

thioglycolate, 5.12 pcr of dioctyle phthalate and 0.0064 pcr of zinc octoate.

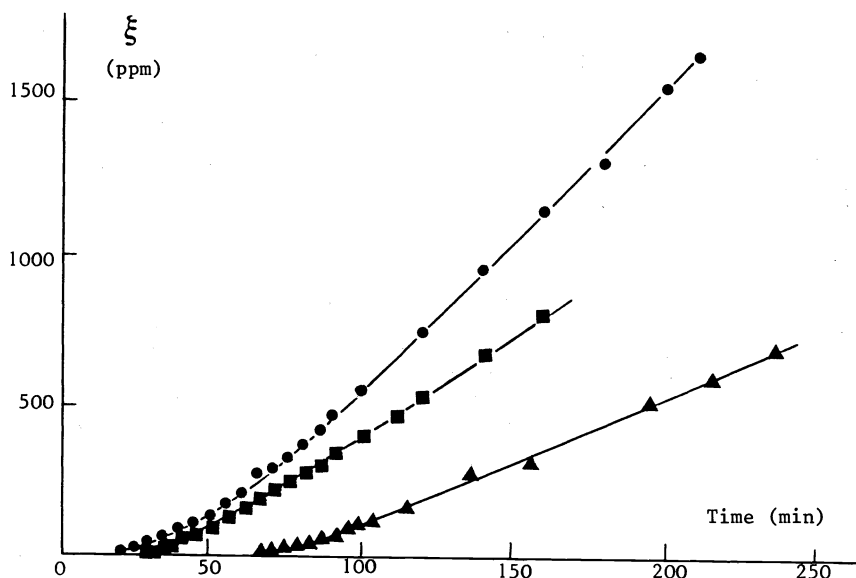


Fig. 1. Thermal dehydrochlorination test in solution. Dehydrochlorination ratio ξ at 175°C, for samples III (▲), VIII (■) and IX (●)

UNSATURATIONS

The titration of total double bonds has been carried out, according to Boissel (Ref. 6), by bromination in the presence of mercuric acetate as catalyst in dichloroethan solution. The excess of bromine is back-titrated through iodometry. For the internal double bonds, the details of the ozonolysis method, carried out at -25°C have seen already described (Ref. 7). The results are obtained as the number \bar{Y} of chain scission for 1000 monomer units from viscosity measurements.

$$\bar{Y} = \frac{62.5 \cdot 10^3}{(\eta_0/K)^{1/\alpha}} \left\{ \left(\frac{\eta_0}{\eta} \right)^{1/\alpha} - 1 \right\}$$

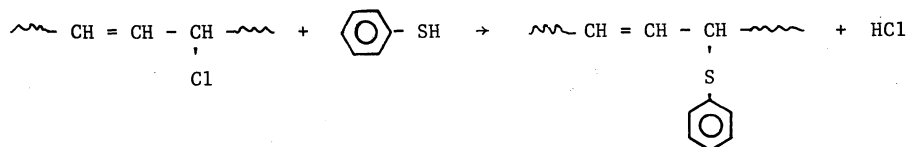
where η_0 is the initial limiting viscosity number, η is the limiting viscosity number after ozonolysis, $\alpha = 0.822$ and $K = 1.5 \cdot 10^{-2}$ are the Mark-Houwink viscosity coefficients.

Attempts to use the olefin metathesis reaction, although practiced with stoichiometric rather than catalytic amounts of tungsten compounds, failed.

LABILE CHLORINE ATOMS

According to Caraculacu (Ref. 8), treatment of PVC with phenol is able to give an account of both allylic and tertiary chlorine atoms. A study with a model compound chloro-4-hex-2-ene, has shown to us that the reaction with allylic chlorine follow a nucleophilic substitution mechanism, involving an intermediate carbocation so that a successful competition of the elimination reaction (dehydrochlorination) takes place. In addition various reaction products can be separated, suggesting the simultaneous occurrence of O and C-alkylation of the hexenyl group.

