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Characterization and Degradation of Poly(Vinyl Chloride-*g*-Isobutylene) Carrying Tertiary Chlorine and Cyclopentadienyl Branch Termini

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SUMMARY

Poly(vinyl chloride-g-isobutylene)s have been synthetized by using PVC backbones containing relatively high concentration of allylic chlorines [PVC(A)] in conjunction with BCl_3 coinitiator. Since graft-termination occurs by ion-collapse, graft copolymers with tertiary chlorine branch termini [PVC(A)-g-PIB-Cl] were formed. The presence of terminal tertiary chlorines has been demonstrated by degradation and cyclopentadienylation experiments. UV-visible spectra of ungrafted and grafted PVC(A), molecular weight data, and branching frequency as a function of concentration of allylic chlorines indicate chain transfer to polyenes. Thermal and thermooxidative stability of PVC(A) increases upon grafting due to the replacement of allylic chlorines by PIB branches. The introduction of highly oxidizable Cp groups in PVC(A)-g-PIB-Cl by Me_2CpAl-treatment decreases the thermooxidative stability.

INTRODUCTION

A wide variety of novel block and graft copolymers exhibiting unique physical properties have been prepared during the past decade by cationic techniques (KENNEDY, 1977). For example, grafting and/or blocking of rubbery and glassy polymers may produce thermoplastic elastomers, materials that possess elastomeric behavior in the absence of chemical crosslinks.

Recent studies have demonstrated (KENNEDY, 1977; KENNEDY et al., 1977) that labile chlorines, e.g., tertiary and/or allylic, in conjunction with suitable cationic coinitiators provide initiation sites for grafting. Although PVC could be used as a starting material (initiator) for cationic grafting and interesting new PVC graft-copolymers have been synthesized (KENNEDY, 1977; GUPTA and KENNEDY, 1979; TRIVEDI and SCHULTZ, 1980, SHARMA and VARMA, 1980; IVÁN et al., 1981b, 1981d), grafting efficiency and the extent of grafting from virgin PVC i.e., grafted branches/PVC chain, remained low because the concentration of labile chlorines is extremely low in commercially available resins. GUPTA and KENNEDY (1979) have shown that the labile chlorine concentration can be increased by mild NaOH treatment in the absence of objectionable discoloration of the resin.

In the course of our continuing investigations on the degradation and cationic modification of PVC, we have developed a chemical dehydrochlorination method (IVÁN et al., 1981a)

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which led to PVC's containing short polyenes terminated with allylic chlorines [PVC(A)] (IVÁN et al., 1981c).

IVÁN et al. (1981b) have shown that PVC(A)/BCl_3/$\underline{i}$-C_4H_8 systems yield high grafting efficiencies (∿90%) even at relatively low allylic chlorine concentrations.

In view of the mechanism of termination of BCl_3-coinitiated isobutylene polymerization [$\sim CH_2C^{\oplus}(CH_3)_2BCl_4^{\ominus} \longrightarrow \sim CH_2C(CH_3)_2Cl + BCl_3$] the branch termini are expected to carry tert.-chlorine atoms (KENNEDY et al., 1977). Indeed cyclopentadienylation of PVC-$\underline{g}$-PIB's produced by BCl_3 led to reversible networks (IVÁN et al., 1981b) most likely because of Diels-Alder addition of the dangling Cp termini.

This paper concerns characterization (molecular weights, branching frequencies, composition) and degradation of poly(vinyl chloride-$\underline{g}$-isobutylene)'s, the PIB branches of which carry terminal tertiary chlorine atoms and cyclopentadienyl groups.

EXPERIMENTAL

A. Materials A commercially available suspension PVC (Geon 103, B.F. Goodrich Chemical Co.) has been used. It was purified by three precipitations from THF solution into methanol and dried under vacuum at ambient temperature. The preparation and purification of dimethylcyclopentadienylaluminum (Me_2CpAl) has been described (KENNEDY and CASTNER, 1979); it was used within a few hours after purification (sublimation). Solvents were dried and distilled by standard methods. The preparation of PVC(A) has been described (IVÁN et al., 1981a).

B. Techniques Grafting experiments and cyclopentadienylation by Me_2CpAl were carried out in a stainless steel enclosure under a dry nitrogen atmosphere. Grafting was carried out under vigorous stirring using 2 w% PVC solutions in dry CH_2Cl_2, 1.1 mole/dm^3 $\underline{i}$-C_4H_8 and $0.92 \cdot 10^{-2}$ mole/dm^3 BCl_3 at -50° for 30 minutes. Reactions were quenched by dry prechilled methanol. The separation of PVC-$\underline{g}$-PIB grafts from PVC and PIB homopolymers has been described (KENNEDY and DAVIDSON, 1977).

