Diels–Alder reactions of partially dehydrochlorinated PVC in solution and in the melt

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Maleates were shown to decrease but not prevent polyene formation from PVC. Diels–Alder adducts were confirmed between partially dehydrochlorinated PVC and dihexadecylmaleate and dioctadecylmaleate both in solution and under extrusion processing conditions by ^1H n.m.r. and i.r. spectroscopy. The ^1H n.m.r. spectra allowed an estimation of the degree of incorporation of the maleate groups.

(Keywords: PVC; Diels–Alder reaction; polyene; ^1H n.m.r.; maleate)

INTRODUCTION

PVC is known to lose HCl on heating to give polyenes, for example during processing if stabilizers are not present. It is generally accepted that after the loss of the initial HCl molecule from the polymer chain, further loss of adjacent HCl groups occurs. This leads to the formation of extended polyene sequences. This is normally referred to as the 'zipper' mechanism[1–5]. It can be represented as:

$$\sim CHCl\text{–}CH_2\text{–}CHCl\text{–}CH_2\text{–}CHCl\text{–}CH_2 \sim$$
$$\Big\downarrow \ \text{–HCl}$$
$$\sim CH{=}CH\text{–}CHCl\text{–}CH_2\text{–}CHCl\text{–}CH_2 \sim$$
$$\Big\downarrow \ \text{–HCl}$$
$$\sim CH{=}CH\text{–}CH{=}CH\text{–}CHCl\text{–}CH_2 \sim$$
$$\Big\downarrow \ \text{–HCl}$$
$$\sim CH{=}CH\text{–}CH{=}CH\text{–}CH{=}CH \sim$$

etc.

The initial loss of HCl probably takes place from positions where labile (tertiary and allylic) chlorine atoms are present. HCl is known to catalyse the further loss of HCl[1–5].

To what extent the Diels–Alder reactions can occur between dienes (polyenes) formed on dehydrochlorination of PVC and dienophiles is still not clear, although many studies over a number of years have been carried out. It has been suggested[4,6–8] that the stabilization ability of organotin maleates, which are efficient stabilizers for PVC, is partly due to the Diels–Alder reaction between these stabilizers and the diene system formed on partial degradation of PVC. Diels–Alder adducts have been obtained between a tin maleate (triphenyltin methyl maleate) and 2,3-dimethylbuta-1,3-diene[9]. Organotin maleates are also effective HCl acceptors[2]. This is of paramount importance for PVC stabilizers due to the catalytic effect of HCl on the degradation of this polymer. Exchange reactions between organotin compounds and allylic chlorine atoms in PVC may also play a part in the stabilization ability of these tin compounds[10].

For the Diels–Alder reaction to occur the diene must be in the cisoid conformation, whereas the expected preferred conformation of polyene sequences in partially dehydrochlorinated PVC is *trans*. Nevertheless Diels–Alder adduct formation has been reported between partially dehydrochlorinated PVC and suitable dienophiles in solution. Wirsen and Floddin[11] claimed from u.v. studies that the presence of maleic anhydride reduces the formation of polyene sequences when PVC is dehydrochlorinated with base. In closely related work Kelen *et al.*[12,13], used u.v. spectroscopy to show a reduction in the PVC polyene concentration after reaction with chloromaleic anhydride at 140°C. The presence of a Diels–Alder adduct of PVC and dibutylmaleate was indicated by the presence of a carbonyl band in the i.r. spectrum of the resulting sample after heating PVC in dibutylmaleate for 1 h at 250°C and then 14 h at 205°C (ref. 14). Diels–Alder addition of conjugated polyenes is also considered to be important in the crosslinking of PVC during degradation[15].

However, it is still not possible to predict how readily and to what extent Diels–Alder adducts can be formed when PVC is partially dehydrochlorinated. If the Diels–Alder reaction occurs rapidly in comparison to the further loss of HCl, then this approach could be a possible route for the modification of PVC during processing. This paper reports our studies on Diels–Alder addition reactions between partially dehydrochlorinated PVC and maleates both in the melt (under simulated processing conditions in a Brabender Plastograph) and in solution.