The reaction with the more nucleophilic thiophenol is cleaner: there is only S-alkylation with no trace of elimination. Further, in dichloroethan solution at 60°C, the thiophenol does not react with the chloro-2-methyl-2-butane, which is a model compound for tertiary chlorine atoms. The reaction on PVC should be:



Three events should be observed: consumption of thiophenol, production of HCl, grafting of aromatic rings onto the PVC. The reaction is carried out at 60°C in dichloroethane solution

(2.5 %) for 30 h. A stream of nitrogen carry the evolved HCl in a water solution. The consumption of thiophenol can be followed by coulometric titration using samples taken from the cell, while coulometric titration is used also for chloride ions in the water. Finally UV analysis of the polymer can be used to measure the substitution of the thiophenol groups. Excellent agreement is obtained between the three analysis, provided the temperature of the reaction is kept below 80°C ; at higher temperature, some dehydrochlorination takes place.

MATERIALS

A serie of polymer have been prepared by Rhône Poulenc at a laboratory scale but in conditions quite similar to those used in the industrial bulk process. The polymerization temperature was kept at 55°C. Final stages of the polymerization were varied, the final conversion varying between 51.5 and 85 %. In some cases, the temperature has been increased at the end of the polymerization in order to keep the pressure constant for a longer time. Due to autoacceleration (Tromsdorff effect) a final rise in the temperature may be observed, which can be more or less controlled. Finally, a degazing treatment has been carried out, to lower the amount of residual monomer in some cases. The results concerning these polymers are reported in Table 1. Among the samples, two (II and VIII) were used for the IUPAC group.

TABLE 1. Characterization of "industrial" samples

Sample	I	II ^(d)	III	IV	V	VI	VII	VIII ^(e)	IX
Final conversion %	51.5	56.5	75	75	77	80	81.7	82.5	85
Maximal temperature (°C) during polymerization	60	60	52	83	89	74	89	89	90
Degazing temperature (°C)	55	60	52	77	55	78	87	85	88
\overline{M}_n	--	39 100	35 900	32 500	32 000	36 900		26 000	35 100
\overline{M}_w	--	96 600	75 000	78 000	87 300	91 000	--	82 900	82 700
Initial DHC rate ^(a)	Rd	2.7	3.1	4.8	5.8	4.0	--	4.8	7.2
Color test min. ^(b)	--	60	60	50	45	55	--	30	40
Total double bond ^(c)	--	1.43	1.19	1.82	1.63	1.43	--	1.93	1.98
Internal unsaturation ^(c)	--	0.3	0.16	0.42	0.15	0.14	--	0.44	0.77
Labile Cl ^(c)	--	1.53	1.50	2.18	1.92	1.60	--	2.54	2.15

(a) ppm/min. at 170°C ; (b) time for blackening at 190°C ;

(c) defect number per 1000 monomer unit ; (d) sample II of IUPAC working party

(e) sample IV of IUPAC working party

Another sample (X) of the IUPAC group has been used : it has been prepared by Sörvik (Ref. 9) from a latex of emulsion polymer with vapors of monomer at subsaturation pressure (6.2 atm at 55°C). That sample ($\overline{M}_n = 21\ 300$; $\overline{M}_w = 74\ 700$) is a model for a polymer produced at the end of the polymerization (conversion higher than 70 %).

Fractionation of samples III, IV, VII and IX have been carried out through preparative GPC. Five fractions have been produced, as shown in Fig. 2. Fractions F_I and F_V being too small, analysis has been carried out only on the central fractions. The results concerning for each samples fraction F_{II} and F_{IV} are reported in Table 2.