Cyclopentadienylation by Me_2CpAl (0.16 Me_2CpAl/VC units) was carried out under stirring in CH_2Cl_2 solution at -40°C for 90 minutes.

Molecular weights were determined by GPC (five Microstyragel columns), a Waters 6000 A pump and osmometry (Mecrolab-502 high-speed membrane osmometer).

Experimental details of thermal and thermooxidative dehydrochlorination have been described (IVÁN et al., 1981d).

RESULTS AND DISCUSSION

A. Characterization of PVC(A)-$\underline{g}$-PIB-Cl's Substituted allylic chlorines in conjunction with BCl_3 are efficient initiators in carbocationic polymerization. BCl_3-coinitiated isobutylene polymerizations are free from chain transfer and yield tertiary chlorine termini by ion-collapse (KENNEDY et al., 1977, 1979). Thus PVC(A)/BCl_3/i-C_4H_8 systems lead to poly(vinyl chloride-$\underline{g}$-isobutylene)'s carrying terminal tertiary chlorines [PVC(A)-$\underline{g}$-PIB-Cl]. Scheme I helps to visualize this process. IVAN et al. (1981b) have shown that grafting efficiencies are close to 100% in these systems.

Scheme I. Formation of PVC(A)-g-PIB-Cl

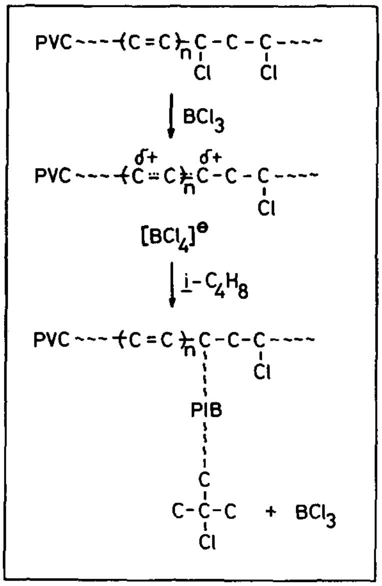


Figure 1. Branching frequency (b) as a function of concentration of internal allylic chlorines (S)

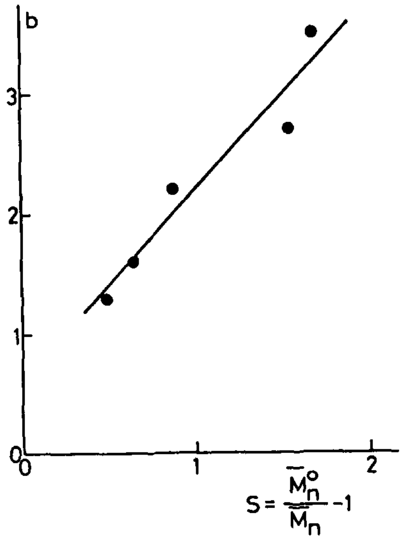


Figure 2.. UV-visible specta of a PVC(A) (sample 6) before and after grafting polyisobutylene by BCl_3 coinitiator

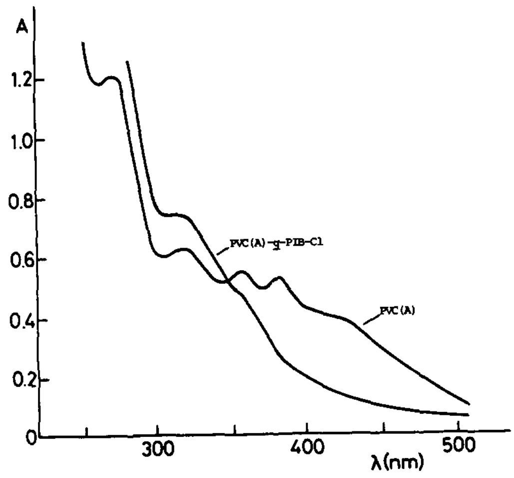


TABLE I

Effect of allylic chlorine concentration
(S, determined by ozonolysis) in PVC(A) on the grafting of isobutylene

Sample	S	$\overline{M}_n^o \cdot 10^{-3}$ (PVC)	*i*-C_4H_8 yield (%)	GE[a] (%)	$\overline{M}_n \cdot 10^{-3}$ (homo-PIB)	$\overline{M}_n \cdot 10^{-3}$ (PVC-*g*-PIB)	b[b]	PIB in the graft (%)
control	0.11	64.2	6	∿2	-	-	-	-
1	0.49	65.2	22	48	49.4	131	1.3	50
2	0.64	64.9	19	61	44.1	138	1.6	53
3	0.88	63.1	29	79	41.2	155	2.2	59
4	1.55	64.9	34	83	38.9	170	2.7	62
5	1.69	63.7	40	89	38.2	200	3.5	68
6	3.70	64.4	64	91	24.1	300	9.7	76

