Cyclopentadienylation of Allyl-Chlorine Enriched PVC and Degradation Thereof

Béla Iván*[1], Joseph P. Kennedy[1], Tibor Kelen*[1] and Ferenc Tüdős[2]

[1] Institute of Polymer Science, University of Akron, Akron, OH 44325, USA

[2] Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, POB 17, Hungary

SUMMARY

Pendant cyclopentadienyl groups (Cp) have been introduced by treatment with Me_2CpAl into poly(vinyl chlorides) the allyl chlorine contents of which was augmented by mild chemical dehydrochlorination [PVC(A)]. Heating the cyclopentadienylated products [PVC(A)-Cp] led to gels, most likely by Diels-Alder addition, because the networks could be broken by strong dienophiles, e.g., maleic anhydride. The thermal stability of PVC(A)'s was improved upon Me_2CpAl treatment due to the substitution of thermally unstable allylic chlorines by Cp groups. The thermooxidative stability of PVC(A)-Cp was reduced relative to that of PVC(A) on account of the high oxidizability of Cp groups in the resin.

INTRODUCTION

Understanding and control of the mechanism of initiation, termination, and chain transfer in carbocationic polymerization led to the synthesis of various novel modified polymers exhibiting unique properties (KENNEDY, 1977, 1979). For example, cyclopentadienylated chlorobutyl rubber, ethylene-propylene copolymer (KENNEDY and CASTNER, 1979), and polychloroprene (IVÁN et al., 1980) have been obtained by cyclopentadienylation with Me_2CpAl. Treatment of these polymers by Me_2CpAl results in substitution of labile (tertiary and/or allylic) chlorines by Cp groups which may participate in Diels-Alder/retro Diels-Alder reactions. It has been demonstrated (KENNEDY and CASTNER, 1979, IVÁN et. al., 1980a, 1980b) that pendant Cp functions yield useful thermally reversible networks.

In the course of our investigations on cationic modification of PVC, we have decided to prepare PVC's with relatively high concentration of pendant Cp groups. Earlier studies have shown (IVÁN et al., 1981a) that cyclopentadienylation of commercially available resins and/or laboratory samples by Me_2CpAl produced PVC's containing insufficient amount of Cp groups for Diels-Alder network formation. Evidently the concentration of labile chlorines substituted by Cp Groups was extremely low. Recently we have synthetized colorless PVC's, PVC(A)'s, containing relatively high concentration of reactive allylic chlorines (IVÁN et al., 1981b, 1981c) useful for subsequent derivatizations, i.e., for the synthesis of reversible networks by cyclopentadienylation (IVÁN et al., 1981d).

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* Visiting scientist; permanent address: Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, POB 17, Hungary

This paper concerns cyclopentadienylation by Me_2CpAl of PVC's containing relatively high concentration of allylic chlorines [PVC(A)-Cp], and an examination of the thermal and thermo-oxidative degradation of these modified resins.

EXPERIMENTAL

A. Materials A commercially available suspension PVC, Geon 103 (from B.F. Goodrich Chemical Co.) has been used. The sample was purified by three precipitations from THF solution into methanol and dried under vacuum at ambient temperature.

Dimethylcyclopentadienylaluminum (Me_2CpAl) was synthesized by adapting the procedure for the preparation of diethylcyclopentadienylaluminum (GIANNI and CESCA, 1961). Me_2CpAl was used within a few hours after purification, i.e., sublimation at $\sim 120°C$ and ~ 2 mmHg.

Solvents were thoroughly dried and distilled.

B. Techniques Preparation of PVC(A)'s has been described in detail (IVÁN et al., 1981b). Great care was exercised during purification and handling of PVC(A)'s since traces of the base, t-BuOK, used for the synthesis of PVC(A)'s and protogenic impurities may seriously affect cationic reactions. Samples were twice precipitated from THF into methanol, filtered, then Soxhlet-extracted with methanol under a dry nitrogen atmosphere for 2 days.

Concentrations of polyenes in PVC(A)'s were determined by ozonolysis (MICHEL et al., 1975) followed by molecular weight determination by GPC (cf. Table I). These values, S, give also the concentrations of allylic chlorines in the polymer (IVÁN et al., 1981c).

