

# Chemical Modification of Chlorinated Rubbers. II.

## Study of Chlorinated Natural Rubber Modified by Amino-Esters

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### Synopsis

The synthesis of ethyl-11-aminoundecanoate and ethyl-3-aminobutyrate and the chemical modification of chlorinated natural rubber by these amino-esters were investigated in order to find useful materials for long-life antifouling paints free from toxic moieties. Detailed reactions and fractionation schemes are described for isolating pure products; their structure was characterized by IR and NMR spectrometries.

### INTRODUCTION

In the first part of this series,<sup>1</sup> we reported the results concerning some structural changes in chlorinated natural rubber (CR) and in related products under various experimental conditions.

The purpose of the present investigation is the chemical modification of CR by some amino esters to obtain useful products to make CR compatible with polyamides and to manufacture of a long-life antifouling paint free from toxic agents.

Indeed the products providing antifouling protection to underwater areas are of importance since the vegetable and animal species, which usually proliferate on hulls and submerged equipments, create problems due to the increase of both weight and roughness, thus to increasing resistance to moving water and currents. For instance, improving the lifetime and efficiency of marine antifouling paints is a very important goal for energy saving since the fuel used for the propulsion of a ship could be decreased by 20% if its bottom is continuously kept clean of marine fouling.<sup>2</sup>

Efficient protection against marine animal fouling can be obtained by the inclusion of hydrolyzable toxic moieties in the coating. This creates a continuous layer of biocid agents in the immediate neighborhood of the surface to be protected. To improve control of lixiviation, i.e., the release of the toxic compound in the aqueous phase, the use of coatings where the biocid agent is chemically bonded to a polymer has been developed in recent years.

However, the development of a second generation of antifouling paints not containing toxic agents remains of great interest for the biological

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protection of the marine environment, as well as for a further increase in lifetime of the coatings. This goal seems feasible as the result of previous research on the attachment mechanism of foulings on a surface. Indeed, besides preventing initial attachment by using specific biocid chemicals or repellents, another technical approach can be taken, namely, interfering with the hardening of the binding cement and developing surfaces having free energy values such that fouling cements cannot adhere.

Our initial observations about the adverse effect on marine organism attachment caused by some polyamides prompted us to search for polyamide materials applicable, as a coating to which these organisms would not adhere by means of their proteinaceous cement.<sup>3</sup>

However, taking into account the poor adhesion of polyamides on the CR layer most often used as a primer for protection against corrosion, we investigated the synthesis of polyamide-modified CR either as an antifouling paint coating or as a compatibilizing layer promoting adhesion between the CR layer and a polyamide sheet. On this basis, the chemical modification of CR was studied, mostly by amino esters which are more soluble than amino acids in the usual solvents for CR.<sup>4</sup>

## EXPERIMENTAL

### Synthesis of Ethyl-11-Aminoundecanoate

A mixture of 11-aminoundecanoic acid (30 g), absolute ethanol (350 cc), toluene (200 cc), and hydrochloric acid (12*N*, 20 cc) is refluxed for 5 h. All solvents are then evaporated, and the residual compounds dried off. Reaction water is eliminated as a ternary mixture (water-ethanol-toluene). Then an ethanol-toluene mixture is added, and, after a 5-h reflux, the mixture is dried off. After a third addition of ethanol and toluene, the solvents are distilled off and the aminoester hydrochloride (AEHC) dissolved in chloroform. After the elimination of chloroform, AEHC is crystallized in methyl acetate. Its main characteristics are mp 144–146°C (lit. 145°C).

ANAL. Calcd. for  $C_{13}H_{28}O_2NCl$ : C 58.76, H 10.53, O 12.5, Cl 13.37 wt %. Found: C 58.7, H 10.7, N 5.5, O 12.2, Cl 13.7 wt %.

To obtain free amino ester, a chloroformic AEHC solution is neutralized by the addition of an aqueous solution of sodium carbonate and dried on sodium sulfate. The chloroform is then distilled off and an amino, amido mixture (mp 68°C) is obtained. The sublimation of this mixture gives ethyl-11-aminoundecanoate: mp 72°C.

ANAL. Calcd. for  $C_{13}H_{27}O_2N$ : C 68.12, H 11.79, N 6.11, O 13.97 wt %. Found: C 65.9, H 10.9, N 5.7, O 17.7, Cl 0.30 wt %.

### Ethyl-3-Aminobutyrate

We used Aldrich compound, which is a liquid containing some solid particles of oligomers.

ELEMENT. ANAL. Calcd. for filtrate  $C_6H_{13}O_2N$ : C 54.96, H 9.92, N 10.68 wt %. Found: C 54.4, H 9.9, N 10.1 wt %.

The small divergence between theoretical and experimental value may be due to the presence of dimer and trimer in the monomer, since only the

tetramer is insoluble. For the chemical modifications, we mostly used the filtrate as such, but we were able to purify it further by a distillation under reduced pressure.

### Reaction of Chlorinated Polymers with Amino-Esters and Amines

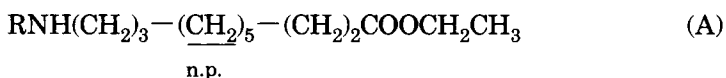
The following compounds are successively introduced into a reaction flask: chlorinated polymer (5.6 g), amino ester or amine (8 g), toluene or chlorobenzene (50 cc). The solution is heated to the reaction temperature under nitrogen and with permanent stirring.