(a) GE = grafting efficiency

(b) Branching frequency: $b = \frac{\overline{M}_n(\text{PVC-}\underline{g}\text{-PIB}) - \overline{M}_n(\text{PVC})}{\overline{M}_n(\text{PIB})}$

Table I and Figures 1 and 2 show important characteristics of the grafting process and products. According to the data in Table I, $\underline{i}$-C_4H_8 yield and PIB content in the graft increase with increasing concentrations of allylic chlorines in PVC(A). In contrast, M_n's of homo-PIB's decreases as concentrations of allylic chlorines in PVC(A)'s increase. High branching frequencies (b>1) may be obtained with PVC(A)/BCl_3/$\underline{i}$-C_4H_8 systems (cf. Table I and Figure 1). Earlier research in which commercially available resins were used (KENNEDY and DAVIDSON, 1977), resulted in branching frequencies of about unity.

Figure 1 shows branching frequency, i.e., PIB branches/PVC chains in the graft, as a function of allylic chlorine concentration. According to the data, the slope of the b versus S plot is somewhat higher (1.56) than the expected unity slope. This may be attributed to various branch-forming reactions in addition to the expected grafting-from process, e.g., chain transfer to polyene sequences present in PVC(A)'s. Molecular weight data of homopolyisobutylenes (cf. Table I) also support this possibility. Therefore, we have decided to prepare a PVC(A) sample (No. 6) containing a relatively high concentration of polyenes and subsequently graft isobutylene from it. Figure 2 shows UV-visible spectra of the ungrafted and grafted PVC(A) (sample 6). Absorbances are lower in the visible region and higher somewhat in the UV region for PVC(A)-$\underline{g}$-PIB-Cl. This means that the length of polyene sequences, at least in part, decreased upon grafting. Evidently, the probability of branch formation increases with increasing polyene sequence length. The branching frequency obtained with this sample (b=9.7, see Table I) indicates a faster than linear increase in branching at high polyene contents. This is not surprising since conjugated olefins are known to be very active in carbocationic polymerizations (KENNEDY, 1975). Similar conclusions have been published by others (SIGWALT et al., 1976) for grafting of chlorobutyl rubber.

Subsequent modification of PVC(A)-$\underline{g}$-PIB-Cl's by Me_2CpAl yielded graft copolymers with reactive Cp branch termini, PVC(A)-$\underline{g}$-PIB-Cp, which yielded reversible networks by Diels-Alder/$\underline{\text{retro}}$-Diels-Alder reactions (IVÁN et al., 1981b). Scheme II helps to visualize the processes that result in PVC(A)-$\underline{g}$-PIB-Cp.

B. Thermal degradation of PVC(A)-g-PIB-Cl and PVC(A)-g-PIB-Cp It was of interest to study the degradation behavior of our graft copolymers. Figure 3 shows the extent of HCl loss (ξ_{HCl}) as a function of time for two PVC(A)'s (4 and 5 in Table I), and the corresponding PVC-$\underline{g}$-PIB-Cl's and PVC-$\underline{g}$-PIB-Cp's during thermal degradation. Extent of HCl loss is normalized to the PVC content of graft copolymers. According to the data, the thermal stability increases upon grafting. PVC-$\underline{g}$-PIB-Cl exhibits two dehydrochlorination phases, a relatively fast initial phase which is followed by a slower phase.

The increase in stability may be due to the disappearance of thermally unstable allylic chlorines which rapidly initiatie zip-elimination of HCl along the PVC chain. According to Scheme I during grafting allylic chlorines are replaced by PIB branches carrying tertiary chlorine termini. These termini are also unstable and eliminate HCl upon heating, but do not lead to fast zip-elimination of HCl. Thus, the relatively fast initial dehydrochlorination phase may be attributed to HCl loss from PIB branch termini carrying tertiary chlorine. PVC-*g*-PIB-Cp's show a slight increase in thermal stability relative to the corresponding PVC-*g*-PIB-Cl's. This result may be due to the absence of tertiary chlorines, i.e., substitution of labile tertiary chlorines by Cp groups during cyclopentadienylation by Me_2CpAl (see Scheme II).

C. *Thermooxidative degradation of PVC(A)-g-PIB-Cl and PVC(A)-g-PIB-Cp* Figure 4 shows the extent of HCl loss as a function of time for PVC(A) samples 4 and 5 and the corresponding PVC-*g*-PIB-Cl's and PVC-*g*-PIB-Cp's during thermooxidative dehydrochlorination (180°C, O_2). The thermooxidative stability of PVC-*g*-PIB-Cl is much higher than that of pure PVC(A)'s. The two dehydrochlorination phases apparent during thermal degradation are absent. The stability of PVC(A)-*g*-PIB-Cp is below that of PVC-*g*-PIB-Cl but is higher than that of PVC(A) during the early stages of thermooxidative degradation.