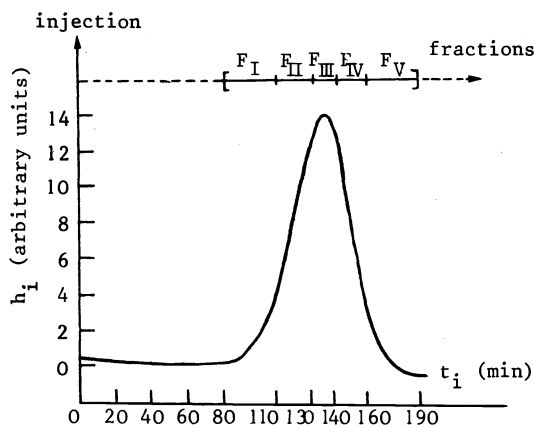


Fig. 2. Fractionation by GPC

TABLE 2. Defects in fraction from preparative GPC

Sample		III	IV	IX	VII
Color test stability (minutes)		60	50	40	30
Internal double bond	low MW fraction F _{IV}	0.20 (25 000)	0.81 (19 000)	1.06 (28 000)	1.96 (28 000)
	high MW fraction F _{II}	1.74 (73 000)	0.35 (79 000)	0.24 (63 000)	0.14 (75 000)
Total double bond	low MW fraction F _{IV}	1.20 (18 000)	1.37 (17 000)	6.21 (10 000)	5.6 (14 000)
	high MW fraction F _{II}	4.05 (96 000)	5.35 (86 000)	0.85 (72 000)	4.3 (99 000)

in brackets : number average molecular weight of the fractions

Another kind of fractionation has been carried out through successive extractions with ethyl ether (F₁) benzene (F₂) and acetone (F₃), leaving an insoluble residue (F_{IV}). A complete fractionation have been carried out with samples II and VIII. The more interesting fraction is F_I; however infrared analysis show that it does contain all the residual peroxides and also the small amount of plasticizer (dioctyl phtalate) used to introduce the initiator homogeneously. For that reason, the two samples I and VIII have been prepared without the plasticizer and only ethyl-ether extraction has been carried out. The results are reported in Table 3.

TABLE 3. Fractionation through extraction procedure

Sample	Fraction	Weight (%)	\overline{M}_n	\overline{M}_w	Peroxide ₋₄ mole/g.10	Internal double bond	Total double bond	Labile Cl
I	F ₁	0.38			0.33	--	--	87.5
II	F ₁	0.19	1 000	1 910	0.26	--	26.5	48.7
	F ₂	1.43	6 000	9 300	0	0	1.5	3.07
	F ₃	13.66	23 700	39 100	0	0.3	1.06	0.4
	F ₄	83.77	54 900	90 000	0	0.08	0.89	1.66
VII	F ₁	0.71	1.230	2.330	0.50	--	--	50.6
VIII	F ₁	0.74	1 140	2 210	0.43	--	27.7	30.2
	F ₂	4.34	6 100	9 000	0	1.8	1.46	6.4
	F ₃	12.46	17 400	28 400	0	0	0.74	9
	F ₄	79.97	59 300	98 000	0	0.6	1.28	0

Two other sets of polymer have been used : both have been prepared by D. Sonderhof at the Darmstadt Kunststoff Institut. The first set is a serie of four copolymers of vinylchloride and phenylacetylene (Table 4). They are model compounds for isolated internal double bond ; however owing to the presence of a pendant aromatic ring they are not excellent models. Although increasing the proportion of phenylacetylene (PA) cause a decrease of the molecular weight, most of the double bonds are actually inside the backbone. The second set are polymer prepared in the presence of oxygen. Their characteristics are reported in Table 5). It may be seen that the presence of oxygen causes a rather large increase of the internal double bonds (more than of carbonyl groups).

