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DETERMINATION OF ALLYLIC CHLORINE IN PVC BY A RADIOCHEMICAL METHOD

E. C. BURUIANĂ, V. T. BĂRBÎNŢĂ and A. A. CARACULACU
Institute of Macromolecular Chemistry "Petru Poni", Aleea Gr. Ghica Vodă nr. 41A, Jassy, Romania

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Abstract—Allylic chlorine in PVC can be determined by isotopic exchange with $SOCl_2^{36}$. The number of allylic chlorines in PVC is between 0.12 and 0.16 for 100 monomer units. The selective exchange of chlorine in the polymer was verified by experiments with model compounds.

Allylic chlorine in PVC may occur either at chain-ends as a result of disproportionation [1] or of transfer to monomer [2] or in the chains as a result either of random dehydrochlorination or of copolymerization with acetylenic impurities in the monomer [3]. We now propose a rapid and selective method for determination of allylic chlorine in PVC.

RESULTS AND DISCUSSION

Selective exchange of chlorine with $SOCl_2^{36}$ was verified for PVC micromodels having secondary, tertiary or allylic chlorine. The following compounds were used as models: 3-chloropentane, 3-chloro-3-ethylpentane and 3-chloropentene-1. From this study, exchange of ^{36}Cl for chlorine bound to tertiary carbon (Cl_T) and between allylic type chlorine (Cl_A) was indicated. It was shown that this reaction did not occur for secondary chlorine (Cl_S). It is thought that the selective exchange is due to fact that structures with Cl_T and Cl_A are in equilibrium with partially ionized structures. To make use of these findings for study of PVC, it was necessary first to examine PVC macromodels with known Cl_A and Cl_T contents. For this purpose, we synthesized copolymers with double bonds in the chain by copolymerization of vinyl chloride with 4-chloro^{36}-pentine-l [3].

The characteristics of the copolymers are presented in Table 1.

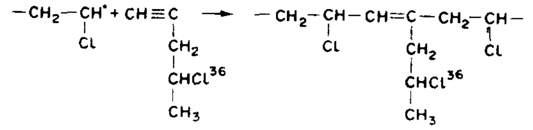
$$-CH_2-\underset{Cl}{CH^{\bullet}} + CH\equiv\underset{\underset{\underset{CH_3}{|}}{\underset{CHCl^{36}}{|}}}{\underset{CH_2}{\underset{|}{C}}} \longrightarrow -CH_2-\underset{Cl}{CH}-CH=\underset{\underset{\underset{CH_3}{|}}{\underset{CHCl^{36}}{|}}}{\underset{CH_2}{\underset{|}{C}}}-CH_2-\underset{Cl}{CH}-$$

Table 1 shows that the copolymers contain 0.12% Cl^{36} and 0.72% Cl^{36} respectively meaning that the copolymers also have Cl_A contents of 0.12% and 0.72% respectively. If exchange between allylic chlorine and Cl^{36} is complete, it should be possible to obtain a copolymer with double radioactivity, indicating that the radioactivity is entirely due to exchange involving Cl_A and not to secondary reactions.

The results for the copolymer with 0.12% Cl_A are presented in Table 2. Increase of the radioactivity (see Table 2) corresponded to a Cl_A content of 0.15%, confirming a quantitative exchange between Cl_A in the copolymer with Cl^{36}. A similar result was found for the copolymer with 0.72% Cl^{36}.

Table 1. Radioactivity of PVC macromodels with Cl_A and Cl_T obtained by copolymerization of vinyl chloride with 4*-chloropentine-1 and 2,4*-dicholoropentene-1

		Comonomer radioactivity				*Macromodel radioactivity*			
Comonomer	W_1 g	B_1 counts/min	R_1 counts/min	$ACl^*_{(M)}$ counts/g.min	W_2 g	B_2 counts/min	R_2 counts/min	$ACl^*_{(cop)}$ counts/g.min	$\frac{ACl^*_{(COP)}}{ACl^*_{(M)}} \times 100$
4*-chloropentine-1	0.09	45	1516	47,717	1.7963	39	96	55	Cl_A% = 0.12
		43	1519			41	97	55	
		47	1518			40	96		
4*-chloropentine-1	0.09	27	5820	188,211	0.7995	26	650	1367	Cl_A% = 0.72
		26	5850			26	653		
		26	5849			26	650		
		27	5822			26	640		
		26	5845			27	643		
2,4*-dichloropentene-1	0.2	27	5729	111,826	0.8855	34	965	1853	Cl_T% = 1.66
		28	5719			34	969		
		29	5751			33	965		
		28	5762			34			
		29				34			

$$ACl^*_{(M)} = \frac{(R_1 - B_1)}{W_1} \times \frac{100}{\%Cl^*}$$

$ACl^*_{(M)}$ = specific activity of chlorine in the comonomer.
$\%Cl^*$ = percentage of Cl^* in the comonomer.