At the end of the reaction, the products are separated according to the following scheme: the reaction mixture is poured in an excess of methanol and then filtered off via a glass plate funnel to isolate the insoluble fraction, which is thoroughly washed several times with methanol and dried under reduced pressure till constant weight is obtained. This insoluble fraction in methanol corresponds to a high molecular weight graft copolymer. On the other hand, the soluble fraction in methanol is evaporated under reduced pressure till dryness is obtained, and the residual solid is then dissolved in methyl-ethyl-ketone (MEK). Again this solution is filtered off to isolate an insoluble fraction corresponding to the unreacted amino compound, and a soluble fraction which is evaporated under reduced pressure till dryness is obtained and which corresponds to a low molecular weight graft copolymer.

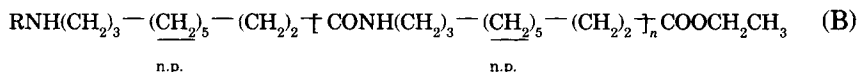
### Characterization of the Products

$^{13}\text{C}$ -NMR (qualitative and quantitative),  $^1\text{H}$ -NMR, and IR spectroscopies were carried out as reported in Paper I.<sup>1</sup> The determination of amide content was performed in both the amino ester (which is in fact a mixture of monomer amino ester and of polycondensed amino-amido-ester), and the grafted CR.

Two types are considered:



and



where  $\text{R} = \text{H}$  or  $\text{CR}$ .

Let  $a$  and  $b$  be the number of A and B species, respectively. Then  $(a + b)$  is the number of carbonyl groups which can be identified by  $\text{C}=\text{O}$ ,  $\text{CH}_2$ , and  $\text{CH}_3$  groups binded to ester functions. The central  $\text{CH}_2$  groups, non-perturbed (n.p.) by amine or amide groups are observed at the same frequency and their numbers are equal to  $5a$  in A species and to  $5b + 5bn$  in B species.

The areas of both peaks can be compared if they correspond to carbon atoms during approximately the same relaxation time. We chose to compare nonperturbated  $\text{CH}_2$  with ester  $\text{CH}_2$ . Let  $y$  and  $z$  be the areas of peaks,

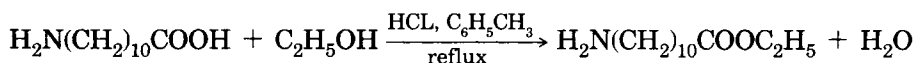
respectively, relative to ester  $\text{CH}_2$  (59.9 ppm) and to n.p.  $\text{CH}_2$  (29.2 ppm),  $a + b = \alpha y$  and  $5(a + b + bn) = \alpha Z$

$$\text{leading to } bn \% = \frac{z - 5y}{z} \times 100$$

## RESULTS AND DISCUSSION

### Ethyl-11-Aminoundecanoate

According to Carriere,<sup>5</sup> the compound can be obtained by a standard esterification process:

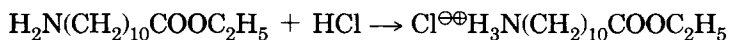


which gives a white product (mp 68°C).

By using this experimental process as described,<sup>5</sup> we obtained the same compound (mp 68°C), but we found that its characteristics were not those expected for ethyl-11-aminoundecanoate.

In fact, two side reactions can take place:

- (1) Protonation of the amine group by the catalyst



This reaction is confirmed by both the IR spectrum (Fig. 1) of the hydrochloride which exhibits absorption bands  $\nu\text{NH}_3^{\oplus}$  at 3200–3000  $\text{cm}^{-1}$  and  $\nu\text{C}$  [ester at 1730  $\text{cm}^{-1}$ , as well as the  $^{13}\text{C}$ -NMR spectrum (Fig. 2) which shows the following peaks ( $\delta$  ppm): 173.1 (carbonyl), 59.5 ( $\alpha$ -methylene carbon of an ester group), 39.9 (carbon in  $\alpha$ -position of  $-\text{NH}_3^{\oplus}\text{Cl}$ ).

(2) Polycondensation of the aminoester. To obtain the free amine, the hydrochloride is treated with an aqueous solution of sodium carbonate. The IR spectrum of the resulting compound (Fig. 3) shows absorption bands clearly showing that it is not the expected amino ester. There is only one absorption band at 3250  $\text{cm}^{-1}$  instead of the three bands which would correspond to the  $-\text{NH}_2$  group. Moreover, two  $\text{C}=\text{O}$  bands are observed:  $\nu_{\text{C}=\text{O}}$  (ester) at 1750  $\text{cm}^{-1}$  and  $\nu_{\text{C}=\text{O}}$  (amide) at 1630  $\text{cm}^{-1}$ .

