Polymer Bulletin 23, 425–430 (1990)

Polymer Bulletin

Infrared evidence for the grafting of ester groups on polyvinyl chloride stabilised by Zinc and Calcium stearates

Michel Bartholin, Naima Bensemra, Tran van Hoang, and Alain Guyot*

CNRS, Laboratoire des Matériaux Organiques, B.P. 24, F-69390 Lyon-Vernaison, France

SUMMARY :

Careful FTIR analysis of PVC samples heated in trichlorobenzene solution at 187 °C in the présence of mixture of zinc and calcium stearates for various times were carried out . A special accessory allowing identical flushing of several samples with dry nitrogen was used . The samples were thoroughly purified before examination . The very weak carbonyl absorption , after an initial decrease , increases as a sharp band near 1734 cm^{-1} progressively shifting towards lower wave numbers and then decreases with simultaneous broadening . A corresponding C-H band is seen near 2850 cm^{-1}.

INTRODUCTION :

The Frye and Horst theory (1,2) explaining the stabilisation mechanisms of polyvinyl chloride (PVC) with metal soaps by the substitution of labile chlorine atoms at the end of a growing polyene sequence or directly on the labile chlorine atoms contained as irregular structures in PVC , with the ester group of the metal carboxylates , was recently questionned (3,4) . The ester band at 1740 cm^{-1} in the infrared spectra reported by Frye and Horst was not observed after polymer purification in recent studies of Vymazal et al (3) who suggest that it should be assigned to monomeric carboxylic acid residues formed upon reaction of HCl with the metal soaps . However the so-called blocking and deblocking theory opposed to the Frye and Horst mechanisms (4) does not offer any comprehensive mechanisms for the blocking process involved in the teporary stabilisation of PVC by the metal soaps . We would like to report here more precise FTIR studies which conclude to support the Frye and Horst mechanisms .

EXPERIMENTAL .

PVC sample XII of the IUPAC working party on characterisation of structural defects in PVC (5) was chosen . Chemicals , solvents and details for the experimental procedure have been described previously (6) . Spectra were taken with FTIR Nicolet 20 SX apparatus using a 2 cm^{-1} resolution on KBr pellets with 5 % of purified polymer . A special accessory enabling the examination of 7 samples on a cylinder run by a small electric motor with an outside control without opening the sample compartment was designed for this purpose ..

All samples were flushed overnight with dry nitrogen before taking the background and the spectra ; in this way all samples had the same state of dryness which is an absolute requirement for quantitative comparisons .

All absorbance data were corrected using the internal reference band at 4332 cm^{-1} as suggested by McKenzie et al (7) ; the dehydrochlorination being limited to less than 2% , the results are close to those obtained using the 1426 cm^{-1} band of CH_2 groups .

First and second derivatives of the spectra were taken followed by deconvolution and simulation treatments using the program established by Cameron et al (8) . By this

---

*To whom offprint requests should be sent procedure it was possible to separate the different constituent bands of the spectra .

RESULTS AND DISCUSSION :

Three series of spectra are shown in Figure 1. They correspond respectively to three series of samples taken at different heating time at 187°C of PVC solutions treated in the presence of three different ratios of Zn and Ca stearates , the total amount of stearate being kept constant (4% in weight) .

The initial polymer shows a dissymetric carbonyl band with a maximum at 1742 cm^{-1} , which probably corresponds to some oxygenated structure introduced in the polymer either during the polymerization (initiator residue , product from reaction of oxygen traces in the monomer ...) or during the process of elimination of residual monomer or also upon further reaction with air . During the first minutes of thermal treatment some of these structures are destroyed because the intensity of the band decreases with practically no modification in shape . Later on , the whole intensity of the band increases and the band becomes sharper , its maximum being progressively shifted towards lower wave numbers . The position of the observed maxima are reported in Table I . When the ratio Zn/Ca increases the shift extends more rapidly up to more than $20cm^{-1}$ from the initial position . The band becomes broader in figures 1b and 1c for the last spectra .