$$ACl^*_{(cop)} = \frac{(R_2 - B_2)}{W_2} \times \frac{100}{\%Cl}$$

$ACl^*_{(cop)}$ = specific activity of chlorine in the copolymer labelled by synthesis.
$\%Cl$ = percentage of chlorine in the copolymer.
W_1, W_2 = weight.
B_1, B_2 = background.

Table 2. Determination of Cl_A and Cl_T contents in the macromodels

	$SOCl_2^{36}$				Polymer after labeling				
Weight W_1, g	B_1 counts/min	R_1 counts/min	$\Lambda Cl^*_{(SOCl_2^*)}$ counts/g.min	Sample nr[a]	W_2 g	B_2 counts/min	R_2 counts/min	$\Lambda Cl^{**}_{(cop)}$ counts/g.min	Content of Cl_A and Cl_T
						54	142		
				1	0.8427	53	140	182	$Cl^*_A\% = 0.15$
	47	9939				55	140		
0.198	45	9993	82,893						
	44	9909				27	478		
				2	0.3756	29	467	2090	$Cl^*_T\% = 0.29$
						29	478		

$$\Lambda Cl^*_{(SOCl_2^*)} = \frac{(R_1 - B_1)}{W_1} \times \frac{100}{\%Cl^*}$$

$$\Lambda Cl^{**}_{(cop)} = \frac{(R_2 - B_2)}{W_2} \times \frac{100}{\%Cl}$$

$$Cl_A\%, Cl_T\% = \frac{\Lambda Cl^{**}_{(cop)} - \Lambda Cl^*_{(cop)}}{\Lambda Cl^*_{(SOCl_2^*)}} \times 100$$

[a] 1—copolymer with 0.12% Cl_A obtained by synthesis.
2—copolymer with 1.66% Cl_T obtained by synthesis.

$\Lambda Cl^*_{(SOCl_2^*)}$ = specific activity of chlorine in $SOCl_2^*$.
$\%Cl^*$ = percentage of Cl^* in the $SOCl_2^*$.
$\Lambda Cl^{**}_{(cop)}$ = specific activity of chlorine in the copolymer after labelling with $SOCl_2^*$.
$\%Cl$ = percentage of chlorine in the copolymer.
$\Lambda Cl^*_{(cop)}$ = specific activity of chlorine in the copolymer labelled by synthesis.
W_1, W_2 = weight.
B_1, B_2 = background.

The copolymer obtained by copolymerization of vinyl chloride with 2,4*-dichloropentene-1 was used as PVC macromodel with Cl_T [4]. The characteristics of this copolymer are shown in Table 1.

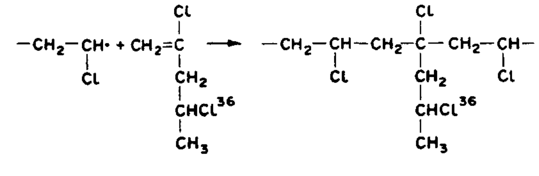

Table 1 shows that a copolymer with 1.66% Cl^{36} was obtained, and this must also be the Cl_T content.

As a result of the reaction between the copolymer with 1.66% Cl_T and $SOCl_2^{36}$, there is an increase of Cl^{36} (0.29%); results are presented in Table 2. The low content of Cl^{36} may be due either to the Cl_T not being labelled in the polymer or to it being lost as a result of dehydrochlorination.

To establish what happened to Cl_T after the polymer was treated with $SOCl_2^{36}$, a phenolysis reaction was undertaken to determine the labile chlorine content of the polymer [5]. Using the phenolysis, a value of 0.6% for the labile chlorine content was found; this result indicates dehydrochlorination of the copolymer with Cl_T, leading to a product with conjugated double bonds. These data indicate that chlorine in the vicinity of a double bond system is neither labelled with $SOCl_2^{36}$ nor is phenolysed, but has low reactivity.