In the  $^{13}\text{C}$ -NMR spectrum (Fig. 4), two peaks located at  $\delta$  ppm 173.7 and

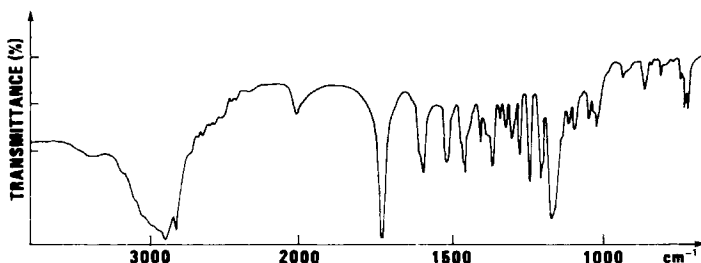


Fig. 1. Infrared spectrum of ethyl-11-aminoundecanoate hydrochloride (KBR pellet).

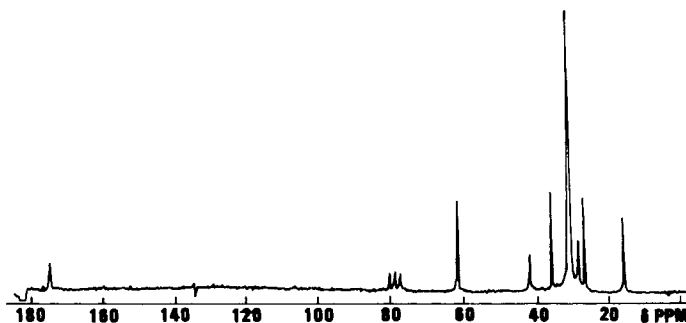
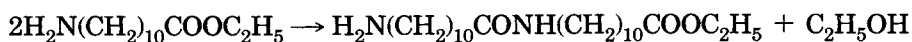


Fig. 2.  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR spectrum of ethyl-11-aminoundecanoate hydrochloride in solution in  $\text{CDCl}_3$  ( $\delta_{\text{CDCl}_3} = 76.9$  ppm).

173.1 confirm the presence of two CO groups. In fact, the presence of both ester and amide groups could result from the following reaction:



which could be catalyzed by  $\text{Na}_2\text{CO}_3$ .  $^{13}\text{C}$ -NMR quantitative analysis of the mixture showed an amide group content equal to 45 wt %.

We succeeded in obtaining amide-free ethyl-11-aminoundecanoate (mp  $72^\circ\text{C}$ ) by sublimating the mixture. To our knowledge, this is the first time that this amino ester has been isolated as a pure product. Unfortunately, a large part of this compound was self-polycondensated during the sublimation treatment. That is the reason why the overall yield remains below 20 wt %.

The main characteristics of the IR spectrum of pure ethyl-11-aminoundecanoate (Fig. 5) are given in Table I. It is very important to point out that there is only one CO band (ester at  $1760\text{ cm}^{-1}$ ), and two bands between  $3260$  and  $3400\text{ cm}^{-1}$ , and a shoulder which are characteristic of primary amino groups. This observation proves unambiguously that the compound is free of amido groups. The characteristics of  $^{13}\text{C}$ -NMR spectrum (Fig. 6) are given in Table II.

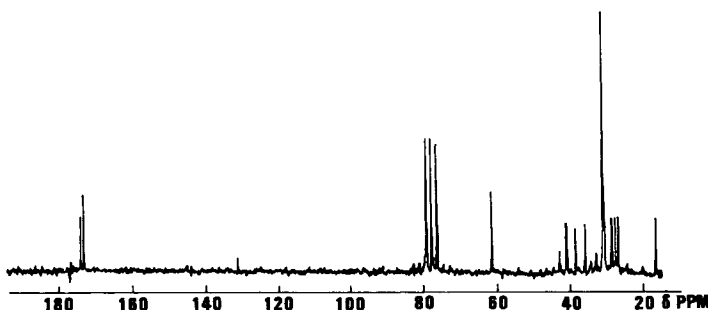


Fig. 3. Infrared spectrum of the EA mixture resulting from the treatment of ethyl-11-aminoundecanoate hydrochloride by aqueous  $\text{Na}_2\text{CO}_3$  solution (KBr pellet).

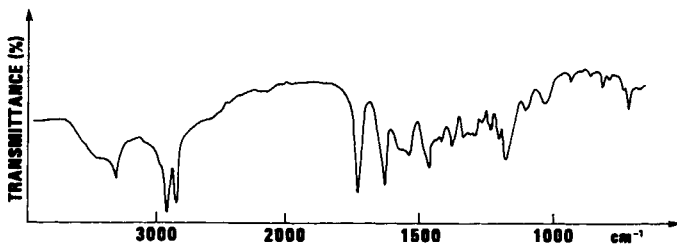


Fig. 4.  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR spectrum of the same mixture as in Figure 3.

The characteristics of  $^1\text{H}$ -NMR spectrum of pure ethyl-11-aminoundecanoate are given in Table III.

The attribution of  $\text{NH}_2$  protons is confirmed by the addition of deuterated water,  $\text{D}_2\text{O}$ , which suppresses the peak located at 4.5 ppm.