TABLE 4. Model polymer with internal double bond vinylchloride - phenyl acetylene copolymer

Sample	% PA	\overline{M}_n	Internal unsaturation (a)	R_d 140°C ppm/min
PA I	0.094	46 400	1.02	128
PA II	0.445	29 800	3.2	412
PA III	0.634	24 100	6.0	484
PA IV	1.04	20 500	9.02	637

(a) number per 1000 monomer unit

TABLE 5. PVC samples prepared in the presence of oxygen

Sample	O ₂ in the VC monomer (mole %)	$\geq C=O$ in the polymer (mole %)	Internal double bonds	\overline{M}_n	R_d 170°C ppm/min
1 - 0	0	0	0.08	53 100	6.8
2 - 0	0.057	0.048	0.09	44 900	9.8
3 - 0	0.66	0.093	0.20	42 200	14.2
4 - 0	4.75	0.26	0.51	35 450	18.7

RESULTS AND DISCUSSION

From the results reported in Table 1 a plot of the various defect concentration versus the initial dehydrochlorination rate, show very rough linear correlations. The correlation indices are 0.78 for total unsaturation, 0.65 for internal unsaturation and finally 0.63 for labile chlorine. Clearly the number of labile chlorine atoms is higher than the total number of unsaturations so that the thiophenol reaction might involve other structures than the allylic chlorine but it is not possible at the present time to be more precise.

The correlation with the internal double bond has some support however. It seems, at first that the differences in sample stabilization might be correlated with the differences in their internal unsaturations. Another interesting result is the fact that the number of internal polyene sequences is not changed after moderate degradation. For instance, for a DHC yield of 1700 ppm of sample II, the number of chain scission per polymer chain upon ozonolysis remains at 0.2 ± 0.003 , whatever the degradation temperature between 150 and 190°C. So it may be concluded that polyene sequences are initiated from preexisting internal unsaturation without creations of new unsaturated structures. The same kind of results has been observed with the phenylacetylene copolymers; however these copolymers are less stable than the "industrial" polymers (see Fig. 3 where the data for samples II to IX have been calculated taking into account the activation energy of 27 kcal/mole) and the substitution of a phenyl ring may give a specially unstable structure, very keen to initiate the DHC process. However, the results shown in Fig. 4, concerning the polymers prepared in the presence of oxygen, suggest that the initial DHC rate is more clearly dependent on the internal unsaturation than on the oxygenated structures.

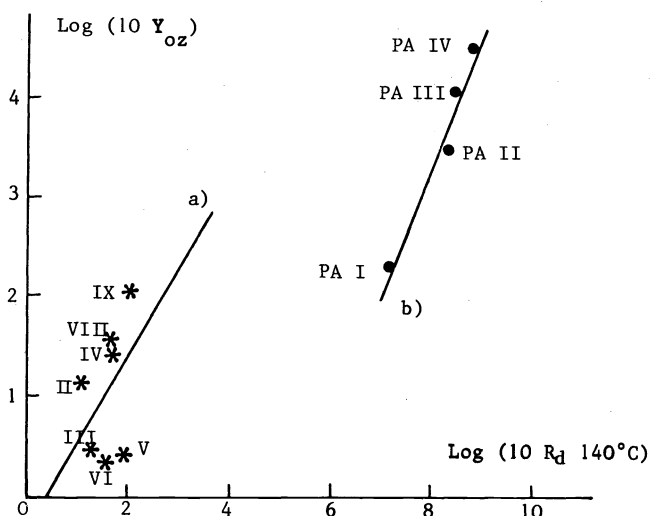


Fig. 3. Log-Log plot of internal unsaturation versus DHC rate for the bulk process PVC (a) and the phenylacetylene copolymers (b)

