

Thermal Stability, Fractionation, and Chemical Modification of Chlorinated Rubbers. I. Infrared and ^{13}C -NMR Study of the Structure of Chlorinated Natural Rubber Modified under Various Experimental Conditions

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Synopsis

The structure of chlorinated natural rubber (CR) was studied by infrared and NMR spectroscopy. It was shown that the structure proposed by Troussier (thèse de Docteur-Ingénieur, Lyons, 1954) does not fit the ^{13}C -NMR characteristics of this compound. CR was fractionated and each fraction was characterized. The thermal stability of CR and the evolution of its structure in various experimental conditions was studied by NMR.

INTRODUCTION

Our purpose is both a fundamental study of the reaction of chlorinated natural rubber (CR) with aminoesters and an attempt to prepare antifouling coatings free from toxic agents.

The chemical modification of chlorinated polymers has been the subject of numerous studies during recent years. The ionic modifications have been received by Kennedy and Marechal.¹ On the other hand, the direct reaction of chlorinated polymers with amines and alcohols, which has already been widely studied,^{2,3} should undergo new and further development due to phase transfer techniques.^{4,5} Radical modifications are highly varied, but the most important are probably those which associate a chlorinated polymer with a metal, or a metal derivative, to generate free radicals. These were reviewed by Marechal.⁶ Their application to the modification of chlorinated natural rubber was the subject of a fundamental study by Nogues et al.,⁷ and they were used in the preparation of antifouling paints by Dawans et al.⁸

The present article reports a spectroscopic study of CR structure and of its dependence on experimental parameters. The second part of the series will describe the chemical modification of CR by aminoesters, and the third, its chemical modification by polyamides.

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EXPERIMENTAL

Infrared Spectroscopy

IR spectra were registered on a Perkin-Elmer 577 Spectrometer. Samples were either films between pellets of KBr or pellets prepared from ground polymer and KBr.

NMR Spectroscopy

¹H-NMR: Spectra were registered on a Varian A 60 Spectrometer, TMS as internal reference.

¹³C-NMR: Spectra (natural abundance) were registered on Fourier transform spectrometers (Brüker) at 25 and 62 MHz.

¹³C{¹H} experiments use a randomly modulated field to distribute the available power over the whole proton spectrum.

Off resonance, which results in a partial ¹³C{¹H} decoupling, was used to assign carbon resonances; it preserves the multiplicity of the signal.

Coupling constants J_{13C-H} were obtained by gated decoupling experiments; decoupling took place during a waiting period between the end of the acquisition time and before the excitation pulse.

¹³C-NMR Quantitative Analysis

It is a well-known fact that in routine ¹³C-NMR the area of a peak is not proportional to the number of nuclei which resonate at the corresponding frequency. Quantitative analysis is, however, possible provided that some precautions are observed:

—Addition of a relaxation reagent Cr(acac)₃ with [polymer]/[Cr(acac)₃] < 1 and [polymer] \simeq 30 g L⁻¹.

—Use of a flip angle = $\pi/2$ and a delay = 5 s.

CR Purification

CR (112 g) is dissolved in toluene (1 L), and this solution is poured into methanol (5000 mL); the precipitate is filtered off (95 wt %; Cl %: 64.5) and the residual soluble fraction (5 wt %; Cl %: 46.3) recovered by evaporation of the filtrate.

Thermal Stability of CR

CR (\simeq 5.5 g) dissolved in toluene (50 mL) is placed in a flask (250 mL) swept by a nitrogen stream and heated at a controlled temperature for 8 h. Experimental conditions used for each sample are given in Table I.

RESULTS AND DISCUSSIONS

Bibliographic Survey

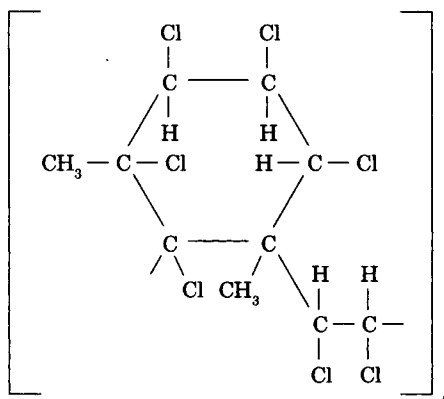
Chemical modification of chlorinated polymers by amines has been the subject of several fundamental studies (see Refs. 9–12). However, we could not find any such work relative to the reaction of amines with CR; this is

TABLE I

CR (g)	Ca stearate (g)	T (°C)	Yield (wt %)		Cl (%) precip.
			Precipitated	Nonprecipitated	
5.6	—	50	94	6	63.5
5.6	—	80	91	9	62
5.6	—	100	90	10	62.2
5.6	—	120	95	5	62.6
5.5	1.12	120	94	6	58.2

probably due to the characteristics of this compound which make its chemistry particularly difficult.