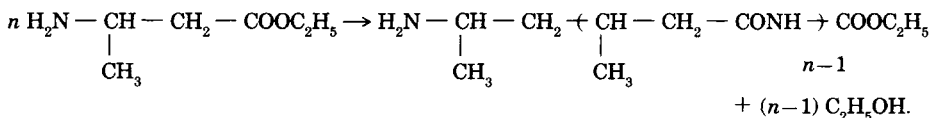
In conclusion, all the results reported in Tables I-III fully confirm the structure of the amino-ester.

However, ethyl-11-aminoundecanoate polycondenses so easily that a partial polycondensation cannot be avoided during its reaction with CR. Thus, we carried out most of the modifications starting from the mixture (mp  $68^\circ\text{C}$ ), labeled further as AE, and contained amino ester together with some amido, amino ester.

The solubility of AE in toluene was determined at several temperatures:  $0.8 \text{ g L}^{-1}$  ( $20^\circ\text{C}$ ),  $2.83 \text{ g L}^{-1}$  ( $50^\circ\text{C}$ ),  $27.89 \text{ g L}^{-1}$  ( $80^\circ\text{C}$ ).

### Ethyl-3-Aminobutyrate

We used a commercial compound which is partly oligomerized at room temperature:



$^{13}\text{C}$ -NMR spectrum of the monomer containing oligomers shows peaks due to CO (amide and ester) groups in the range of 170–172 ppm.

IR spectrum of pure ethyl-3-aminobutyrate obtained by distillation under reduced pressure (17 torr,  $78^\circ\text{C}$ ) shows absorption bands at frequencies given in Table IV. Peaks of  $^{13}\text{C}$ -NMR spectrum are given in Table V.

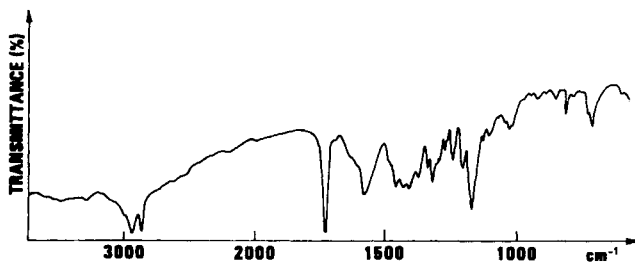


Fig. 5. Infrared spectrum of pure ethyl-11-aminoundecanoate.

TABLE I  
Main Frequencies of the Infrared Spectrum of Pure Ethyl-11-Amino-Undecanoate<sup>a</sup>

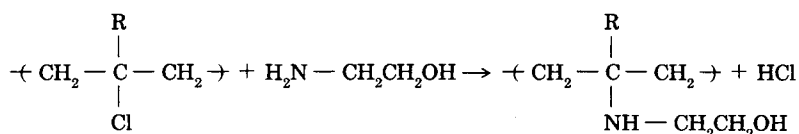
Wave number (cm <sup>-1</sup> )		Attributions
3360 } 3260 }	Broad bands	$\nu_{\alpha, N-H}$ $\nu_{s, N-H}$ Fermi resonance
2920 w		
2840 w		
1760 vs		$\nu_{C=O}(\text{ester})$
1580 m		$\delta_{N-H}(\text{amine})$
1410 m		$\delta_{C-H}$
1175 vs		$\nu^{\beta}_{C-O-C}$
1030 w		$\nu_{C-N}(\text{amine})$
725 m		$\delta_{N-H}(\text{amine})$

<sup>a</sup> vs = very strong; s = strong; m = medium; w = weak.

### Reaction of CR with Amino-Esters

Several previous publications have been concerned with the reaction of chlorinated polymers with amino esters. Among them, we review here some basic studies. Noda and Kagawa<sup>6</sup> have studied the kinetics of the quaternization of chloromethylated polystyrenes by aliphatic tertiary amines. Investigating the kinetics of the amination of chlorinated polystyrenes by secondary and primary amines, Kawabe and Yaganita<sup>7</sup> have defined the optimal conditions for getting a quantitative amination, as follows: low polymer concentration; use of an amine with a bulky alkyl group.

Kriston et al.<sup>8</sup> studied the chemical modification of chlorinated polystyrenes by amines to improve the anticorrosion properties of these compounds. They used mono-, di-, and triethanolamine, butylamine, diethylamine, and triethylamine. The best results were obtained with monoethanolamine and butylamine. According to these authors, the following reaction takes place:



Salomon and Ultee<sup>9</sup> studied the reaction of piperidine with chlorinated paraffins. Depending on the temperature, two reactions can take place:

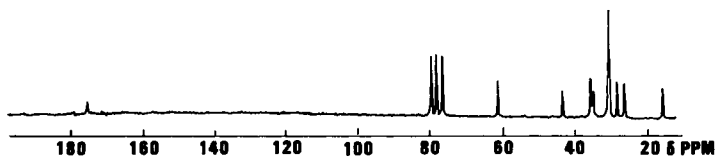
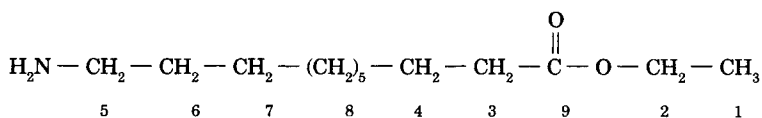


Fig. 6. <sup>13</sup>C (<sup>1</sup>H) NMR spectrum of pure ethyl-11-aminoundecanoate (CDCl<sub>3</sub>, Ref.  $\delta_{\text{CDCl}_3}$  = 76.9 ppm).

