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Degradation, Cyclopentadienylation, and Grafting of Vinyl Chloride/2-Chloropropene Copolymers

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ABSTRACT

Poly(vinyl chloride)s containing relatively high concentrations of tertiary chlorines (~ 0.8 -6.5 mol%) have been synthesized by heterogeneous free radical copolymerization of vinyl chloride with 2-chloropropene (VC/2-CP). Copolymerization rates and \overline{M}_n 's of VC/2-CP decreased with increasing initial 2-CP concentration in the monomer feed, which indicates that 2-CP is a retarder in VC polymerization. Initial dehydrochlorination rates of thermal and thermo-oxidative degradation of VC/2-CP copolymers have been found to be proportional with the concentration of 2-CP in the copolymer. However, other type of irregularities, e.g., unsaturations and/or random initiation of HCl loss from stable $-\text{CH}_2-\text{CHCl}-$ structures, also influence these

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processes. A linear relationship exists between the rates of initial thermal and thermo-oxidative dehydrochlorination processes. VC/2-CP containing pendant cyclopentadienyl (Cp) groups (VC/2-CP-Cp) has been prepared by treating the copolymer with dimethylcyclopentadienylaluminum (Me_2CpAl). VC/2-CP-Cp gelled on drying, however dissolved in the presence of strong dienophiles, e.g., maleic anhydride or dimethyl acetylenedicarboxylate. Evidently gelation is due to Diels-Alder addition of pendant Cp groups and may lead to thermally reversible networks. While the introduction of oxidizable Cp groups into VC/2-Cp decreases the thermo-oxidative stability, it increases the thermal stability of the copolymer because thermally unstable tertiary chlorines are replaced by Cp and/or Me groups. Grafting of isobutylene from VC/2-CP with Et_2AlCl coinitiator yielded poly(vinyl chloride-co-2-chloropropene-g-isobutylene) (VC/2-CP-g-PIB), graft copolymers with relatively high PIB content (60-90%) but low branching frequency (~ 1.27). Grafting of isobutylene increased both thermal and thermo-oxidative stability of the copolymer because of the replacement of unstable tertiary chlorines by PIB branches.

INTRODUCTION

During our continuing investigations on cationic modification of polymers we became interested in the synthesis of modified PVC's containing relatively high concentrations (several percent) of functional groups and/or grafted branches. Although PVC can be readily derivatized by cationic techniques [1-3], the concentration of the labile allylic and/or tertiary chlorines is extremely low in commercial resins [4]. On account of this fact the concentration of functional groups and/or grafted branches are also low in cationically modified PVC's [3, 5-9]. Recently we prepared PVC's containing relatively high concentrations of allylic chlorines and demonstrated their use in a variety of modifications, e.g., cyclopentadienylation, grafting [10]. Therefore, we set out to prepare PVC's carrying higher concentrations of active labile (tertiary and/or allylic) chlorines and to study the cationic modification and degradation behavior of these resins. We hoped that by increasing the concentration of active sites in PVC we could also increase the concentration of functional groups and/or grafted branches in the resin, which in turn would extend our range of control of properties of these materials.

This paper concerns the preparation of PVC's with relatively high amounts of tertiary chlorines ($\sim 1-5$ mol%), their cationic modification, and degradation behavior. According to recent ^{13}C NMR studies [4] the tertiary chlorine content in commercial and laboratory

PVC's is only 0.1-0.5%. Copolymers containing higher levels of tertiary chlorines have been synthesized by the free radical copolymerization of vinyl chloride (VC) and 2-chloropropene (2-CP) [11-15], and some properties of such VC/2-CP copolymers have been investigated. Previous workers, however, did not study the modification and thermo-oxidative degradation behavior of these copolymers.