We have used several solvents (cyclohexanone, tetrahydrofuran, dichloroethane, tetrachloroethane) for determining the optimum conditions for isotopic exchange between labile chlorine in PVC with $SOCl_2^{36}$. It has been established that cyclohexanone and tetrahydrofuran are not good solvents for this purpose because of secondary reactions, and that dichloroethane may be used as solvent for PVC labelling at room temperature.

Because the isotopic exchange is complete in 200 hr (Fig. 1), tetrachloroethane was used as solvent for reaction of PVC with $SOCl_2^{36}$ at 60°; under these conditions, approx. 90% isotopic exchange occurs in 1 hr (Fig. 1).

The results for PVC samples by this isotopic method are presented in Table 3; the allylic chlorine content lies between 0.12–0.16%, in good agreement with results by the u.v. method of phenolysed PVC [5].

The fact that the radioactivity of PVC treated with $SOCl_2^{36}$ is due to Cl_A labelling and not to a secondary reaction was verified by treating labelled PVC with

Table 3. Determination of allylic chlorine content in PVC

Sample	W, g	B counts/min	R counts/min	$\Lambda Cl^*_{(PVC)}$ counts/g.min	$\Lambda Cl^*_{(SOCl_2^*)}$ counts/g.min	$Cl_A\%$
		54	116			
Turda	0.7753	53	109	132	82,893	0.16
		56	110			
		54	121			
Breon	0.8723	53	115	129	82,893	0.16
		56	117			
		54	98			
Vipla	0.7406	53	101	100	82,893	0.12
		56	90			

$$\Lambda Cl^*_{(PVC)} = \frac{(R - B)}{W} \times \frac{100}{\%Cl}$$

$$Cl_A\% = \frac{\Lambda Cl^*_{(PVC)}}{\Lambda Cl^*_{(SOCl_2^*)}} \times 100$$

$\Lambda Cl^*_{(PVC)}$ = specific activity of chlorine in the PVC after labelling with $SOCl_2^*$.
$\%Cl$ = percentage of chlorine in the PVC.
W = weight.
B = background.

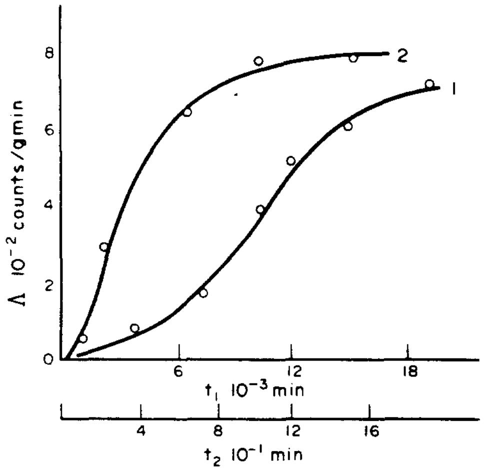

Fig. 1. Isotopic exchange in dichloroethane at 20° (1) and in tetrachloroethane at 60° (2).

unlabelled $SOCl_2$. Assay of the resulting PVC showed that the residual activity did not exceed 10% of the initial value.

EXPERIMENTAL

Copolymers with Cl_A and Cl_T in the chain were synthesized as previously [3, 4]. The copolymers and PVC were labelled thus: 1 g PVC was dissolved in 30 ml tetrachloroethane and 0.3 ml $SOCl_2^{36}$ were added to this solution. The reaction mixture was stirred for 3 hr at 60°. The samples were reprecipitated from tetrachloroethane–petroleum ether several times to give polymers with constant radioactivity. Measurements of radioactivity of PVC solutions in tetrahydrofuran were made with a liquid counter.

CONCLUSIONS

(1) Selective exchange of chlorine in PVC with $SOCl_2^{36}$ allows determination of allylic chlorine.

(2) $SOCl_2$ causes dehydroclorination of Cl_T structures in PVC.

(3) Chlorine in the vicinity of a conjugated double bond system is neither labelled with $SOCl_2^{36}$ nor phenolysed; this type of chlorine has a reactivity close to that of a secondary chlorine.

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