Its structure remains widely unknown, in spite of several studies.¹³⁻¹⁶ From these, and particularly from Refs. 14-16, it has been concluded¹⁶ that CR contains mainly cyclized units:



This structure corresponds to the general formula $(C_{10}H_{11}Cl_7)_n$ and to a chlorine content of 65.5%, in agreement with the values relative to industrial compounds (63-68%).

However some recent IR and ^{13}C -NMR studies of CR with different chlorine contents (13.3-57.5%) by Wartenberg¹⁷ showed that the real structure of CR is probably very different. This study not only showed that CR contains side vinyl groups such as $\sim CH - \underset{CH_2}{C} - CH_2CH_2 \sim$ but, above all, that the

presence of the cyclic structures previously claimed does not fit spectroscopic data, since ^{13}C -NMR spectroscopy shows that only two types of quaternary carbons (vinylic and chlorinated) are present. No quaternary carbon belonging to a ring was observed. It can be put forward that CR could contain nonchlorinated six-membered rings; however, an exhaustive review of all the possibilities showed that this is impossible. Another objection is that macrocyclic structures with nonchlorinated quaternary atom could exist; this is not in opposition with our spectroscopic observations since such structures might not be detected by ^{13}C -NMR, the concentration of the characteristic atoms being far below the sensitivity of this technique. However, the probability of formation of such structures is very slight.

Whatever the real structure of CR is, it was important to dispose of an accurate analytical techniques to follow its structural evolution as the chlorination proceeds.

We will now examine the two main technics that we used: IR spectroscopy and $^{13}\text{C-NMR}$.

Infrared Study of CR

Main characteristics of the IR spectrum of nonpurified CR are reported in Table II.

The very weak absorptions at 1730 and 1630 cm^{-1} are due to impurities and are no longer present in purified CR Wartenberg¹⁷ concluded from a study of the evolution of the spectrum with chlorine content that bands at 780, 750, and 730 cm^{-1} are respectively due to the secondary C—Cl, the primary C—Cl, and the rocking of CH_2 .

$^{13}\text{C-NMR}$ Study of CR

Description of the Spectrum. $^{13}\text{C-NMR}$ spectrum (solution C_6D_6) is reported in Figure 1 and its main characteristics are given in Table III.

C_6D_6 spectrum overlaps the unsaturated carbon patterns; however, the spectrum of CR in CDCl_3 revealed that no unsaturated carbons are present in this compound. To identify the various peaks, we used Velichko's results relative to different chlorinated hydrocarbons.^{18,19}

Examination of $^{13}\text{C-NMR}$ spectrum leads to several remarks:

(1) Peaks are very broad and remain so when temperature increases. The chemical shift of a carbon atom is very sensitive to the substitution of one or several hydrogens by chlorine, whether this takes place on the carbon itself (35.5 ppm) or on a carbon in α (+ 10 ppm) or even in β position (− 3.5 ppm). The width of the peaks is due to the very large number of structures present in CR. However, we were to identify most patterns and attributions fit those of Velichko et al.^{18,19}

(2) Peaks at 74 and 77 ppm are due to the quaternary carbons linked to

TABLE II
Main Characteristics of the IR Spectrum of Nonpurified CR^a

cm^{-1}	Assignments
2940 m	$\nu_{\text{C-H}}$
1730 vw	$\nu_{\text{C=O}}$
1630 vw	$\nu_{\text{C=C}}$
1430 s	$\delta_{\text{C-H}}$
1375 m	
1260 s	
1180 m	
930 m	
780 s	$\nu_{\text{C-Cl}}$
750 s	
+ 730 s	
660 m	r_{CH_2}

^a s = strong, m = medium, vw = very weak.

