

THERMAL DEGRADATION OF CHEMICALLY CROSSLINKED POLY (VINYL CHLORIDE)

A. H. K. Yousufzai, Ruqia Mahmud and Shabihul Hasan

PCSIR Laboratories, Karachi-39.

(Received February 18, 1985; revised February 13, 1986)

Studies have been made of thermal degradation of chemically crosslinked poly (vinyl chloride) at 202°. It has been found that the rate of dehydrochlorination of chemically crosslinked poly (vinyl chloride) was inhibited while that of the previously gelled PVC was faster. A possible explanation has been given.

INTRODUCTION

It is now generally believed [1-3] that the process of dehydrochlorination of poly (vinyl chloride) is free-radical in nature. Though sufficient evidence is now available in support of the above point, there is always room for more experimental proof. C.H. Bamford [4] was the first to obtain a definite evidence of active free radicals participating in these degradations of PVC by degrading PVC in the presence of toluene α -t and toluene x -¹⁴C at 180°. It was observed that both materials became incorporated into the polymer chain and dehydrochlorination was found to be directly related to the extent of their incorporation. Ph₃P (triphenyl phosphine) markedly catalyzed the dehydrochlorination at 120° and a graft copolymer of methyl methacrylate and PVC was obtained in the presence of Ph₃P.

The presence of free radical in the process of the dehydrochlorination of poly (vinyl chloride) was positively identified for the first time by Yousufzai *et al.* [5]. When PVC was degraded in the presence of chloromercury acetaldehyde (CMA), this compound decomposed alone [6] thermally at around 200° to give mercurous chloride, acetaldehyde and ketene by a free radical process, the mercurous chloride being formed by the combination of two HgCl radicals. When PVC was decomposed in the presence of CMA, mercuric chloride was formed as an additional product. Since no trace was found of mercuric chloride when CMA was decomposed in an atmosphere of hydrogen chloride, it was concluded that in degrading PVC, chlorine atoms were present which reacted with HgCl radicals to give mercuric chloride.

The thermal degradation of PVC is always accompanied by crosslinking and gelation prior to dehydrochlorination. The present paper deals with the thermal degradation of chemically crosslinked PVC.

EXPERIMENTAL

Materials. Polyvinyl chloride: An emulsion grade PVC was used, manufactured by M/s Geon Japan Ltd. It was purified by dissolving it in cyclohexanone and precipitating in methanol. Solvents such as methanol, xylene and cyclohexanone were purified by the usual methods. A.R. grade kaolin (Merck), zinc chloride, stannic chloride and anhydrous aluminium chloride (B.D.H.) were used as such.

Methods. Crosslinking of PVC: Crosslinking of PVC was carried out in the presence of a Friedel-Craft catalyst [9]. The PVC was suspended in solvents such as xylene, dioxane, benzene, toluene; catalysts were added in 0.5 – 1.5 vol. % and kaolin was about 18 %. The mass was refluxed for 4 hr. at SnCl₄ (50 – 90°), ZnCl (70 – 140°) and FeCl₃ (130 – 170°). The crosslinked PVC was then precipitated in methanol and dried at 60° under vacuum. The kaolin used was previously dried to 0.1 % moisture over 6 hours at 120°

Determination of Intrinsic Viscosities of the Polymer. The viscosities of plain and crosslinked PVC were determined in cyclohexanone using an Ubbelohde viscometer. The results were as follows:

RESULTS AND DISCUSSION

Poly (vinyl chloride) was crosslinked chemically by using a Friedel-Craft catalyst. The degree of crosslinking was determined by measuring their intrinsic viscosities in cyclohexanone, which are given in Table 1. The increase in the intrinsic viscosity is an indication of crosslinking prior to gelation, in which case the polymer will become insoluble in solvents. The crosslinked polymer was then degraded and the results are given in Table 2 and Fig. 1. It is evident from Fig. 1 that the degradation of PVC