Scheme II. Cyclopentadienylation of PVC(A)-*g*-PIB-Cl by Me_2CpAl

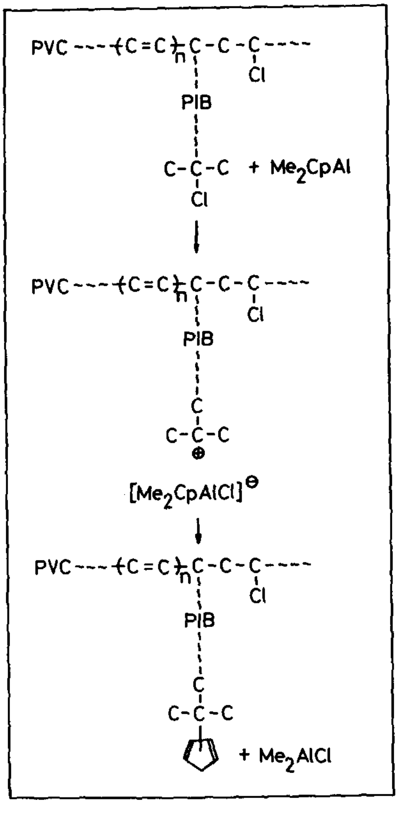


Figure 3. Extent of HCl loss as a function of time for PVC(A) (samples 4 and 5) and the corresponding PVC-g-PIB-Cl and PVC-g-PIB-Cp during thermal degradation (190°C, N_2)

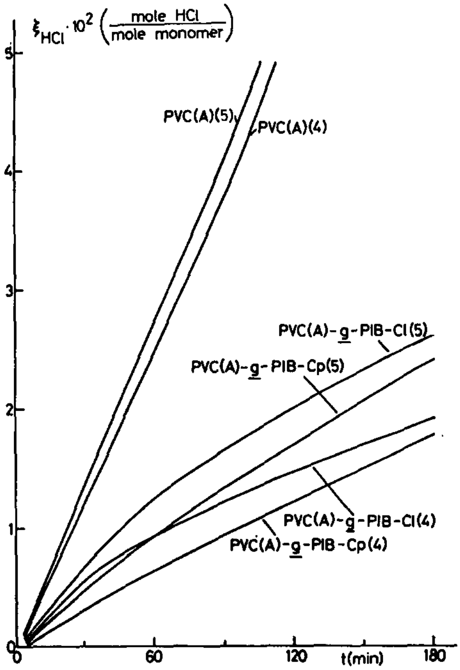
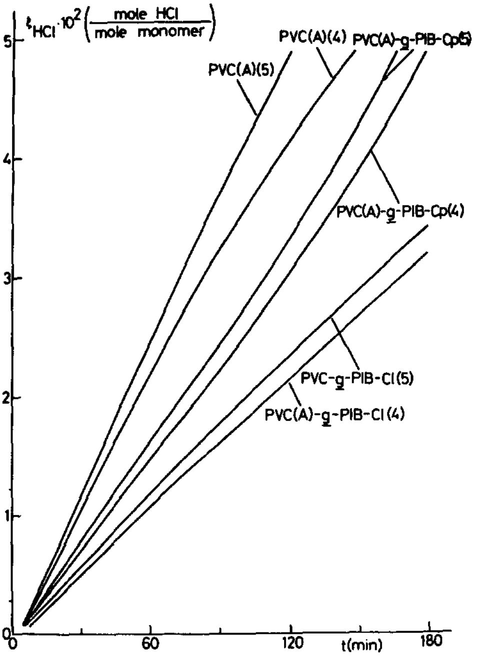


Figure 4. Extent of HCl loss as a function of time for PVC(A) (samples 4 and 5) and the corresponding PVC-g-PIB-Cl and PVC-g-PIB-Cp during thermooxidative degradation (180°C, O_2)



The increased thermooxidative stability of PVC-g-PIB-Cl may be attributed to the disappearance of allylic chlorines by grafting. On the other hand, the stability decrease of PVC-g-PIB-Cl by cyclopentadienylation is due to the introduction of highly oxidizable Cp groups into the graft copolymer. Thus, fast oxidation of Cp groups may produce peroxy radicals which may attack regular repeat units in the PVC chain and lead to initiation of HCl zip-elimination. These findings support earlier proposals (TÜDÖS et al., 1979) according to which the main process during thermooxidative degradation of PVC is due to the polyene → peroxide → peroxy radical sequence.

In sum, grafting of polyisobutylene branches from PVC(A) by BCl_3 coinitiator enhances thermal and thermooxidative stability of PVC. This improvement is due to replacement of relatively labile allylic chlorines during grafting. Changes in the morphology of the resin upon grafting (KENNEDY, 1977; KENNEDY and DAVIDSON, 1977) most likely also contributes to the enhanced stability.

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