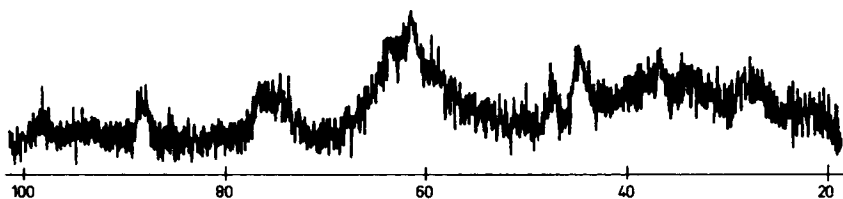


Fig. 1. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of nonpurified CR (C_6D_6 , room temperature). Ref. $\delta_{\text{C}_6\text{D}_6} = 128$ ppm.

a single chlorine atom; carbons linked to several chlorine atoms would appear at lower fields.

(3) Peaks at 63 and 64 ppm are due to $>\text{CHCl}$ groups since coupling constants $J_{^{13}\text{C}-\text{H}}$ do not exceed 150 Hz excluding the presence of $-\text{CHCl}_2$ groups whose coupling constants would be in the range 170–180 Hz.

Troussier's cyclic structure¹⁶ implies that to each ring corresponds a non-chlorinated quaternary carbon; this point has already been discussed⁴ and is confirmed by the results reported in the present article.

(4) Nogues²⁰ mentioned the presence of residual CCl_4 in nonpurified CR. However, ^{13}C -NMR spectrum does not exhibit the corresponding sharp peak at 96 ppm.

Determination of the Empirical Formula. Spectra are recorded in conditions (see Experimental) such that the areas of peaks are proportional to the number of the corresponding atoms; this allows the determination of empirical formulae which are reported in Table VIII.

Purification of CR Analysis of the Different Fractions

Purification is carried out by adding methanol to a solution of CR in toluene or chlorobenzene, which results in precipitation of most of the polymer. The characteristics of each fraction are reported in Table IV.

Like Nogues²⁰ we observed that a very small fraction of CR (0–5%) is insoluble in toluene. IR spectrum of this fraction shows that it contains species with a high degree of insaturation (1630 cm^{-1}) and oxydation (1730 cm^{-1}) and a very low chlorine content.

Since nonfractionated CR has a chlorine content equal to 67.5, it appears that part of the chlorine has been lost during fractionation. This could be due to the diminution of very light compounds during the evaporation of methanol (degradation product or impurity).

TABLE III
Main Characteristics of the $^{13}\text{C}\{^1\text{H}\}$ -NMR Spectrum of Nonpurified CR

Chemical shifts (ppm)	Assignments	Multiplicity ^a	$J_{\text{C}-\text{H}}$ (Hz)
28–33–37	$-\text{CH}_2-$, $-\text{CH}_3$	Multiplet	
45–48	$-\text{CH}_2\text{Cl}$	Triplet	
62–64	$-\text{CHCl}-$	Doublet	151
74–77	$>\text{CCl}-$	Singlet	
87	$>\text{CCl}_2$	Singlet	
98	$-\text{CCl}_3$	Singlet	

^a Determined by off-resonance technique.

TABLE IV
Characteristics of the Precipitated and Nonprecipitated Fractions in CR

Fraction	Yield (wt %)	% Cl ^a	$\eta_{(\text{toluene})}$ (100 cc g ⁻¹)
Precipitated	95	64.5	0.2
Nonprecipitated	5	46.3	—

^a % Cl was obtained by elementary analysis.

TABLE V
Main Characteristics of the IR Spectrum of PCR^a

Wave number (cm ⁻¹)	Assignment
2940 m	$\nu_{\text{C-H}}$
1600 vw	$\nu_{\text{C-C}}$
1480 vw	
1430 s	$\delta_{\text{C-H}}$
1370 w	
1260 s	
1180 w	
930 m	
780 m	$\nu_{\text{C-Cl}}$ + ν_{CH_2}
730 s	
690 m	
460 vw	

^a s: strong; m: medium; w: weak; vw: very weak.

In this article most experiments will be carried out on the precipitated fraction which will be labeled purified CR or PCR. The main characteristics of the IR spectrum of PCR are reported in Table V. With respect to the spectrum of non-purified CR we observed a very important decrease of the absorption at 750 cm⁻¹.

On the other hand, we recorded the infrared spectrum of the fraction soluble in methanol which exhibits a strong absorption at 1720 cm⁻¹ and a medium absorption at 1610 cm⁻¹; these two bands are present in the spectrum of nonpurified CR. In C—Cl vibration area, absorptions are observed at the same frequencies both in precipitated and nonprecipitated fractions. The band 780 cm⁻¹ has a very low intensity in nonprecipitated CR whereas its absorption is very high in nonpurified CR. The ¹³C-NMR spectrum of PCR is reported in Table VI. The main difference between the spectra of purified and nonpurified CR is the absence of >CCl₂ and —CCl₃ groups.