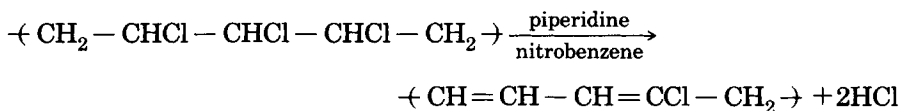
TABLE II  
Characteristics of  $^{13}\text{C}$  ( $^1\text{H}$ ) Spectrum of Pure Ethyl-11-Aminoundecanoate<sup>a</sup>:



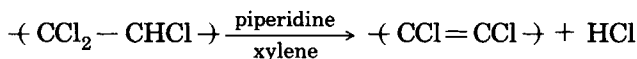
$\delta$ (ppm)	Attributions
14.1	1
24.8	4
26.7	7
29.2	8
33.7	6
34.7	3
42.1	5
59.9	2
173.7	9

<sup>a</sup>  $\text{CDCl}_3$  solution, Ref.  $\text{CDCl}_3$ ,  $\delta = 76.9$  ppm.

— at  $100^\circ\text{C}$ :



— at  $20^\circ\text{C}$ :



They are dehydrochlorination reactions catalyzed by a secondary amine.

We carried out the same reaction on CR in toluene at  $25^\circ\text{C}$ .  $^{13}\text{C}$ -NMR spectrum of the insoluble fraction in methanol showed some unsaturation peaks but also peaks characteristic of piperidine, indicating that part of the amine is bonded to CR. Thus both elimination and substitution reactions take place at room temperature. In fact, the simultaneous existence of these two concurrent reactions played an important role in our work.

TABLE III  
Characteristics of  $^1\text{H}$ -NMR Spectrum of Pure Ethyl-11-Aminoundecanoate<sup>a</sup>

$\delta$ (ppm) (ref. TMS)	Multiplicity	Attribution (numbers as in Table II)
1.10	Broad peak	$\text{CH}_3^1$
1.30	—	$\text{CH}_2^{4-8}$
2.25	Triplet	$\text{CH}_2^3$
2.80	Broad peak	$\text{CH}_2^5$
4.18	Quadruplet	$\text{CH}_2^2$
4.50	Broad peak	$-\text{NH}_2, \text{H}_2\text{O}$

<sup>a</sup>  $\text{CDCl}_3$  solution; Ref. TMS.



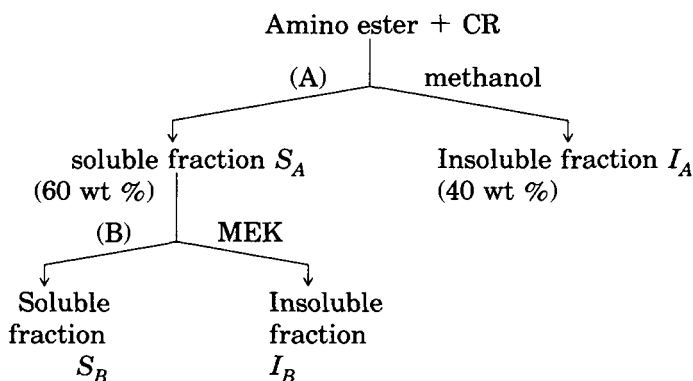
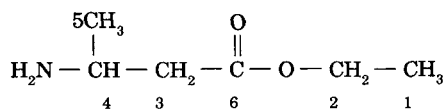
TABLE IV  
 IR Spectrum of Pure Ethyl-3-Aminobutyrate

Wave number (cm <sup>-1</sup> )	Attribution
3340 m	N—H (amine)
3260 w	
2960 vs	C—H
1720 vs	C=O (ester)
1580 w	N—H
1440 w	C—H
1360 m	C—H (methyl)
1300 m	C—O—C
1170 m	
1030 m	C—N

<sup>a</sup> vs = very strong; s = strong; m = medium; w = weak.

*Reaction of CR with Ethyl-<sup>11</sup>-Aminoundecanoate*

**General Behavior of the Reactional Systems.** In Experimental, we gave a detailed scheme describing the successive steps in the separation of the different components formed in the reaction mixture. This is essential for the interpretation of both structural and kinetic results. For easy reading, we summarize below the main steps as well as the referenced products of the above-mentioned scheme:


 TABLE V  
 Characteristics of <sup>13</sup>C (<sup>1</sup>H)-NMR Spectrum of Pure Ethyl-3-Aminobutyrate:


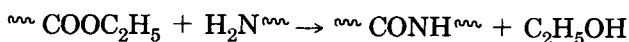
$\delta$ (ppm)	Attribution
14.3	1
23.7	5
44.5	4 <sup>a</sup>
44.8	3 <sup>a</sup>
59.9	2
172.1	6

<sup>a</sup> These attributions were confirmed by off-resonance techniques. CD Cl<sub>3</sub> solution; Ref. CD Cl<sub>3</sub>,  $\delta = 76.9$  ppm

The soluble fraction  $S_B$  contains both unreacted amino ester and grafted amino ester on highly chlorinated CR. In its IR spectrum, an intense band is present at  $790\text{ cm}^{-1}$ , which is also observed in the spectrum of raw CR but which is far less intense in the spectrum of purified CR (see Ref. 1). The IR spectrum of the insoluble fraction  $I_B$  shows that the product is mainly amino ester hydrochloride.