EXPERIMENTAL

Materials

Vinyl chloride (VC), 2-chloropropene (2-CP), isobutylene, and solvents were purified by standard methods. The synthesis and purification of dimethylcyclopentadienylaluminum (Me_2CpAl) has been described [16]. Diethylaluminum chloride (Et_2AlCl) has been stirred over dry NaCl at 80°C for 2 h to remove alkylaluminum dichloride and vacuum distilled. Maleic anhydride (MA) and dimethyl acetylenedicarboxylate (DMADC) were used as received.

Procedures

Copolymerization

Copolymerizations of VC and 2-CP were carried out at 40°C using azobisisobutyronitrile (AIBN) initiator (for details, see Table 1). The polymerization kinetics was followed by dilatometry. The dilatometers were filled with carefully purified AIBN and 2-CP. The mixtures were freed from oxygen by vacuum freeze-thawing, and vinyl chloride was condensed into the ampules. Polymerizations were heterogeneous. After polymerization, the samples were washed with ethanol, precipitated from THF into methanol, dried, and Soxhlet extracted with dry methanol under dry nitrogen to remove initiator, monomer, and/or cationogenic residues. Finally, the purified samples were dried under vacuum at ambient temperature.

Cyclopentadienylation [16, 17]

Cyclopentadienylation of VC/2-CP with Me_2CpAl has been carried out in methylene chloride solutions (~1 wt% polymer) using 0.16 Me_2CpAl /monomer unit at -40°C for 90 min and vigorous stirring under a dry nitrogen atmosphere in a stainless-steel enclosure. Reactions were quenched by prechilled methanol. Further details and purification are given in Ref. 9.

TABLE 1. Polymerization Conditions and Characterization of Vinyl Chloride/2-Chloropropene Copolymers

Sample	Polymerization conditions ^a		Amount of 2-CP in copolymer ^b m (mol%)	Yield (%)	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n
	$[\text{AIBN}] \times 10^2$ (mol/dm ³)	$[\text{2-CP}]_0$ (mol%)				
1	1.34	-	-	13.7	78.4	2.01
2	1.39	0.50	0.78	12.0	73.4	1.71
3	1.31	1.12	1.42	10.0	59.4	1.87
4	1.52	2.25	3.45	9.0	53.2	1.82
5	1.47	4.80	6.46	6.7	31.5	2.05

^aTemperature: 40°C (heterogeneous polymerization).

^bDetermined by elemental analysis.

Grafting

Grafting experiments were carried out using stirred solutions of VC/2-CP in CH_2Cl_2 (~1 wt%), 1.9 mol/dm³ i-C₄H₉, 4.1×10^{-2} mol/dm³ Et₂AlCl coinitiator at -50°C for 30 min. Quenching, purification, and homopolymer separation have been described [10].

Dehydrochlorination

Thermal and thermo-oxidative dehydrochlorination techniques have been described [9].

GPC and Osmometry

Molecular weights have been determined by GPC (Waters 6000A equipment) and osmometry (Mechrolab-502 high-speed instrument).

RESULTS AND DISCUSSION

Copolymerization of Vinyl Chloride and 2-Chloropropene

Table 1 and Figs. 1-3 summarize VC and 2-CP copolymerization results. Copolymerization kinetics has been followed by dilatometry, and the time dependence of conversion is shown in Fig. 1. Conversions obtained by dilatometry were in good agreement with those determined by gravimetry. Polymerizations were heterogeneous from the onset of reaction. Figure 1 shows that initial rates of copolymerization and acceleration decrease significantly by increasing the concentration of 2-CP. According to the data in Fig. 2 and Table 1, molecular weights markedly decrease with increasing initial 2-chloropropene concentration [2-CP]₀. Evidently 2-chloropropene is a retarder in vinyl chloride polymerization. In the presence of 2-CP both initial rates and acceleration decrease significantly.

According to Fig. 3, a linear relationship exists between *m*, i.e., 2-CP content in $\text{-(CH}_2\text{-CHCl)}_n\text{(CH}_2\text{-C(CH}_3\text{)Cl)}_m$ copolymers (determined by elemental analysis) and [2-CP]₀ (cf. also Table 1). The data, however, are insufficient for low error determination of reactivity ratios *r*₁ and *r*₂ because of the very narrow monomer and copolymer composition range studied.