TABLE VI
¹³C-NMR Spectrum of PCR

Chemical shift (ppm)	Assignment
21.5–28–34.7–37.4	CH ₂ + CH ₃
45.4–48	—CH ₂ Cl
62–64	>CHCl
74–77	>CCl—

TABLE VII
¹³C-NMR Study of Thermal Behavior of CR in Different Experimental Conditions Used for Grafting^{17,a}

Group	CR	PCR	CR 50°C, 8 h	CR 80°C, 8 h	CR 100°C, 8 h	CR 120°C, 8 h	CR + CaSt, 120°C, 8 h	CR (70%) + CaSt (7%) + Φ Cl ₃ (13%), 120°C, 20 min	CNC + piperidine, 25°C, 17 h
—CCl ₃	3.3	—	—	—	—	—	—	—	—
>CCl ₂	3.3	—	—	—	—	—	—	—	—
>CCl—	8.5	15.6	16.6	13.4	11.2	10	18.6	8.7	15
—CHCl—	35	31	34.7	37	33.3	30	38.6	28.8	24.5
—CH ₂ Cl	12.4	21.9	18.3	15	15.4	17	19.4	14.7	14.8
—CH ₂ + —CH ₃	37.6	31	30	34.6	40	43	23.6	47.8	45.7

^a CaSt is calcium stearate. CR is nonpurified chlorinated rubber. Solvent is toluene with the exception of last column but one where the reaction was carried out in the bulk for 20 min.

TABLE VIII
Empirical Formulas of the Samples Before and After Different Thermal Treatments

Experimental conditions	Empirical formulas ($^{13}\text{C-NMR}$)	% Cl, elem anal	% Cl, $^{13}\text{C-NMR}$
CR	$\text{C}_{10}\text{H}_{14.5}\text{Cl}_{6.4}$	67.5	66.1
PCR	$\text{C}_{10}\text{H}_{13.7}\text{Cl}_{6.8}$	64.5	64.4
CR in toluene/ N_2 , 8 h			
50°C	$\text{C}_{10}\text{H}_{13.2}\text{Cl}_{6.9}$	63.5	64.8
80°C	$\text{C}_{10}\text{H}_{13.6}\text{Cl}_{6.5}$	62	63.3
100°C	$\text{C}_{10}\text{H}_{14.4}\text{Cl}_6$	62.2	61.3
120°C	$\text{C}_{10}\text{H}_{14.9}\text{Cl}_{5.6}$	62.6	60.0
CaSt 120°C, 8 h	$\text{C}_{10}\text{H}_{15.2}\text{Cl}_{5.4}$	58.2	58.6
CR in bulk + StCa + ΦCl_3 , 120°C	$\text{C}_{10}\text{H}_{15.4}\text{Cl}_{5.2}$	58.4	57.7

On the whole, these analysis show that the purification of CR by precipitation eliminates the small chains bearing unsaturated oxydized or polychlorinated groups. The highest fractions, which are highly chlorinated, were eliminated during the evaporation of the methanol.

$^{13}\text{C-NMR}$ Study of Thermal Stability of CR

The study was carried out on nonpurified CR. Each sample was heated to a chosen temperature for 8 h (see Experimental); then the polymer was precipitated by addition of methanol, and the precipitated fraction analyzed. Each temperature corresponds to the experimental conditions used in the chemical modification (Paper II²¹).

$^{13}\text{C-NMR}$ determinations relative to the different groups contained in the sample are reported in Table VII and Figure 2.

As soon as temperature rises, $-\text{CH}_2\text{Cl}$ content decreases; however, above 80°C there is no further change, showing that at least two types of $-\text{CH}_2\text{Cl}$ are present and that some are very unstable.