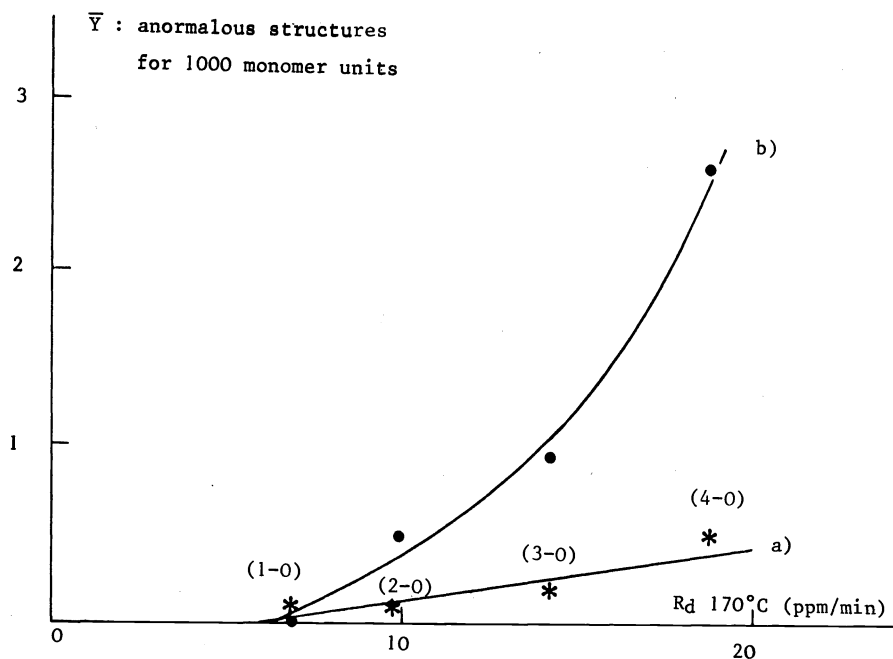


Fig. 4. Anomalous structures (internal unsaturation a, or carbonyl groups b) versus initial DHC rate for samples prepared in the presence of oxygen (Table 5)

Some trials have been carried out in order to eliminate the unsaturations. Catalytic hydrogenation with Pd/carbon catalyst failed to change neither the internal double bonds nor the DHC rate (samples II and X). Better results have been obtained from radical hydrogenation with *p*.toluene sulfonyl hydrazine according to Nakagawa (Ref. 10). For sample VIII the value of \bar{Y} drop from 1.93 to 1.03 while the DHC initial rate drop from 8 to 6.6 ppm/min at 178°C. However the improvement of the thermal stability is lower than expected.

Defect partition according to molecular weight is interesting. Analysis of fractions obtained by preparative GPC (Table 2) by either ozonolysis or bromination shows that for the most stable polymer, unsaturated structures (both internal and terminal) are concentrated in high molecular weight parts; the reverse is true for the most unstable polymer: low molecular weight fractions are rich in double bonds.

Sample results obtained through successive extraction with ethyl ether (F₁), benzene (F₂), acetone (F₃) and of residues (F₄) are shown in Table 3. Here, whatever the sample stability, defects (both unsaturated and labile chlorines) are concentrated in the low molecular

weight fractions, but the main difference lies in the amount of ether soluble fractions. It is interesting to see that there is a rather good linear correlation between dehydrochlorination rate of a whole sample and the amount of ether soluble fraction. The correlation index is rather good (0.93) (Fig. 5). Another good correlation (0.94) (Fig. 6) is obtained between this amount and the highest temperature reached during polymerization, connected with the acceleration often observed when the monomer phase disappears. This fact shows that an important part of unstable structures are created at the final stages of polymerization.