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Table 1 Brabender tests with PVC and long-chain maleates

Conditions						Product	
Maleate							
Substitutes	wt (g)	PVC wt (g)	Temperature (°C)	Time THF soluble (min)	Colour	THF soluble diene sites (wt%)	% possible reacted products
di-C_{16}	7.5	42.5[a]	175	20	Grey/black	55	0.2
di-C_{18}	7.5	42.5[b]	180	20	Light brown	79	0.2
di-C_{16}	6.0	54.0[b]	200	20	Black	29	1.15

[a] Using Corvic K50
[b] Using Corvic 571600
[c] Calculated from n.m.r. spectra

EXPERIMENTAL

Materials

The PVC was ICI Corvic 571600 ($\bar{M}_n$ ca. 40 000) or K50 ($\bar{M}_n$ ca. 30 000) and was unstabilized. Diethylmaleate, dimethylformamide (analytical grade), pyridine (analytical grade) and lithium chloride (laboratory reagent) were obtained commercially. Dihexadecylmaleate (dicetylmaleate) and dioctadecylmaleate were prepared from maleic acid and the respective alcohols using a literature method[16] for preparing esters.

Brabender processing

The PVC/maleate mixtures were mixed in a food blender and then at 120°C in the Brabender Plastograph (190 rev min^{-1}, 10 min).

The PVC blend was then processed in the Brabender at about 23 rpm for 20 min. Processing temperatures are given in *Table 1*.

The processed polymer samples were broken into small pieces, ground in a hammer mill, dissolved in hot tetrahydrofuran (THF) and filtered. Petroleum ether was added dropwise to the cooled THF solution until it became cloudy. This solution was then added slowly to a large excess (10 fold) of petroleum ether (b.p. 60–80°C) to precipitate the PVC, which was filtered off. The precipitation procedure was repeated. The THF insoluble product was removed by filtration, washed with THF and dried under vacuum.

Solution reactions

All the reactions were carried out under an atmosphere of oxygen-free nitrogen. Details of the dehydrochlorination procedures are given in the Results and Discussion section. When a dienophile was used, it was present at the start of the reaction. After completion of the run, the solution was filtered to remove any solid material. The solvent was removed from the filtrate under reduced pressure to give a solid product. This was treated with hot THF in an analogous manner to the work-up procedure for the Brabender tests.

No stabilizers were present during the solution reactions or during the Brabender processing.

Spectra

N.m.r. spectra were recorded in CS_2/acetone (d_6) at 250 MHz on a Bruker WM250 or 90 MHz on a Varian EM390 spectrometer. I.r. spectra were measured as KBr discs on a Mattson Alpha Centauri FT/IR instrument.

RESULTS AND DISCUSSION

The partial dehydrochlorination of PVC in solution under basic conditions to yield conjugated polyene sequences is well known. The dehydrochlorination can be carried out by refluxing a solution of PVC in dimethylformamide (DMF)[17], by refluxing a pyridine solution[18], by treatment of a DMF solution at 80°C with lithium chloride (LiCl)[19,20] or by treatment of a solution of PVC in THF or dioxan with ethanolic potassium hydroxide[18]. These methods were used in our study for the dehydrochlorination of PVC. The formation of polyene sequences is indicated by the deep red colour that develops.

When we dehydrochlorinated PVC with LiCl/DMF, the u.v./vis spectra of the solution showed a broad maximum at 520–540 nm. The increase in intensity of this peak, and therefore the polyene concentration with time, is shown in *Figure 1*. It appears that formation of polyene sequences is a relatively slow process, at least under these conditions. There is a slight increase in the wavelength maxima with time from 520 nm after 20 min to 545 nm after 3 h. This indicates a small change in the length of the polyene sequences, which may alter the extinction coefficient. However, the effect of any variation in extinction coefficient would be expected to be small.

Wirsen and Flodin[11] and Kelen *et al.*[12,13] have shown that when partially dehydrochlorinated PVC is reacted

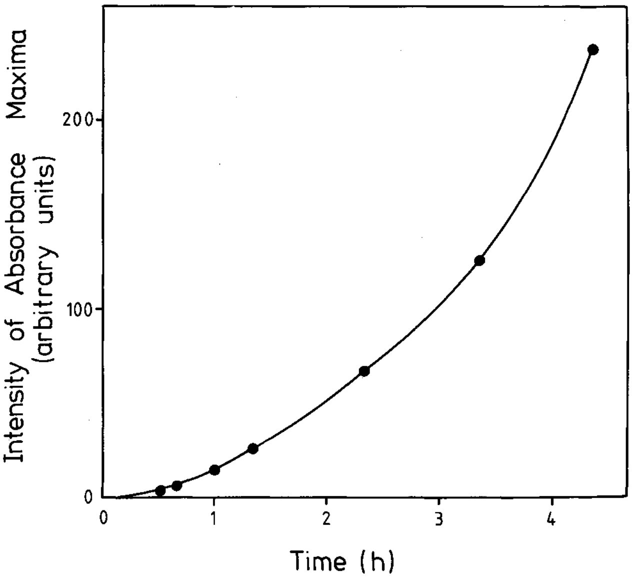


Figure 1 Variation in the absorbance intensity with time. PVC (3 g)/DMF (300 ml)/LiCl (13.7 g) at 80°C