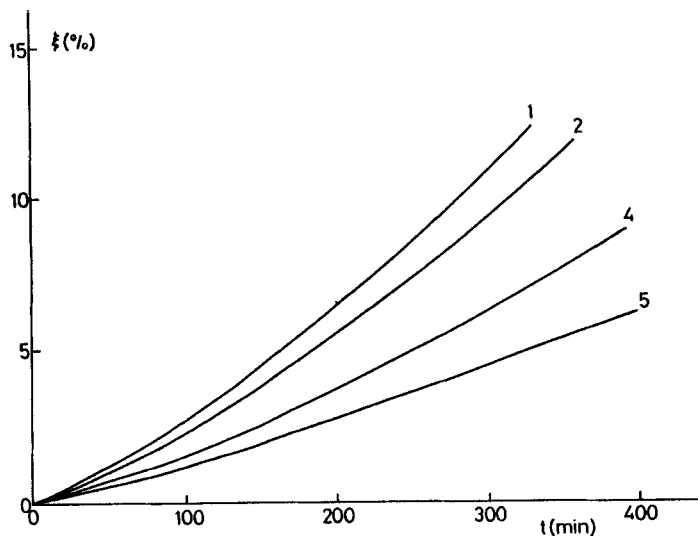


FIG. 1. Copolymerization conversion as a function of time (concentrations applied seen in Table 1).

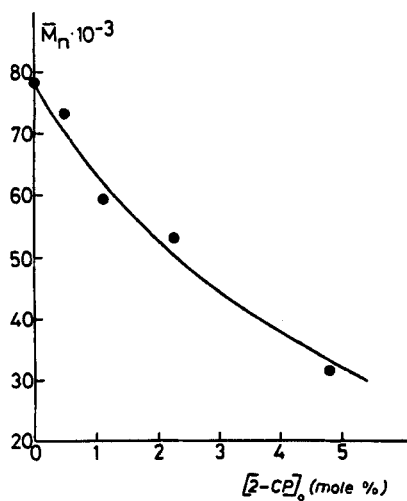


FIG. 2. Number-average molecular weights as a function of initial 2-CP concentration $[2-CP]_0$ in the monomer mixture.

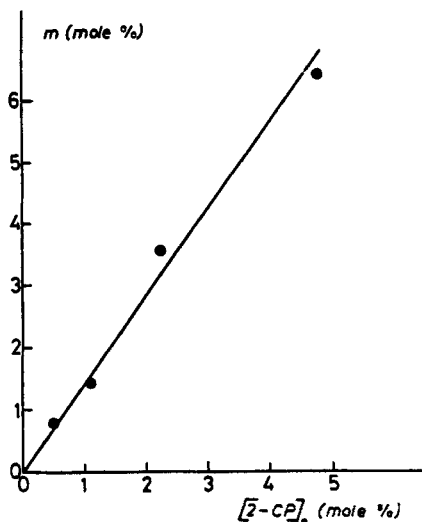


FIG. 3. 2-CP content of the copolymers as a function of initial 2-CP concentration in the monomer mixture.

Thermal and Thermo-oxidative Degradation of VC/2-CP's

Tertiary chlorines in PVC are believed to be thermally unstable defect-sites participating in the initiation of HCl loss during thermal degradation. Therefore it was of interest to study the effect of concentration of $-\text{CH}_2-\text{C}(\text{CH}_3)\text{Cl}-$ units in VC/2-CP copolymers on the thermal and thermo-oxidative stability.

Figure 4 shows the extent of HCl loss, ξ_{HCl} , as a function of time.