TABLE I

Molecular weights (GPC) and concentration of allylic chlorines (polyene sequences) of PVC(A)'s determined by ozonolysis

Exp. No.	$\bar{M}_n^0 \cdot 10^{-3}$	$\dfrac{\bar{M}_w}{\bar{M}_n}$	$\bar{M}_n \cdot 10^{-3}$	$\dfrac{\bar{M}_w}{\bar{M}_n}$	$S = \dfrac{\bar{M}_n^0}{\bar{M}_n} - 1$
	after dehydro-chlorination		after ozonization		
Control	64.2	1.77	57.8	1.80	0.11
1	63.2	1.76	21.8	1.84	1.90
2	62.8	1.81	18.6	1.83	2.37
3	66.1	1.84	13.3	1.80	3.96

Me_2CpAl treatments were carried out by stirring $\sim 1\%$ by weight PVC(A) with 0.16 Me_2CpAl/VC unit in dry CH_2Cl_2 under a dry N_2 atmosphere at $-40°C$ for ninety minutes. Details of purification and handling are given elsewhere (IVÁN et al., 1981a).

Sol fractions were determined by the use of repeatedly freshly distilled, peroxide free THF. THF solutions were filtered and collected in preweighed flasks, then the THF was removed by rotovac and finally the samples were dried to constant weight under vacuum at room temperature.

Degradation experiments were carried out using carefully weighed (0.02 - 0.03 g) powdery PVC samples placed into U-shaped glass tubes (6 mm i.d.). The extent of dehydrochlorination was determined by conventional conductivity measurements of HCl solutions. The techniques have been described in detail (IVÁN et al., 1981a).

RESULTS AND DISCUSSION
A. <u>Cyclopentadienylation of PVC(A)'s</u> In contrast to commercially available PVC's, PVC(A)'s contain a relatively high concentration of allylic chlorines (IVÁN et al., 1981c) expected to be active sites in carbocationic reactions (KENNEDY, 1977; KENNEDY and CASTNER, 1979; IVÁN et al., 1980). Scheme I shows the proposed path of cyclopentadienylation of PVC(A)'s with Me$_2$CpAl. According to earlier studies (KENNEDY and CASTNER, 1979, IVÁN et al., 1980, 1981a) undesired methylation and/or deprotonation are essentially absent in the presence of high concentration of Me$_2$CpAl at low temperatures (-40°C).

Guided by the above facts, PVC(A)'s containing different concentrations of allylic chlorines have been cyclopentadienylated as described in the Experimental. It has been shown (IVÁN et al., 1980b) that cyclopentadienylated PVC(A)'s, PVC(A)-Cp, formed networks upon drying; however, the networks dissolved upon treatment by strong dienophiles, e.g., maleic anhydride. This phenomenon was regarded to prove reversible Diels-Alder network formation involving pendant Cp groups and polyene sequences introduced into PVC(A)'s by controlled chemical dehydrochlorination.

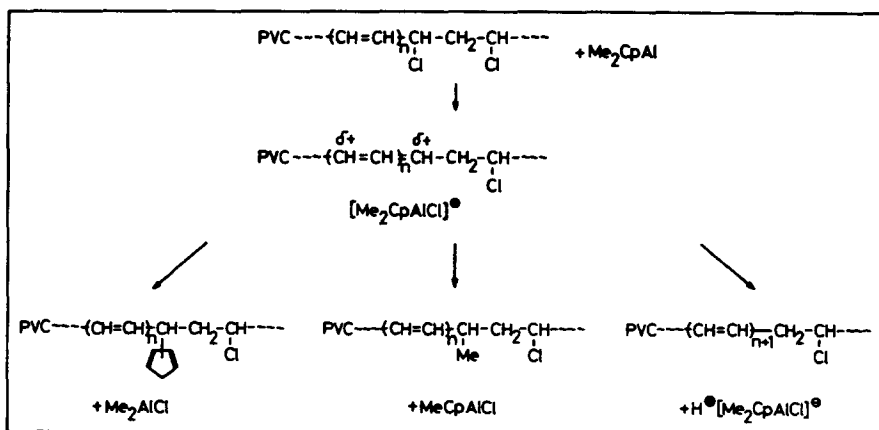<u>Scheme I.</u> Reaction between PVC(A) and Me$_2$CpAl.