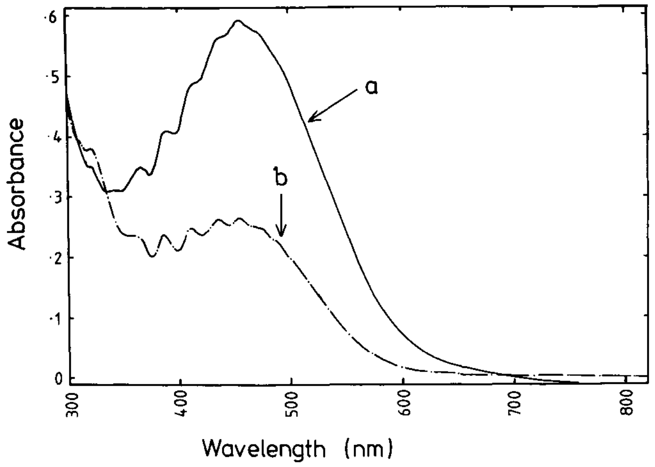


Figure 2 U.v./vis spectra of PVC (3 g); a, refluxed in pyridine (250 ml); b, refluxed in pyridine (250 ml) with diethylmaleate (6 g) for 225 min. Solutions diluted 50 times

with maleic or chloromaleic anhydride a decrease in polyene concentration occurs, as shown by u.v./vis spectroscopy, presumably due to Diels–Alder adduct formation. In our studies, the presence of diethylmaleate reduces polyene formation but does not prevent it, nor does it significantly affect the length of the polyenes (see *Figure 2*). The absorption maxima in curve a in *Figure 2* indicates a chain length of 13 conjugated double bonds. The calculated polyene length is based on the values of Daniels and Rees[21] which show some variation in the absorption wavelengths and the number of double bonds from those of others[22,23]. The intensity of u.v./vis absorption increases with time, in both the absence and presence of diethylmaleate and other similar dienophiles. The intensity of u.v./vis absorption spectra after 1 h reflux with pyridine without maleate was about the same as after 4 h with maleate present.

Although previous work has shown that Diels–Alder adducts can be formed from partially dehydrochlorinated PVC, there has not been a quantitative assessemnt of the extent of adduct formation. It is hard to measure the incorporation of small amounts of a simple dienophile into PVC. We used dihexadecylmaleate (1a) and dioctadecylmaleate (1b) because these are more suitable for quantitative determination by ^{1}H n.m.r. when incorporated into PVC than simple dienophiles. The CH_2 groups of the methylene chains in these maleates are a convenient 'spectroscopic label' for assessing incorporation even at low concentrations. Results from reaction of the long chain maleates with partially dehydrochlorinated PVC in solution and during simulated processing in a Brabender Plastograph are given in *Tables 2* and *1*, respectively. The PVC obtained from these treatments exhibits degradation by its darker colour and reduced solubility in THF compared to the starting PVC, which is totally soluble. Somewhat surprisingly, after these treatments, the lower molecular weight PVC (K50) is less soluble on THF than the higher molecular weight PVC (571 600) as can be seen in *Tables 1* and *2*.

Typical ^{1}H n.m.r. spectra for the THF soluble product from refluxing in pyridine experiments and Brabender processing are given in *Figures 3* and *4*, respectively. These spectra show a strong methylene chain CH_2 signal at 1.3 ppm and a terminal CH_3 of the methylene chains at 0.9 ppm arising from reacted maleate. In the ^{1}H n.m.r. spectra of dioctadecylmaleate and dihexadecylmaleate the signal for the CH_2 groups α and β to oxygen are centred at 4.1 and 1.6 ppm respectively. The signal of the CH=CH protons is at 6.15 ppm. These weaker signals are not distinguishable in the PVC/maleate spectra. The per cent adduct formation was calculated from the intensity of the CH_2 peak at 1.3 ppm compared to the PVC (CHCl) peak centred at *ca.* 4.5 ppm.