Evidently the rate of HCl loss increases with [2-CP] in the copolymer, i.e., the thermal stability decreases significantly with tertiary chlorine content. The effect is even better illustrated in Fig. 5 which is a plot of initial rates of HCl loss (V_{HCl}^0) against m , i.e., tertiary chlorine concentration in VC/2-CP's. Apparently a linear relationship exists between (V_{HCl}^0) and m , i.e., the rate of initiation of HCl loss, neglecting a possible increase in the zip-length of HCl elimination due to 2-CP units in the chain, is proportional to the concentration of tertiary chlorines. The relatively high intercept in the (V_{HCl}^0) versus m plot may be due to the presence of unsaturations, chain-end defects, etc., or to random initiation of HCl loss at regular VC units [4, 18-20].

Figure 6 shows the extent of HCl loss as a function of time for a series of VC/2-CP copolymers in an oxygen atmosphere. Rates of

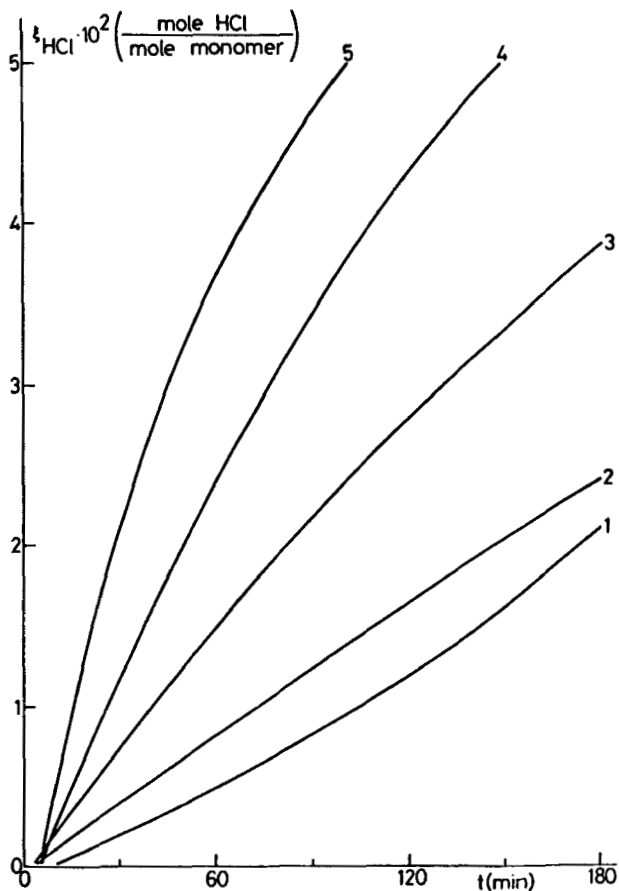


FIG. 4. Extent of HCl loss as a function of time for VC/2-CP's (for identification of curves, see Table 1) during thermal degradation (180°C , N_2).

thermo-oxidative dehydrochlorination are higher for samples containing higher concentrations of tertiary chlorines. Similarly, Fig. 7 depicts the initial rate of HCl loss versus m . Evidently $(V_{\text{HCl}})_0$ is a linear function of m . The intercept in the $(V_{\text{HCl}})_0$ versus m plot for thermo-oxidative dehydrochlorination, similarly to that of the thermal dehydrochlorination, may also be due to irregularities and/or random initiation of HCl loss at regular repeat units.

Interestingly, as Fig. 8 shows, the plot of the initial rate of thermo-oxidative dehydrochlorination (O_2) against that of the thermal

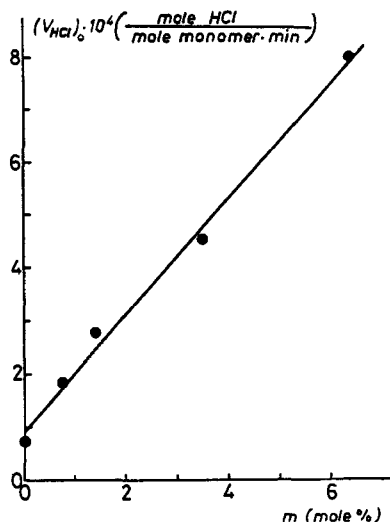


FIG. 5. Initial rate of HCl loss as a function of tertiary chlorine concentrations in VC/2-CP's during thermal degradation (180°C, N₂)