The insoluble fraction  $I_A$  is a graft copolymer formed by bonding the amino ester on a high molecular weight CR, and this fraction was extensively studied.

The characteristics of insoluble fractions  $I_A$  obtained in various experimental conditions, starting from several chlorinated polymers and amino compounds, are described in Table VI. The nitrogen content is directly related to the extent of grafting. However, it is not possible to determine whether the increase in the nitrogen content corresponds to an increase in the number, or length of grafted chains due to a condensation reaction:



The first hypothesis seems the most probable on the basis of the steric hindrance.

The chlorine content determined by experimental analysis in an overall one, i.e., it depends on the molecular weight of the side chains, which cannot be calculated from the nitrogen content, which depends at the same time on the loss of chlorine and the number and length of grafted chains. However it is very useful to compare the chlorine content Cl determined by elemental analysis with the one resulting from spectral analysis.

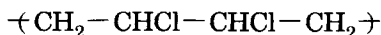
The results gathered in Table VI show that, at room temperature, the reactions carried out in chloroform, which is a better solvent of CR than toluene or chlorobenzene, lead to the highest graft contents.

A temperature increase favors the increase of the nitrogen content. This is probably due to two effects: an increase in amino ester solubility with increasing temperature, which improves the reaction with the chlorinated substrate, and an increase in graft efficiency. This latter would be due either to an increase in the number of labile chlorine atoms with increasing temperature, or to an increase in the growing rate of the grafts.

At  $80^\circ\text{C}$ , the nitrogen content increases clearly with increasing reaction time (Table VII). Most of the experiments were stopped after 8 h.

Apparently, the bulk of the results do not depend on the purification grade of the starting CR. That is the reason why most of the graft reactions were carried on raw CR.

Various chlorinated backbones (Table VI) were studied. The partial maleinization of CR before grafting (MCR) decreases the final graft content. Some interesting results were obtained with poly (2,3-dichloro-1,4-butane-diyl), resulting from the chlorination of 1,4-polybutadiene (CPB),



Indeed, the nitrogen content obtained with CPB and CR in similar ex-

TABLE VI  
Reaction of Amino Compounds with Chlorinated Polymers<sup>a</sup>

Experiment no.	Chlorinated polymer	Cl <sup>b</sup> (wt %)	Amino compound	Solvent	Reaction temp (°C)	Yield (wt %) of fraction		Composition of I <sub>A</sub> (wt %)	
						I <sub>A</sub>	S <sub>A</sub>	N <sup>b</sup>	Cl <sup>b</sup>
1	CR	67.5	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>10</sub> -COOC <sub>2</sub> H <sub>5</sub>	φ Cl	50	37.1	55.1	0.50	57.9
2	CR			CHCl <sub>3</sub>	50	41.6	53.6	0.95	52.9
3	CR			φ Cl	80	40.4	58.5	1.15	50.8
4	CR			φ CH <sub>3</sub>	80	41.9	57.8	1.18	50.0
5	PCR	64.5	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>10</sub> -COOC <sub>2</sub> H <sub>5</sub>	φ Cl	50	40.6	51.5	0.66	55.6
6	PCR			CHCl <sub>3</sub>	50	40.8	52.6	0.63	57.3
7	MCR	58.3	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>10</sub> -COOC <sub>2</sub> H <sub>5</sub>	φ Cl	80	44.5	55.0	0.52	58.3
8	CPB			φ Cl	80	42.1	53.4	0.90	48.0
9	CR	67.5	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>3</sub> -COOC <sub>2</sub> H <sub>5</sub>	φ CH <sub>3</sub>	50	36.9	48.2	0.35	60.9
10	CR			φ CH <sub>3</sub>	80	40.5	57.6	0.38	61.6
11	CR-9	60.9	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>3</sub> -COOC <sub>2</sub> H <sub>5</sub>	φ CH <sub>3</sub>	59	41.3	58.2	0.68	61.8
12	CR			φ CH <sub>3</sub>	25	64.3	35.7	0.69	54.29
13	CR	67.5	Dodecylamine	φ CH <sub>3</sub>	80	42.4	56.5	1.57	48.0

<sup>a</sup> PCR = purified CR as described in Ref. 1; MCR = maleinized CR; CPB = chlorinated 1,4-polybutadiene; CR-9 = CR previously grafted according to experiment no. 9.

<sup>b</sup> Determined by elemental analysis.