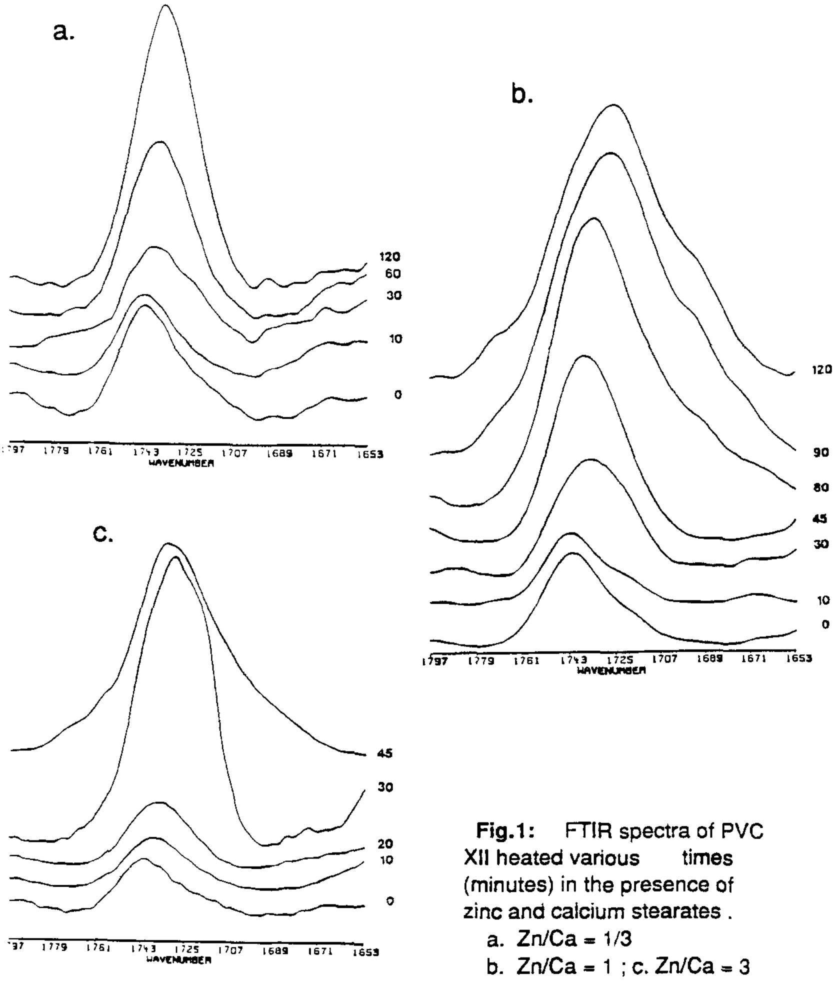

Fig.1: FTIR spectra of PVC XII heated various times (minutes) in the presence of zinc and calcium stearates .
a. Zn/Ca = 1/3
b. Zn/Ca = 1 ; c. Zn/Ca = 3

At these times (90 minutes for Zn/Ca =1 and 45 minutes for Zn/Ca = 3 , a strong formation of HCl is observed , i-e all (or at least most of) the stabilisers have been consumed .

Table I : Position of the Maximum of the Carbonyl Band (in cm^{-1})

Heating Time (Minutes)	0	10	20	30	45	60	80	90	120
Zn/Ca =0.3	1742	1742	--	1739	--	1732	--	--	1730
Zn/Ca = 1	1742	1742	--	1734	1734	--	1731	1727	1725
Zn/Ca = 3	1742	1737	1733	1720	1733	--	--	--	--

In the last case , the intensity of the band has been decreased too . The change in the intensities of the bands with time are shown in Figure 2 as a difference of the actual and initial intensities , integrated from 1700-1770 cm^{-1} .

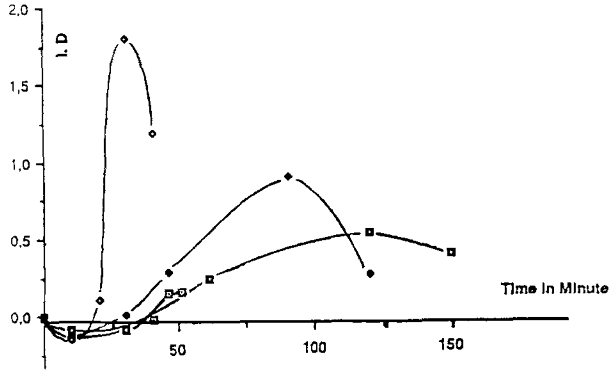

Fig. 2 : Evolution of integral differences (I.D) from 1700-1770 cm-1 versus time for PVC XII heated in the presence of mixture of Zn and Ca Stearates in the following compositions (% weight) : Zn/Ca = 1/3 (◘); Zn/Ca =2/2 (⊡) ; Zn/Ca =3/1 (◇); Zn/Ca = 1/1 (◆).