dehydrochlorination (N₂) gives a straight line with a slope higher than unity and a relatively low intercept. Evidently thermal and oxidative processes leading to HCl loss are closely coupled during thermo-oxidative degradation of PVC. The intercept in this plot, however, indicates that besides the processes included in the "minimum scheme" (introduced by thermal initiation of HCl loss [21, 22]), additional initiating processes are also effective in thermo-oxidative PVC degradation.

Cyclopentadienylation of VC/2-CP's with Me₂CpAl

VC/2-CP's containing relatively high levels of tertiary chlorines are expected to be suitable prepolymers for subsequent cationic derivatizations, such as cyclopentadienylation by Me₂CpAl. Based on earlier findings [8, 9, 16, 17], Scheme 1 shows the proposed path of cyclopentadienylation of VC/2-CP with Me₂CpAl. While simultaneous cyclopentadienylation, methylation, and dehydrochlorination might occur, earlier investigations with PVC's showed that dehydrochlorination is absent [8, 9].

Cyclopentadienylated copolymers (VC/2-CP-Cp) were soluble in CH₂Cl₂ immediately after their synthesis. After quenching, the contents of the reactors were divided into two and maleic anhydride (MA) was added to one part. Then the samples were purified and

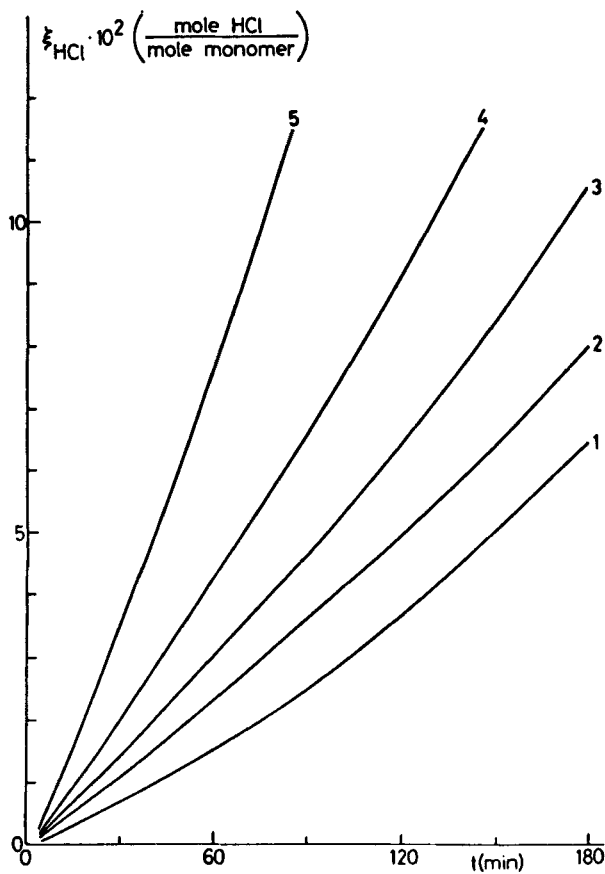


FIG. 6. Extent of HCl loss as a function of time for VC/2-CP's (for identification of curves, see Table 1) during thermo-oxidative degradation (180°C , O_2).

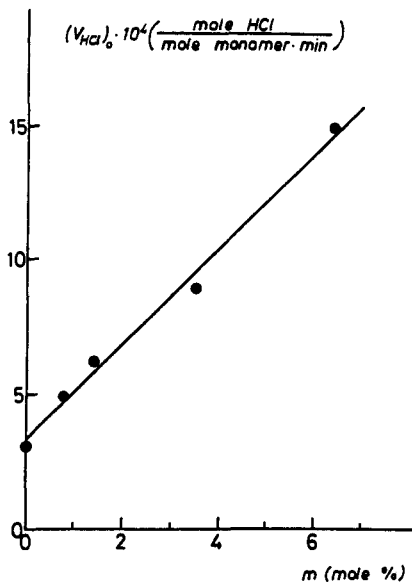


FIG. 7. Initial rate of HCl loss as a function of tertiary chlorine concentrations in VC/2-CP's during thermo-oxidative degradation (180°C, O₂).