The percentages of $-\text{CCl}$ decrease linearly above 50°C and 80°C, respectively. The $^{13}\text{C-NMR}$ spectrum of a sample which was kept at 80°C for 8 h

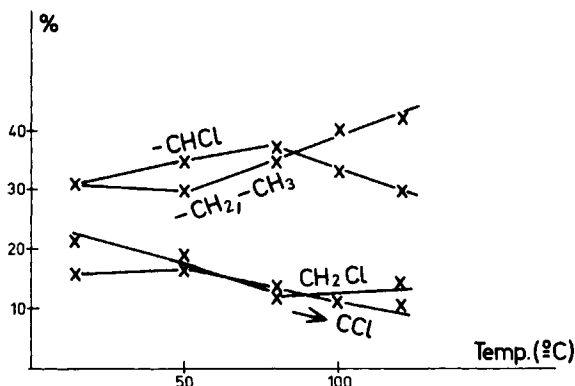


Fig. 2. $^{13}\text{C-NMR}$ study of nonpurified chlorinated rubber. Contribution of the different groups with respect to temperature.

shows that this does not contain unsaturations. From ^{13}C -NMR spectra we determined the empirical formulas of the samples; the results which are reported in Table VIII fit elementary analysis.

Calcium stearate is a stabilizer of poly(vinyl chloride) whose thermal dechlorination processes are probably similar to those of CR. Calcium stearate is not the most efficient stabilizer for PVC, but it does not induce secondary phenomena, which is the reason for our choice. The mechanisms of its action have been analyzed in several articles, one of which, by Michel,²² is particularly important. From the experiments we carried out, it appears that in solution the addition of calcium stearate does not improve the results and it is better to avoid its presence; it would be, however, impossible to carry out reactions in the bulk without it.

References

1. J. P. Kennedy and E. Marechal, *Carbocationic Polymerization*, Wiley, New York, 1981, Chap. 8.
2. H. Kawabe, *Bull. Chem. Soc. Jpn.*, **49**, 2043 (1976) and preceding articles.
3. S. Dragan, I. Petrariu, and M. Dima, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 3077 (1972).
4. T. D. N'Guyen, A. Deffieux, and S. Boileau, *Polymer*, **19**, 423 (1978); *Tetrah. Lett.*, **28**, 2651 (1979).
5. J. M. J. Frechet, *J. Macromol. Sci. Chem. A*, **15**, 877 (1981).
6. E. Marechal, *IUPAC Macromolecules*, H. Benoit and P. Rempp, Eds., Pergamon, New York, 1982, p.85.
7. P. Nogues, F. Dawans, and E. Marechal, *Makromol. Chem.*, **182**, 843, 3481 (1981); **183**, 549 (1982).
8. F. Dawans, M. Devaud, and D. Nicolas (Institut Français du Pétrole), Fr. Pat. 2, 401, 207; U.S. Pat. 4262097 (1977); *Chem. Abstr.*, **90**, 188673g (1979).
9. G. Salomon and A. J. Ultee, *Rec. Trav. Chim.*, **70**, 537-544 (1951).
10. I. Noda and I. Kagawa, *J. Chem. Soc. Jpn.*, **41**, 1518 (1968).
11. H. Kawabe and M. Yaganita, *Bull. Chem. Soc. Jpn.*, **41**, 1518 (1968).
12. P. Kriston, A. Kocskina, and M. Dimitov, *J. Appl. Polym. Sci.*, **14**, 2768 (1970).
13. H. and Hj. Staudinger, *J. Prakt. Chem.*, **162**, 148 (1943).
14. E. H. Farmer, *Adv. Colloid Sci. (N.Y.)*, **2**, 304 (1946).
15. R. Alliot and L. Orsini, *J. Chem. Phys.*, **49**, 422 (1952).
16. M. Troussier, thèse de Docteur-Ingénieur, Lyons, 1954.
17. C. Wartenberg, D.E.A., Université Paris VI, 1981; C. Wartenberg and M. Brigodiot, unpublished results.
18. F. K. Velichko, E. G. Chukovskaya, V. I. Dostovalova, N. A. Kuzmina, and R. Kh. Freidlina, *Org. Mag. Res.*, **7**, 361 (1975).
19. F. K. Velichko, V. I. Dostovalova, N. A. Kzmina, E. I. Fedin, and R. Kh. Freidlina, *Org. Mag. Res.*, **7**, 46 (1975).
20. P. Nogues, Thèse de Docteur-Ingénieur, Paris, 1979; and P. Nogues, F. Dawans, and E. Marechal, *Makromol. Chem.*, **182**, 843 (1981).
21. S. Makani, M. Brigodiot, E. Maréchal, J.-P. Durand, and F. Dawans, *J. Appl. Polym. Sci.*, **29**, 4091 (1984).
22. A. Michel, *J. Macromol. Sci. Chem.*, **A**, **12**, 361 (1978).

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