After small initial decreases , these intensities increase ; a maximum is observed which corresponds rather well to the end of the so-called inhibition period , after which a rapid evolution of HCl is observed (6) , because most of the stabilisers has been consumed ; so the decrease of the intensity of the carbonyl band does correspond to acidolysis of the ester groups by free HCl .

Assuming valid a calibration based on ethyl stearate , typical results are reported in Table II concerning the maximum amount of grafted ester groups .

This amount is clearly dependent on both the total amount of metal stearates (compare run 4 to other runs in Table II) and the relative amount of Zn stearate . Obviously the catalytic effect of $ZnCl_2$ (9) is very important . The initial and the final decreases of the intensity of the carbonyl bands show that some carbonyl structure initially present or formed after , are not stable and may disappear during the process; then the maximum number of grafted ester group give an idea of the minimum number of substitution reaction .

The difference between the total number of available ester groups (in the stabilisers) and that maximum number of grafts give an idea of the maximum number of stabiliser which has been consumed by other reactions , i-e mostly by reaction with HCl produced by the zipping DHC reaction . The efficiency of the grafting reaction is clearly related to the proportion of Zinc in the stabiliser mixture . When it is high , the developpment of polyene sequence is stopped very soon .

Zinc in the stabiliser mixture . When it is high , the developpment of polyene sequence is stopped very soon .

Table II : Maximum Amounts of Grafted Ester Groups

Run	ZnStear. Weight %	CaStear. Weight %	Heating Time (Minutes)	Grafted Ester Groups Mole per gr. of Polymer $x10^6$	Total Amount of Available Ester Groups Mole per gr of Polym.$x10^6$
1	1	3	120	24.0	126.5
2	2	2	90	40.0	126.5
3	3	1	30	79.0	126.5
4	1	1	50	7.2	63.2

The grafting of stearate groups is confirmed by a growth of the C-H stretching bands of the hydrocarbon chain at 2850cm-1 . An example is given for the series with a ratio of Zn/Ca of 3 in Figure 3

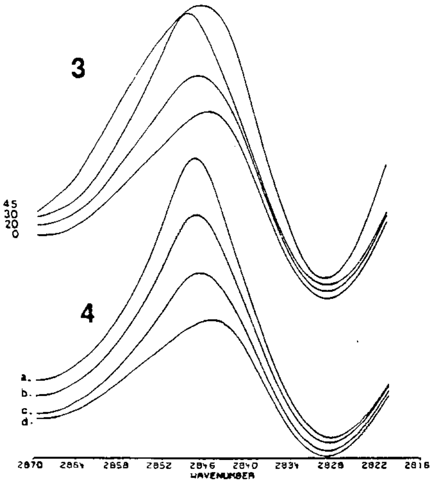

Fig.3 : Evolution of C-H Stretching band versus time for PVC XII heated in the presence of Zn and Ca Stearate (Zn/Ca = 3 % weight).

Fig. 4 : Simulation of C-H stretching band evolution by adding increments of ethyl stearate to PVC XII a=3 ε ; b=2 ε; c= ε ; d=0

; the last spectrum of the serie (45 minutes) shows again a broadening of the band after the maximum of the grafting ; before that maximum , the shape of the bands are very similar to those simulated by adding the spectra of increasing amounts of ester groups from ethyl stearate to the PVC , which are shown in Figure 4 .

Further analysis of the carbonyl bands can be obtained upon deconvolution of the whole band ; an example is given in Figure 5 . Ten bands are necessary to give a perfect account of the whole band . Upon heating , the major growth is observed for a band centered at 1735 cm^{-1}, which corresponds exactly to the main band of a model compound produced by substitution of a stearic group to the chlorine atom of chloro-4hexene-2 (6) ; such compound is a model of an allylic chlorine atom of an isolated internal double bond .