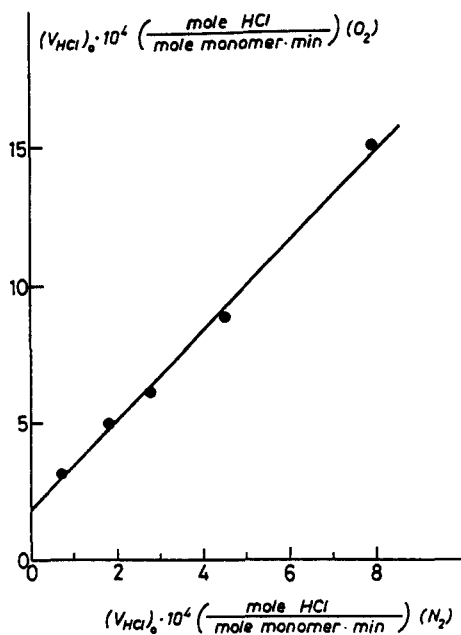
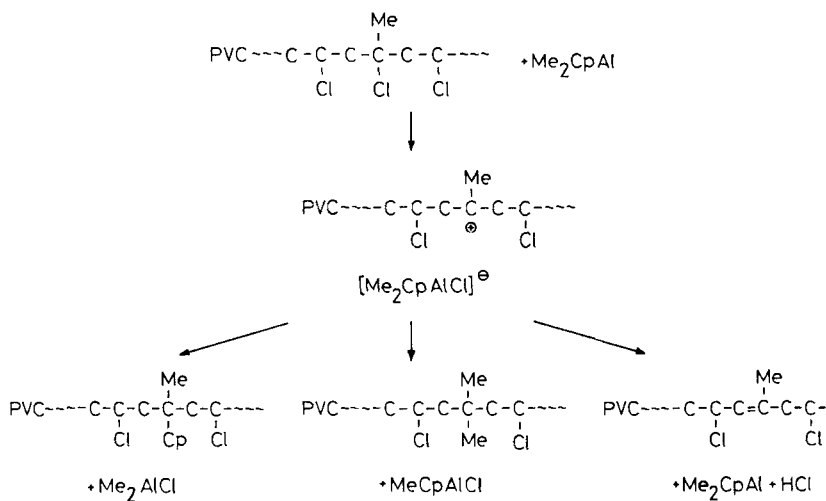


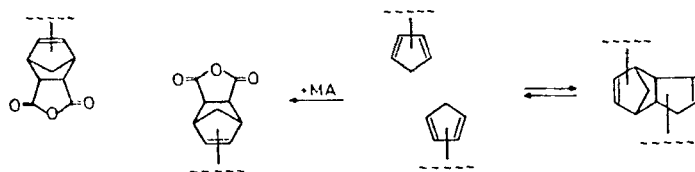
FIG. 8. Initial rate of HCl loss in thermo-oxidative dehydrochlorination (O₂) as a function of initial rate in thermal dehydrochlorination (N₂) for VC/2-CP's (180°C).



SCHEME 1. Cyclopentadienylation of VC/2-CP copolymer by Me_2CpAl .

vacuum dried at ambient temperature in the dark for 2-4 d. While the samples treated with MA were soluble in THF, the untreated samples became insoluble even after prolonged refluxing. Figure 9 shows that the amount of sol fraction rapidly decreases with the tertiary chlorine concentration in the initial resin. Importantly, however, when an excess of a strong dienophile, such as MA or DMADC, was added to swollen VC/2-CP-Cp gels in refluxing THF and/or 1,2,4-trichlorobenzene (TCB) diluents, the products rapidly dissolved. The observations are summarized in Table 2.