To distinguish between physically entrapped and chemically incorporated maleate, controlled and

Table 2 Reaction of PVC (3.0 g) and long-chain maleates (6.0 g) in boiling pyridine (250 ml)

PVC	Maleate	Time at temperature (h)	THF soluble product (wt%)	% of possible diene sites reacted in THF soluble product[a]
571600	di-C_{16}	5.5	50	3.8
571600	di-C_{18}	5	20	1.7
571600	di-C_{16}	7	30	1.9
K50	di-C_{16}	5.5	10	1.7

[a] Based on ^{1}H n.m.r. spectroscopy

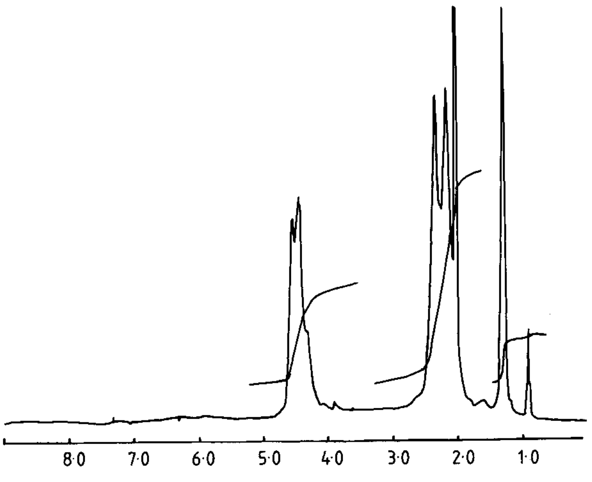


Figure 3 250 MHz ^{1}H n.m.r. of the THF soluble product from the reaction of PVC and dihexadecylmaleate in pyridine

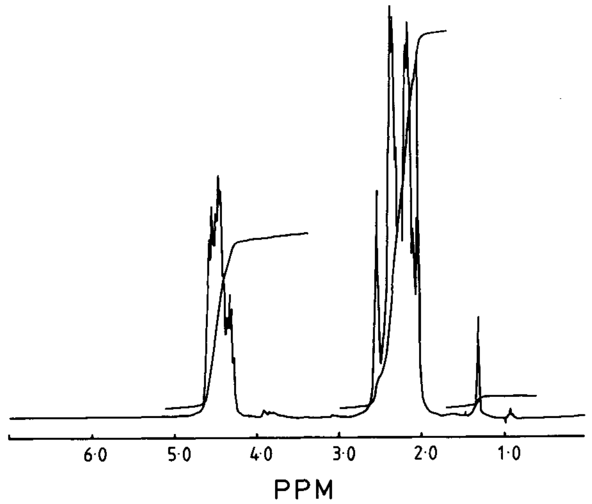
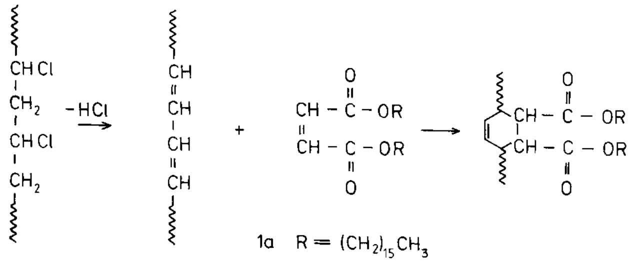


Figure 4 250 MHz ^{1}H n.m.r. of the THF soluble product from the reaction of PVC and dihexadecylmaleate in a Brabender Plastograph

Scheme 1



1a $R = (CH_2)_{15}CH_3$

1b $R = (CH_2)_{17}CH_3$

repeated precipitation of the THF soluble product with petroleum ether was carried out. A mixture of PVC and maleate which had been blended in a high speed mixer at 120°C and was worked-up in the same way showed no peak at 1.3 ppm in the ^1H n.m.r., nor did PVC which was refluxed in pyridine without maleate or processed in the Brabender without maleate. Further evidence that chemical reaction rather than physical entrapment had occurred was that there was no change in the relative intensities of the n.m.r. signals on extraction in a Soxhlet apparatus for 4 h with cyclohexane.