For another possible model compound , vinyl stearate , the carbonyl band is located at 1730cm-1 (10) .Then it is allowed to conclude that , during the heat treatment , the substitution reaction involves mainly these allylic chlorine atoms associated with isolated double bonds ; a part of these does preexist in the initial polymer and come from a side reaction involving Cl radicals during thd polymerization process (11) ; it is interesting to note that their number , 60.8×10^{-6} per gram of PVC in the sample studied here (12) , is of the same order of magnitude than the minimum number of substitution reactions

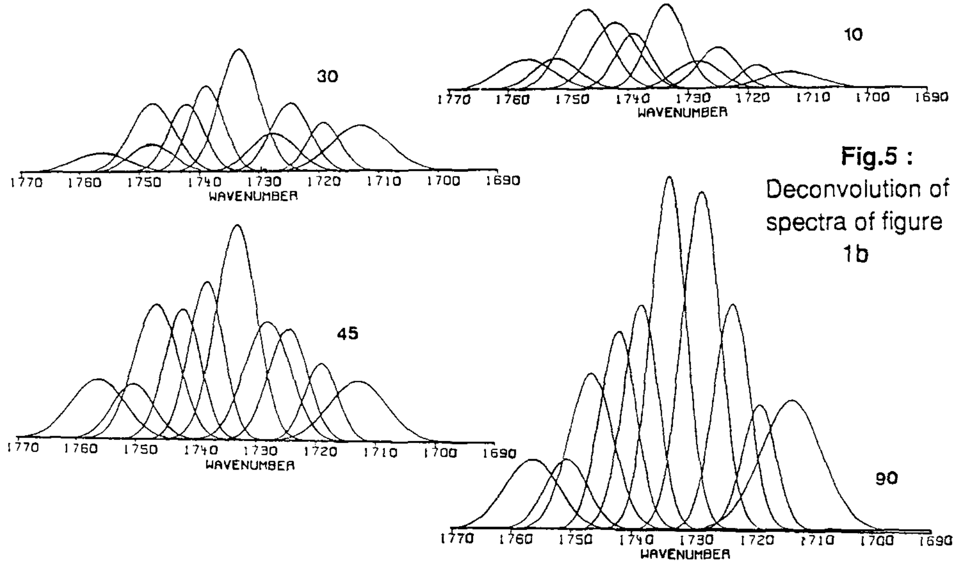

Fig.5 : Deconvolution of spectra of figure 1b

Possibly other substitution can take place after one dehydrochlorination step initiated by labile tertiary chlorine atoms . Upon further heating , other strong bands are growing , chiefly at lower wave numbers , giving account for the shifts in the maxima reported in Table I . It might be suggested that the band corresponding to ester groups substituted at the end of a polyene sequence should be shifted in that direction , according to the length of the sequence ; however there are no available model compounds to check such hypothesis . On the orher hand the shifts might be caused also by accidental oxydation of the polyenes (10) . The growing of these bands give an account for the broadening of the whole band which is observed , begining about at the heating time corresponding to the end of the " inhibition period " . At that moment , the eficiency of the stabiliser for the very fast substitution of the allylic chlorine , after an isolated double bond or at the end of a short growing polyene sequence , decreases and longer sequences can be formed and so detected .

REFERENCES

1. A.H.Frye and R.W.Horst : J.Polym.Science 40 , 419 (1959)
2. Id. : Id 45 , 1 , 1960
3. E.Czako , Z. Vymazal, K.Volka , I.Stibor and J.Stepek : Europ.Polym.J , 15 , 81 , (1979) .
4. B.Ivan ,T. Kelen and F.Tudos : 31st IUPAC MicroSymposium in Prague (July 1988) , to be published in Makromol.Chem.Symposia 1989 .
5. A.Guyot : Pure and Applied Chem. 57 , 833 (1985).
6. N.Bensemra , Tran van Hoang , A. Michel , M.Bartholin and A.Guyot : Polym.Degrad.Stability , 24, 33 (1989).
7. M.W.Mckenzie , H.A.Willis , R.C.Owen and A.Michel : Europ.Polym.J. 19, 511 (1983).

8. J.K.Kauppinen , D.J.Mofatt , H.H. Mantsch , D.G.Cameron : Applied Spectroscopy , 35 , 271 (1981) .
9. Tran van Hoang , A. Michel and A.Guyot : Europ.Polym.J., 12 (1976),337.
10. S.A. Letts , T.Jr.Fort and J.B.Lando : J.of Colloid and Interface Science , Vol. 56 , N° 1 , July 1976 .
11. T.Hjertberg and E.M.Sorvik : Polymer 24 , 685 (1983)
12. M.F.Darricades-LLauro , A.Michel ,A.Guyot , R.Petiaud and Pham quang Tho : J.Macromol.Sci.Chem. A23 ,221 (1986) .

Accepted January 26, 1990 C