Table 1

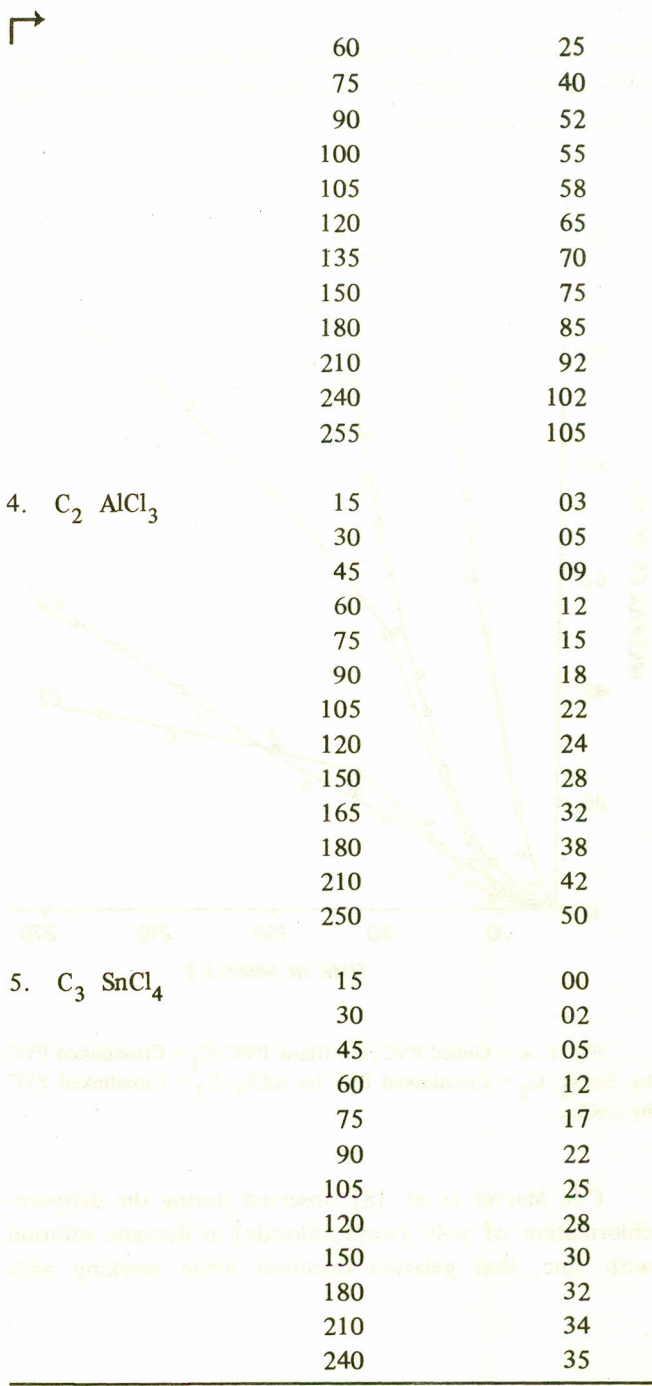
S. No.	Samples No.	Intrinsic viscosities
1.	PVC Blank	0.855 dL/g
2.	C ₁ - ZnCl ₂	1.186 "
3.	C ₂ - AlCl ₃	1.321 "
4.	C ₃ - SnCl ₄	1.311 "

Degradation of PVC: The degradation was carried out as described elsewhere [6].

crosslinked by chemical means is markedly inhibited. The curves C₁, C₂ and C₃ show the degradation pattern of crosslinked PVC by chemical means (C₁ = crosslinked by ZnCl₂; C₂ = crosslinked by AlCl₃ (anhyd); C₃ = crosslinked by SnCl₄). The degradation of blank PVC without any modification is shown by the curve B, while the curve A show the degradation of gelled PVC. The PVC was gelled at 165° for 5 min.

Table 2

S. No.	Sample	Crosslinked by time for degradation (in min.)	Millimoles of HCl
1.	A (Gelled PVC)	15	10
		20	15
		30	28
		45	75
		60	100
		75	112
		90	118
2.	B (PVC only)	15	04
		30	08
		45	15
		60	28
		75	45
		90	68
		100	95
		150	110
3.	C ₁ ZnCl ₂	15	01
		30	02
		45	13



It was also observed from Fig. 1 that the induction period of thermally gelled PVC was much shorter than with either plain PVC or chemically crosslinked PVC. The rates of thermally gelled PVC were higher than those of the plain PVC, while those of the chemically crosslinked PVC were much lower. It is believed that some amount of metallic salts from the decomposed Friedel-Crafts catalyst is trapped or retained by the crosslinked PVC and this reacts with the labile Cl atoms and is, thus, responsible for the inhibition of dehydrochlorination. It has already

been shown [7] that metallic soaps act as stabilisers for PVC, such as cadmium/aluminium, calcium and zinc stearates and are commercially used.

