quantity of these groups. One example is given in Fig. 3, showing the signals belonging to the unsaturation in PVC.

The quantitative results are shown in Table 1. We have tried to measure the unsaturation in four different types of PVC. In the case of two signals at $\delta = 5.55$ and $\delta = 5.95$, there is a lot of uncertainty because the NMR signals of the groups are superimposed. This means that it is not possible to tell which of them are really present. If we compare the three methods (Table 2), there is fairly good agreement between the labile chlorine determination by phenolysis and NMR, and also by phenolysis and radiochemical method. The results obtained by the NMR method are slightly higher, as the NMR method is more precise, because this method does not need any separation or purification, whereas in the case of phenolysis and radiochemical methods, the low fractions, which have a high content of the labile chlorine, have been lost by purification. The methods based on the chemical modifications are always accompanied by loss of the low fractions.

I hope that these data will give us some new information about the structure of PVC and will be of interest in its study.

We also studied the behavior of different types of labile chlorines during the polymerization. We have found that the majority of these unsaturated groups are not inactive during polymerization, and that

some of these products can have an inhibitory effect on the polymerization of vinyl chloride.

REFERENCES

- [1] A. Caraculacu et al., J. Polym. Sci. Polym. Chem. Ed., in press.
- [2] A. Caraculacu et al., Eur. Polym. J., in press.