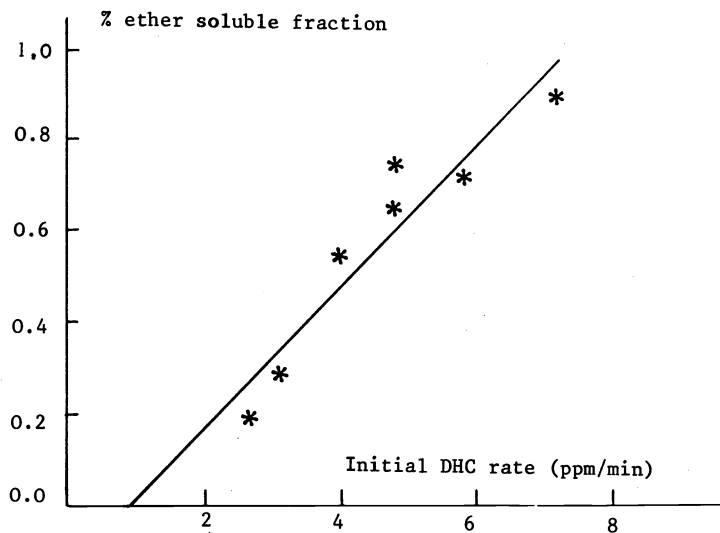


Figure. 5

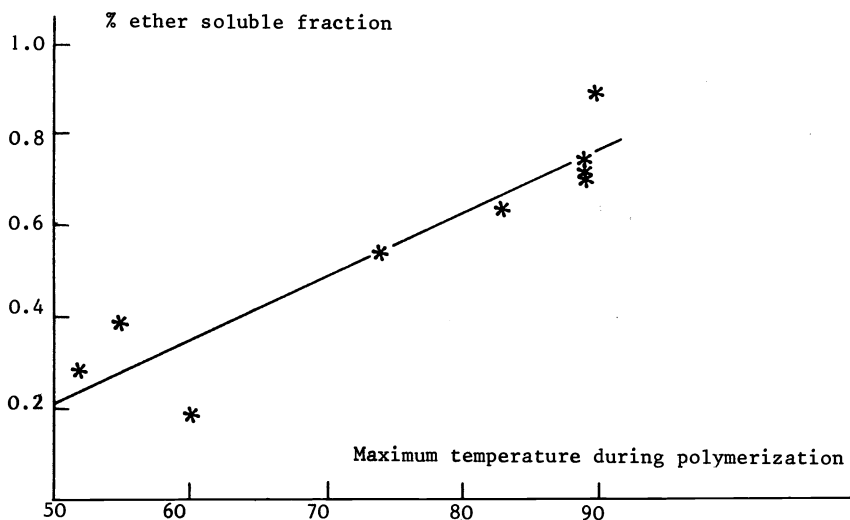


Figure. 6

Analysis of sample X confirm this result, as shown in Fig. 7, that polymer prepared at subsaturation pressure is very unstable ($R_d = 56$ ppm/min at 170°C). Its characteristics are : internal double bond : 0.8, total double bond 3.0, labile chlorine 12.0 for 1000 monomer units.

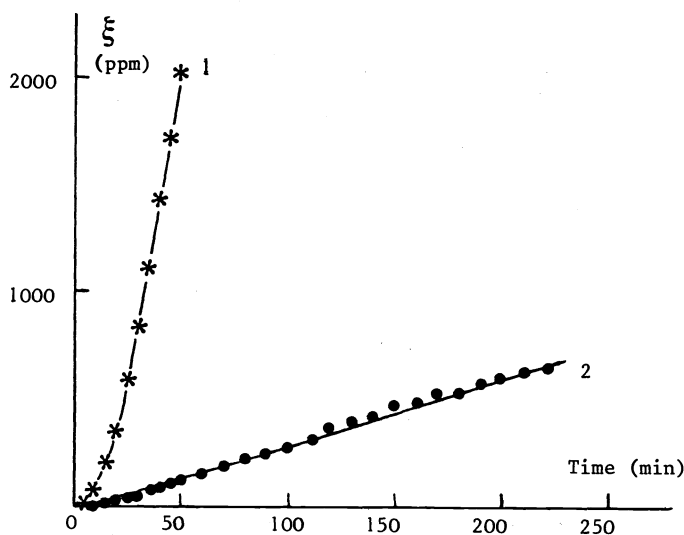
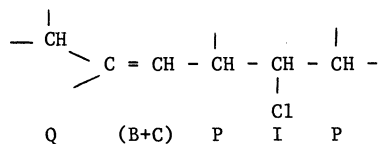


Fig. 7. DHC curves for sample II (2) and sample X (1) at 170°C

After elimination of the ether soluble fraction, the residue is more stable. At 178°C, the initial DHC rate decreases from 8 ppm/min to 5.8 for sample VIII and from 4.5 to 3.7 for sample II. These improvements in thermal stability (respectively 27.5 % and 18 %) are more than proportional to the decrease in labile chlorines (respectively 15 and 10 %). So, low molecular weight fractions are not the only ones responsible for weak thermal stability but their contribution is really a major one.