TABLE VII  
Influence of Experimental Conditions on Composition of Products Obtained during Reaction of CR with Amino Esters in Toluene Solution

Aminoester	Reaction temp (°C)	Composition of the reaction product obtained after various reaction times				
		N <sup>a</sup> (wt %)			Cl <sup>a</sup> (wt %)	
		0.25 h	0.5 h	1 h	8 h	1 h
H <sub>2</sub> H — (CH <sub>2</sub> ) <sub>10</sub> — COOC <sub>2</sub> H <sub>5</sub>	50	—	—	} < 0.1	0.50	61.75
	65	—	—		0.68	—
	80	—	—		0.90	—
$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{H} - \text{CH} - \text{CH}_2 - \text{COOC}_2\text{H}_5 \end{array}$	50	0.25	0.25	0.25	0.25	62.28
	65	0.21	0.19	0.16	0.29	61.67
	80	0.24	0.25	0.30	0.44	61.62

<sup>a</sup> Determined by elemental analysis.

perimental conditions is roughly the same. Since CPB contains only secondary chlorine atoms and CR contains various types of chlorines having different reactivities, it appears that grafting presumably takes place mainly on secondary chlorine atoms.

**Structural Study of Modified CR by Amino-Esters.** IR spectra of the polymers modified by the reaction of amino esters show both absorption bands characteristic of CR (500–800 cm<sup>-1</sup>) and of amine, amide, and ester groups. The absorption frequencies and their attribution are given in Table VIII.

A comparison of IR spectra of grafted CR and of the amino ester leads to the following remarks: The presence of an ester band which is always intense on the modified CR proves that grafting has taken place. The presence of two carbonyl bands (ester at 1730 cm<sup>-1</sup> and amide at 1630 cm<sup>-1</sup>) provides a qualitative estimate of the contribution of self-polycondensation to the overall reaction. At 50°C, this contribution remains low and the grafting is much greater. However, the self-polycondensation increases with increasing reaction temperature.

The characteristics of <sup>13</sup>C-NMR spectrum of CR grafted by amino ester (Fig. 7) are given in Table IX.

TABLE VIII  
IR Spectrum of Modified CR by Aminoesters<sup>a</sup>

Wave number (cm <sup>-1</sup> )	Attribution
3300–3000	N—H + residual methanol
2930, 2860 (vs)	C—H
1730 (vs)	C=O (ester)
1630 (w)	C=O (amide)
1440 (vs)	} Bending of methyl and methylene groups + C—O—C
1370, 1260, 1180 (m)	
1150, 1030, 920 (w)	
780 (m)	} C—Cl + CH <sub>2</sub>
730 (vs)	
660 (m)	

<sup>a</sup> vs = very strong; s = strong; m = medium; w = weak.

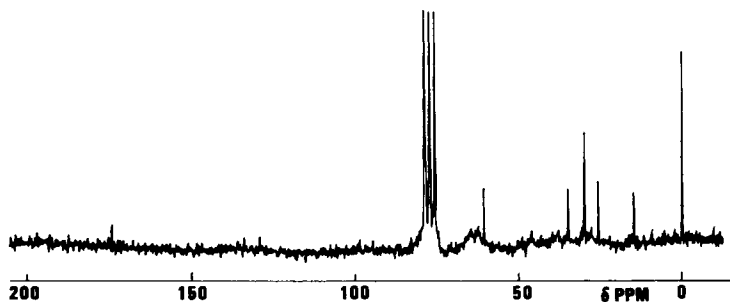
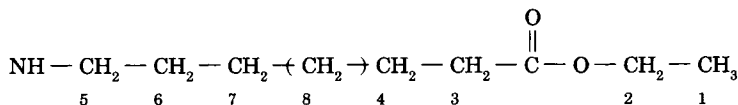


Fig. 7.  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR spectrum of EA-modified CR (fraction  $I_A$ ). Solvent  $\text{CDCl}_3$ , Ref.  $\delta_{\text{CDCl}_3} = 76.9$  ppm.

$^{13}\text{C}$ -NMR spectrum shows four among the six patterns of unpurified CR— $\text{CCl}$ ,  $\text{CHCl}$ ,  $\text{CH}_2\text{Cl}$  and  $\text{CH}_2$ ,  $\text{CH}_3$ —and at the same time, the peaks characteristic of the grafts with the same chemical shifts as in amino ester. The spectrum of a  $\text{CDCl}_3$  solution of the grafted product at  $80^\circ\text{C}$  shows a broad band due to some unsaturations in the 120–140 ppm range. The peaks corresponding to carbons numbered as 5, 6, and 7 in the grafts (located in  $\alpha$ ,  $\beta$ , or  $\gamma$  positions from  $-\text{NH}-$  or  $-\text{CONH}-$ ) could not be attributed.

TABLE IX  
 $^{13}\text{C}$  ( $^1\text{H}$ )-NMR Spectrum of CR Grafted by Amino Ester Graft:<sup>a</sup>



$\delta$ (ppm)	Attribution
14.3	1
24.8	4
26–34	CR: $-\text{CH}_2$ , $-\text{CH}_3$
29.2	8
34.0	3
45–48	CR: $-\text{CH}_2\text{Cl}$
59.9	2
60–64	CR: $-\text{CHCl}-$
76 <sup>b</sup>	CR: $\begin{array}{c} \diagdown \\ \text{C}-\text{Cl} \\ \diagup \end{array}$
120–140	CR: $\begin{array}{c} \diagdown \\ \text{C}=\ \\ \diagup \end{array}$
172.8	9

<sup>a</sup>  $\text{CDCl}_3$  solution; Ref.  $\text{CDCl}_3$ ;  $\delta = 76.9$  ppm.