Figure 1. Sol fraction of
PVC(A)-Cp's as a function of
internal allylic chlorines (S)
in PVC(A)

sol fraction

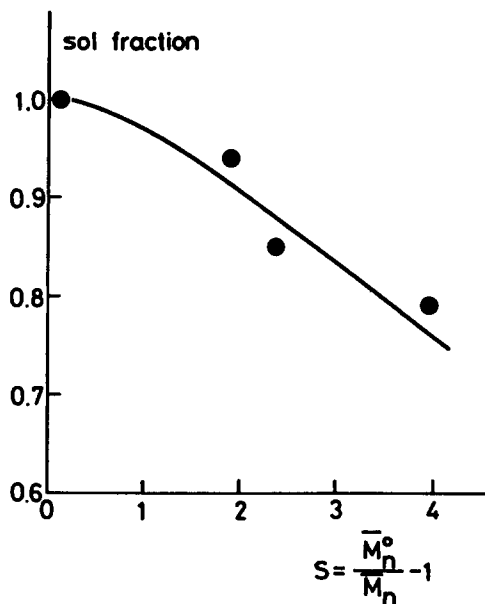$$S = \frac{\overline{M}_n^{\circ}}{\overline{M}_n} - 1$$

Figure 1 shows the sol fraction as a function of internal
allylic chlorine in PVC(A). Evidently, a relatively low
allylic chlorine concentration leads to a significant decrease
in the sol fraction after Me_2CpAl-treatment.

B. Thermal Dehydrochlorination The extent of HCl loss,
ξ_{HCl}, and initial rate of thermal dehydroclorination $(V_{HCl})_0$
of PVC(A)'s have been determined before and after treatment
with Me_2CpAl.

Figure 2 shows ξ_{HCl} as a function of time for PVC(A) and
PVC(A)-Cp. Apparently, the heat stability markedly increases
upon Me_2CpAl-treatment. According to the data in Figure 3, in-
itial dehydrochlorination rate for PVC(A) is a linear function
of S and is higher than that of PVC(A) treated with the cyclo-
pentadienylating agent. Furthermore, the heat stability de-
creases with the concentration of allylic chlorines in PVC(A)
and/or Cp groups in the treated samples.

These results indicate that Cp groups have replaced therm-
ally unstable allylic chlorines upon Me_2CpAl treatment of
PVC(A)'s as shown in Scheme I. Since the concentration of de-
fect sites, i.e., allylic chlorines, decreases with Me_2CpAl
treatment, the rate of initiation of HCl chain elimination (zip-
ping) should also decrease and consequently the thermal stabil-
ity of PVC(A)'s increases by cyclopentadienylation. Similar
observations have been made with cyclopentadienylated vinyl

Figure 2. Extent of HCl loss as a function of time for PVC and PVC-Cp, and for PVC(A) and PVC(A)-Cp during thermal dehydrochlorination(190°C,N_2)
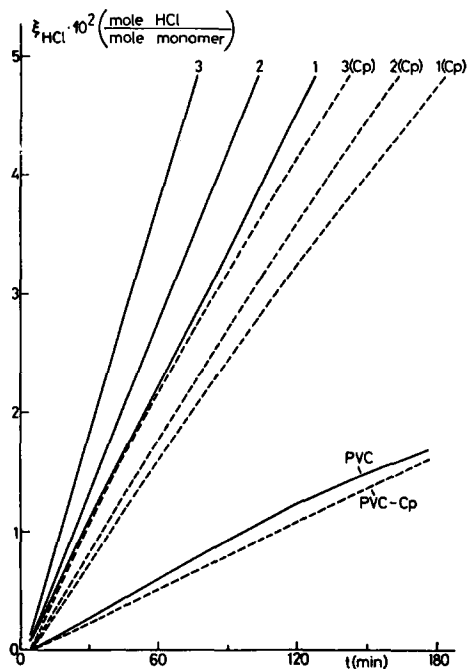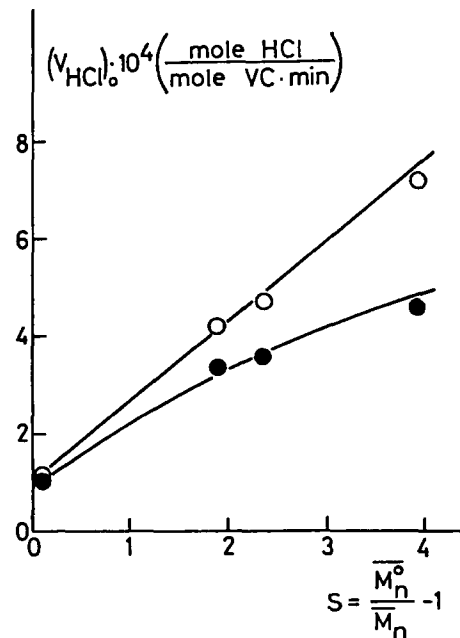
Figure 3. Initial dehydrochlorination rate as a function of S for PVC(A) (o) and PVC(A)-Cp (●) during thermal dehydrochlorination(190°C, N_2)

chloride/2-chloropropene copolymers, in which thermally unstable tertiary chlorines have been replaced by Cp groups by Me_2CpAl-treatment (IVÁN et al., 1981d).