Analysis of these low molecular weight fractions shows several facts. Of course, they may contain other structures than PVC, such as low molecular weight additives introduced with the initiator, as well as peroxide residus (see Table 3). So two samples (I and VIII) were prepared without any other additive than the peroxyde initiator. The ether extracted fraction of the less stable (VII) was analysed by ^1H NMR at 80 and 350 MHz. Some spin decoupling experiment have been carried out in order to make the interpretation of the 350 MHz spectra shown in Fig. 8. In the ethylenic proton region (5.5, 5.9 ppm) the group A, coupled with the doublet H at 4.08 ppm, correspond to the chain end $-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$ already observed in low molecular weight PVC fraction by Pham and Petiaud (Ref. 11). The groups B and C are coupled with group P and Q (Fig. 8) of the CH_2 regions: an irradiation of P + Q, it remains in B and C two singlets of different size, while on irradiation of only Q, it remains two doublets in B and C. On the other hand, the irradiation of P + Q leaves a singlet for the resonance I. So we think that B and C might correspond to the cis and trans isomers of the following structure



Further the groups K and L should correspond to saturated chain ends as $-\text{CH}_2-\text{CH}_2\text{Cl}$ (L) and $\text{HCCl}-\text{CH}_2\text{Cl}$ (K) already observed by Pham (Ref. 11). From quantitative analysis, it may be estimated than for 1000 monomer units, they are 77 saturated chain ends (K+L), 37 unsaturated chain ends (A+H) and 54 internal double bonds (B+C) with a corresponding homoallylic chlorine atom (I). It is interesting to note that the later value does fit well the titration of the labile chlorine atom (50.6). It may be seen, that after reaction with thiophenol, the structure B, C, I and P have disappeared in the spectrum (see in Fig. 9 the comparison of the 80 MHz spectra before and after reaction). In addition aromatic structure at 7-8 ppm are shown. Additionally it may be seen that thiophenol does not react with the chain end chlorine atom.

Although the last study is not yet completed and that some uncertainty remains concerning the interpretation of the NMR spectra, it is clear that the analysis of the low molecular weight fraction with high resolution NMR spectroscopy should be a very powerful key to the understanding of the relationship between the structural defects and the thermal stability of PVC.