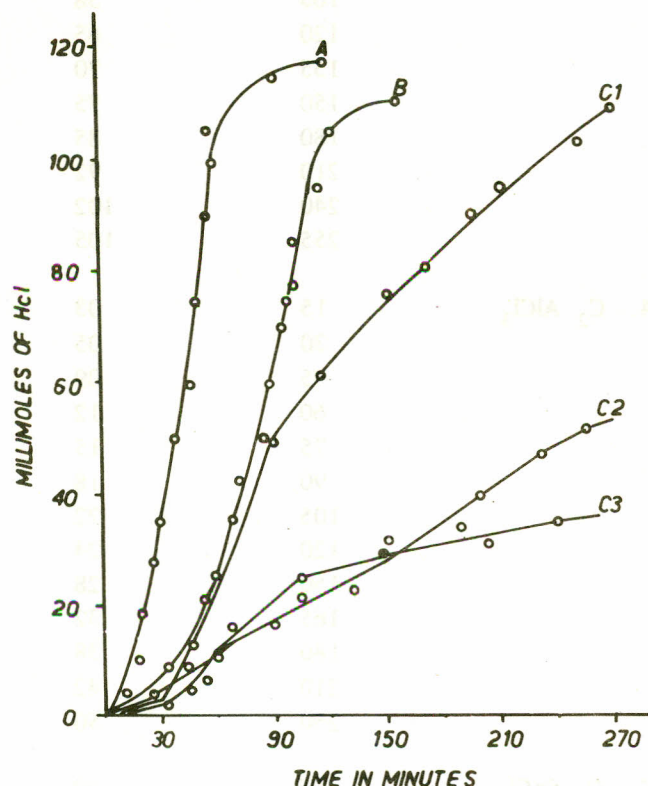
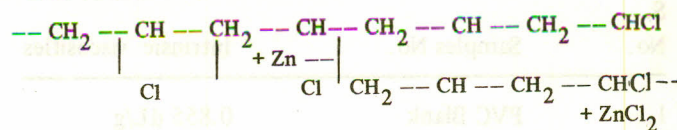


Fig. 1. A = Gelled PVC; B = Blank PVC; C₁ = Crosslinked PVC by ZnCl₂; C₂ = Crosslinked PVC by AlCl₃; C₃ = Crosslinked PVC by SnCl₄.

C.S. Marvel *et al.* [8] observed during the dehydrochlorination of poly (vinyl chloride) in dioxane solution with zinc, that gelation occurred while working with

strong solutions and that Cl reacted with zinc to form zinc chloride.



Probably a similar process takes place in this system also; the initial Cl' radical is trapped by metallic salts left over or trapped inside crosslinked PVC and this does not allow the growth of propagating radical; hence the radical process of degradation is markedly inhibited.

The marked inhibition of the degradation of poly (vinyl chloride) was also observed when PVC was degraded in the presence of chloromercuriacetaldehyde [5]. The inhibition was explained as the interaction of Cl radicals with HgCl radicals in the process, resulting in the inhibition of dehydrochlorination.

REFERENCES

1. M. Onuzaka, *J. Polym. Sci. A* 1, 5, 2229 (1967).
2. G. Arey, B.C. Head and R.C. Polar, *J. Polym. Sci., Macro-Molecular Reviews*, 8, 1-49 (1974).
3. W.C. Geddes, *Europ. Polym. J.*, 3, 267 (1967) B.
4. C.H. Bamford and D.F. Fanton, *Polymer*, 10, 63 (1969).
5. A.H.K. Yousufzai, M.M. Zafar and Shabihul Hasan, *Europ. Polym. J.*, 8, 1231 (1972).
6. W.I. Bengough and H.M. Sharp, *Makromol. Chem.*, 66, 31 (1963).
7. G. Briggs and N.E. Wood, *J. Appl. Polym. Sci.*, 15, 25 (1971).
8. C.S. Marvel, J.H. Sample and M.F. Roy, *J. Am. Chem. Soc.*, 61, 3241 (1939).
9. A.S. Nechaev and V.V. Goldstein, *Plast Massy*, 9, 37 (1976).