Additional support for chemical reaction between partially dehydrochlorinated PVC and dihexadecylmaleate was obtained from i.r. spectroscopy. The i.r. spectra of the THF soluble product (3.8% incorporation) showed weak carbonyl peaks at 1734 and 1724 cm^{-1} compared to 1739, 1730 and 1718 cm^{-1} in the starting maleate. I.r. studies on the isoluble products were inconclusive. We were unable to ascertain whether the product, both from solution experiments and from processing studies, which had undergone degradation crosslinking, had also reacted with the maleate.

The percentage incorporation reported in *Tables 1* and *2* is based on the reactions shown in *Scheme 1*. The number of possible diene sites is calculated on the assumption that complete loss of HCl could occur.

CONCLUSIONS

Conclusive evidence was obtained for the formation of Diels–Alder adducts between partially dehydrochlorinated PVC and a number of maleate esters, both in solution and, for the first time, under processing conditions. However, the results indicated that even the presence of an excess of these reactive dienophiles does not prevent formation of long polyene sequences which result in degradation of PVC. This may be attributed to the slow rate of diffusion within the polymer matrix (especially in the melt), steric hindrance to the approach of the dienophiles and perhaps to a relatively high barrier to the interconversion of *trans* dienes to the required cisoid conformation for the Diels–Alder reaction. As a consequence, the use of the Diels–Alder reaction as a means of modification of PVC during processing by grafting-on a suitable dienophile is unlikely to be a viable approach because of the simultaneous degradation of PVC that occurs.

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REFERENCES

1 Gottesman, R. T. and Goodman, D. *Am. Chem. Soc. Symposium Ser.* 1985, **285**, 383
2 Wypych, J., 'Polyvinyl Chloride Degradation', Elsevier, Amsterdam, 1985
3 Tubos, F., Ivan, B., Kelen, T. and Kennedy, J. P. in 'Developments in Polymer Degradation—6' (Ed. N. Grassie), Elsevier, London, 1985, pp. 147–189
4 Owen, E. D. (Ed.) 'Degradation and Stabilisation of PVC', Elsevier, London, 1984
5 Naqvi, M. K. *J. Macromol Sci.–Rev. Macromol Chem. Phys.* 1985, **C25**, 119
6 Wypych, J. 'Polyvinyl Chloride Stabilization', Elsevier, Amsterdam, 1986, p. 94
7 Wirth, W. O. and Andreas, H. *Pure Appl. Chem.* 1977, **49**, 627
8 Titow, W. V. in 'PVC Technology', 4th Edn. (Edn. W. V. Titow), Elsevier, London, 1984, p. 301
9 Mufti, A. S. and Poller, R. C. *J. Chem. Soc. (C)* 1967, 1767
10 Poller, R. C. *J. Macromol. Sci.–Chem.* 1978, **A12**, 373
11 Wirsen, A. and Floddin, P. *J. Appl. Polym. Sci.* 1979, **23**, 2005
12 Tudos, F., Kelen, T., Nagy, T. T. and Turcsanyi, B. *Pure Appl. Chem.* 1974, **38**, 201
13 Kelen, T. *J. Macromol. Sci.–Chem.* 1978, **A12**, 349
14 Malac, J. *Polym. Lett.* 1971, **9**, 85
15 Kelen, T., Ivan, B., Nagy, T. T., Turcsanyi, B., Tudos, F. and Kennedy, J. P. *Polym. Bull.* 1978, **1**, 79
16 Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G. and Tatchell, A. R. 'Vogel's Textbook of Practical Organic Chemistry', 4th Edn., Longmans, London, 1978, p. 508
17 Wirsen, A. and Floddin, P. *J. Appl. Polym. Sci.* 1978, **22**, 3039
18 Mukherjee, A. K. and Gupta, A. *J. Macromol. Sci.–Chem.* 1981, **A16**, 783
19 Roth, J.-P., Rempp, P. and Parrod, J. *J. Polym. Sci., Part C* 1963, **4**, 1347
20 Sorensen, W. R. and Campbell, T. W. 'Preparative Methods of Polymer Science', 2nd Edn., Wiley–Interscience, 1968, pp. 234–235
21 Daniels, V. H. and Rees, N. H. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 2115
22 Abbas, K. B. and Sorvik, E. M. *J. Appl. Polym. Sci.* 1975, **19**, 2991
23 Lechermeier, G., Revillon, A. and Pillot, C. *J. Macromol. Sci.–Chem.* 1978, **A12**, 285