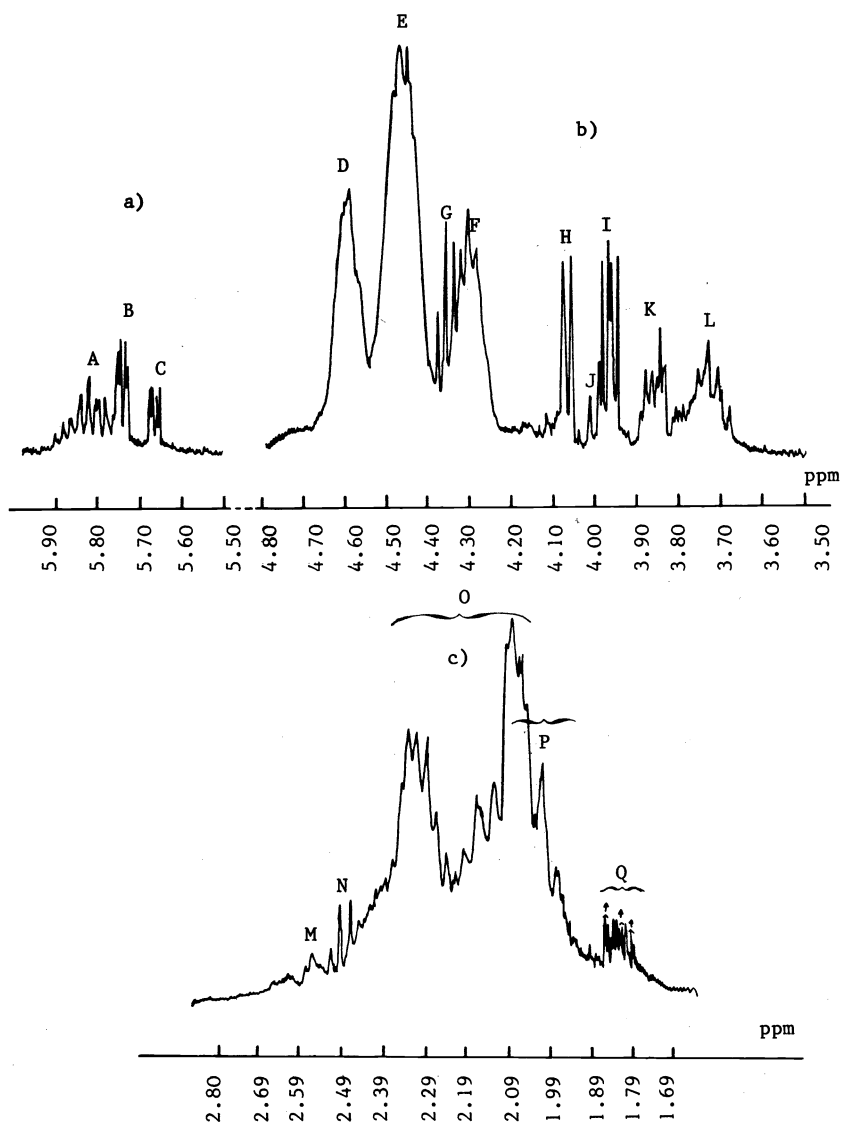


Fig. 8 . ^1H NMR spectrum (350 Mhz) of the ether extract of sample VIII
 a) ethylenic protons (5.5 - 6.0 ppm)
 b) CHCl or CH_2Cl structures
 c) CH_2 or $-\text{CH}$ structures

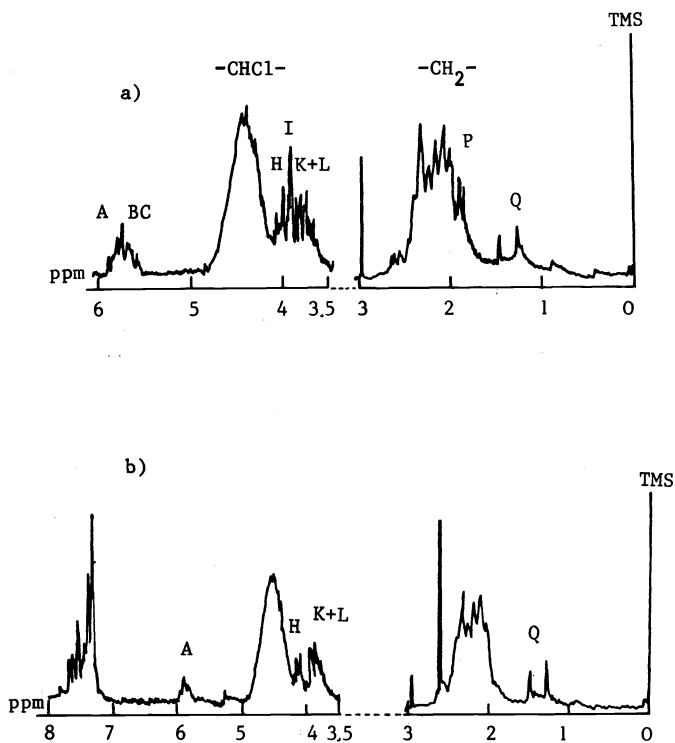


Fig. 9. ¹H NMR spectra (80 MHz) of the ether extract of sample VIII
a) before , b) after reaction with thiophenol

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