C. Thermooxidative Dehydrochlorination In view of the well-known high oxidative sensitivity of substituted cyclopentadienes and conjugated polyenes, it was of interest to examine the thermooxidative behavior of cyclopentadienylated PVC(A)'s.

Figure 4 shows extent of HCl loss (ξ_{HCl}) as a function of time for untreated and Me_2CpAl-treated PVC(A)'s at 180°C under an oxygen atmosphere. Rates of thermooxidative dehydrochlorination are higher for cyclopentadienylated samples than that for untreated PVC(A)'s, i.e., thermooxidative stability decreases upon reaction of PVC(A)'s with Me_2CpAl. Figure 5 depicts the initial rate of HCl loss, $(V_{HCl})_o$, versus S obtained by ozonolysis of PVC(A)'s. According to the data in this Figure, $(V_{HCl})_o$ may be approximated by straight lines as a function of S for both PVC(A)'s and cyclopentadienylated samples. Evidently, the slope obtained for PVC(A)-Cp's is higher than that for PVC(A)'s.

These findings may be explained by the "minimum scheme" of

Figure 4. Extent of HCl loss as a function of time for PVC and PVC-Cp, and for PVC(A) and PVC(A)-Cp during thermo-oxidative dehydrochlorination (180°C, O_2)
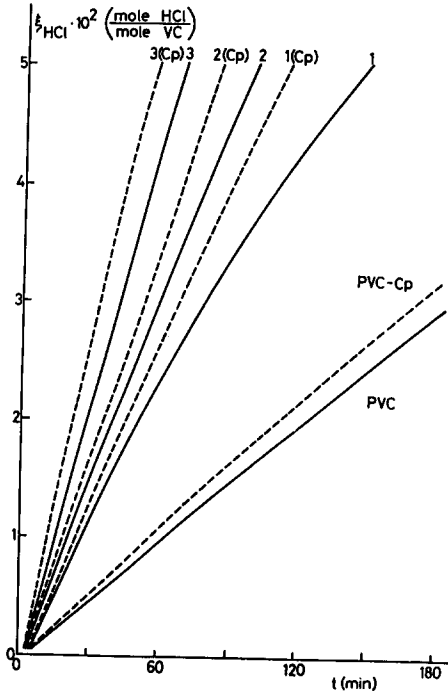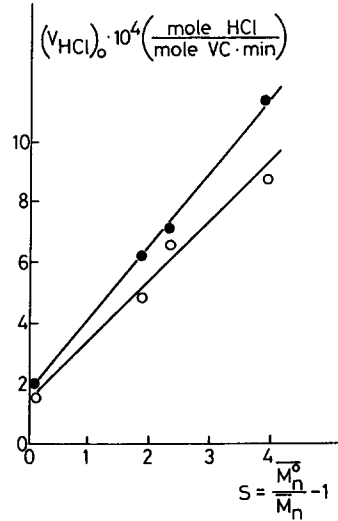
Figure 5. Initial dehydro-chlorination rate as a func-tion of S for PVC(A) (o) and PVC(A)-Cp (●) during thermooxidative dehydro-chlorination (180°C, O_2)

the main processes occuring during thermooxidative degradation of PVC (TÜDÖS et al., 1979). According to this scheme the char-acteristic features of thermooxidative PVC degradation are ther-mal initiation of HCl loss and polyene formation, fast oxida-tion of polyenes, formation of peroxy radicals which may initi-ate sybsequent dehydrochlorination by attacking regular units in PVC. Since PVC-Cp contains less thermally unstable allylic chlorines than PVC(A), the rate of thermal initiation is lower for PVC(A)-Cp than that of PVC(A). However, initiation of HCl loss by peroxy radicals formed during oxidation of Cp groups may compensate for the disappearance of allylic chlorines. According to Figures 4 and 5, this process leads to higher de-hydrochlorination rates for PVC(A)-Cp than for PVC(A). The same phenomenon has been observed with Me_2CpAl-treated commer-cial resins (IVÁN et al., 1981a) and vinyl chloride/2-chloro-propene copolymers (IVÁN et al., 1981d).

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