<sup>b</sup> Determined on  $\text{C}_6\text{D}_6$  solution.

TABLE X  
Elemental and Spectral Quantitative Analysis of CR Grafted by Aminoester

Grafting temp (°C)	Nitrogen content (wt %)		Chlorine content (wt %)		Contents of amide 1 graft (wt %)	
	<sup>13</sup> C-NMR	Elem. anal.	<sup>13</sup> C-NMR	Elem. anal.	<sup>13</sup> C-NMR	Elem. anal.
50	0.60	0.50	57.0	57.9	10.0	10.0
80	1.04	1.09	49.6	50.6	43.0	13.5

Indeed these carbon atoms are very sensitive to the neighborhood of NH groups: This broadens the peaks which become undistinguishable from those due to CR. The peaks due to  $>CCl_2$  and  $-CCl_3$  groups, observed in the raw CR, are no longer present in the grafted CR as they are in the purified CR (see Ref. 1).

The calculation method described in Experimental can be used to determine the nitrogen, chlorine, and amide contents. The results are given in Table X.

There is a good correlation between the results obtained by both analysis methods. By increasing the grafting temperature, both nitrogen and amide contents increase. This observation fits the conclusion reached from IR analysis. However, the respective contribution of the graft reaction and the self-polycondensation remain difficult to determine.

As shown in Table XI giving the modifications of the chlorinated backbone during heating with or without amino ester, a large fraction of unsaturation appears in the course of the graft reaction. A similar observation has already been mentioned concerning the action of piperidine, and this shows that the amino ester behaves both as a nucleophile and a base.

This result fits the correlative decrease of  $CH_2$  and  $CCl$  groups and, to some extent, of  $CH_2Cl$  group since the latter decrease presumably results from the following reactions:

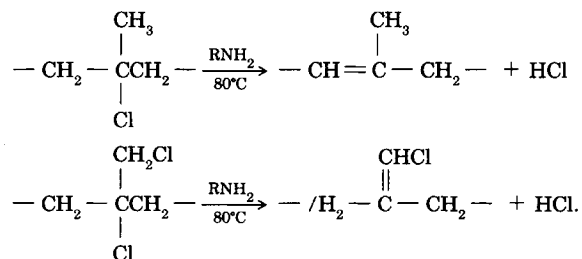


TABLE XI  
Modification of the Chlorinated Backbone under Heating with or without the Aminoester<sup>a</sup>

Type of reaction	Reaction temp (°C)	Group no. (%)				
		$CH_2, CH_3$	$CH_2Cl$	$>CHCl$	$>C-Cl$	$>\tilde{C}=\text{}$
Grafting	50	35.0	17.0	31.0	16.5	~0
	80	16.5	11.8	31.7	8.0	31.7
Blank	50	30.0	18.3	34.7	16.6	~0
	80	34.6	15.0	37.0	13.4	0

<sup>a</sup> Reaction time: 8 h

TABLE XII  
Composition of a Three-Layer Antifouling Coating Based on CR and Polyamide

Layer order no.	Product	Solvent	Polymer (g L <sup>-1</sup> )	Weight of polymer (mg cm <sup>-2</sup> )
1	CR	Toluene	50	4.16
2	AE-modified CR (N = 0.81 wt %)	Toluene	50	1.00
3	Technyl Z20901	$\left. \begin{array}{l} \text{Methanol} \\ \text{(50\% vol)} \\ \text{Xylene} \\ \text{(25\% vol)} \\ \text{n-Butanol} \\ \text{(25\% vol)} \end{array} \right\}$	100	6.33

Previous results have shown that it is possible to modify CR by aminated compounds without deteriorating any of its main properties. On this basis, another technical approach using fatty polyamides such as Versamides instead of the amino ester is in progress.<sup>10</sup> This research work has already brought important improvements to both the graft efficiency and the quality of the materials produced.

Some of the modified chlorinated rubbers were studied for the prevention of foulings attachment, for use as antifouling coatings.

Most of the experiments were carried out on metal test pieces coated by an anticorrosion primer, usually a CR layer, an intermediate layer of amino-ester-modified CR and a superficial layer of a polyamide showing antifouling properties. The purpose of the intermediate layer made from graft copolymers is to bind firmly the other layers, which, as such, do not adhere.

The insolubility of most usual polyamides in the solvents used for painting and the thermal degradation of CR when the temperature is above 100°C, imposed the use of soluble polyamides which can be easily applied by means of the standard paint techniques. This is the reason why we used mostly copolyamides such as Technyl Z-20901, resulting from the copolycondensation of adipic and sebacic acids with hexamethylene diamine, or Versamid 930, resulting from the reaction of a diamine with unsaturated dimers of fatty acids. These copolyamides are sufficiently soluble in various solvents to make coatings of good quality, as shown in Table XII.

Coated test pieces were immersed in the upper sea at COB (Centre Océanographique de Bretagne) and at CREO (Centre de Recherches et d'Etudes Océanographiques), in France. The observations made after 3 and 12 months clearly showed that the separation of the layers which takes place when CR and polyamide are put directly in contact does not occur when they are separated by an intermediate layer of CR modified by the amino ester.

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