Gelation during the drying of VC/2-CP-Cp's is not due to undesirable permanent network formation but to Diels-Alder addition between pendant Cp groups. Addition of MA or DMADC affects dissolution because these strong dienophiles trap the free Cp functions and thus displace the Diels-Alder/retro-Diels-Alder equilibrium:



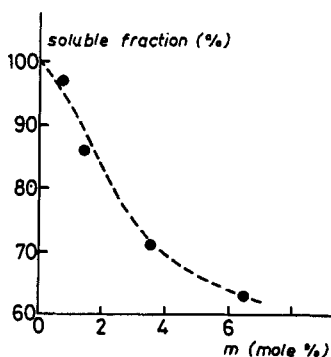


FIG. 9. Sol fractions of vacuum-dried VC/2-CP-Cp's as a function of tertiary chlorines in the untreated VC/2-CP's.

TABLE 2. Solubility of Cyclopentadienylated VC/2-CP-Cp's^a

Sample	MA added after Me ₂ CpAl-treatment, THF	VC/2-CP-Cp's			
		THF	Refluxing THF + MA	TCB (120°C) + MA	TCB (120°C) + DMADC
1	s	s	s	s	s
2	s	g	s	s	s
3	s	g	s	s	s
4	s	g	g	s	s

^as = soluble, g = gel.

Cyclopentadienylated VC/2-CP copolymers may yield useful thermally reversible networks and by subsequent modifications may lead to other valuable derivatives as well.

The thermal and thermo-oxidative dehydrochlorination of cyclopentadienylated copolymers were also studied. Figure 10 shows the extent of HCl loss, ξ_{HCl} , as a function of time for Sample 4 (see Table 1) and for the cyclopentadienylated sample (4-Cp) during thermal (N₂) and thermo-oxidative (O₂) degradation. According to the data in this figure, the thermal stability increases upon cyclopentadienylation, which is most likely due to the replacement of labile tertiary chlorines in VC/2-CP by more stable Cp and/or methyl groups. In contrast, the thermo-oxidative stability decreases

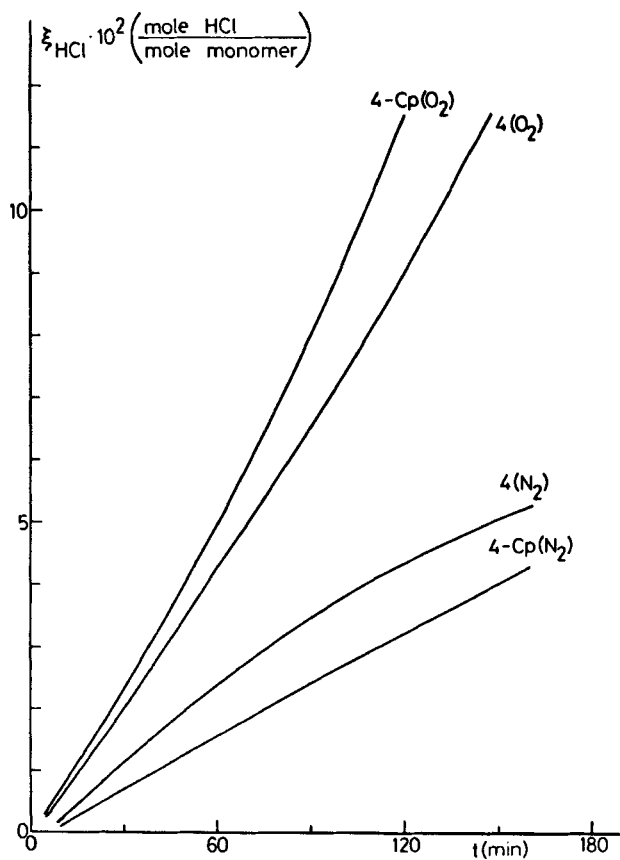
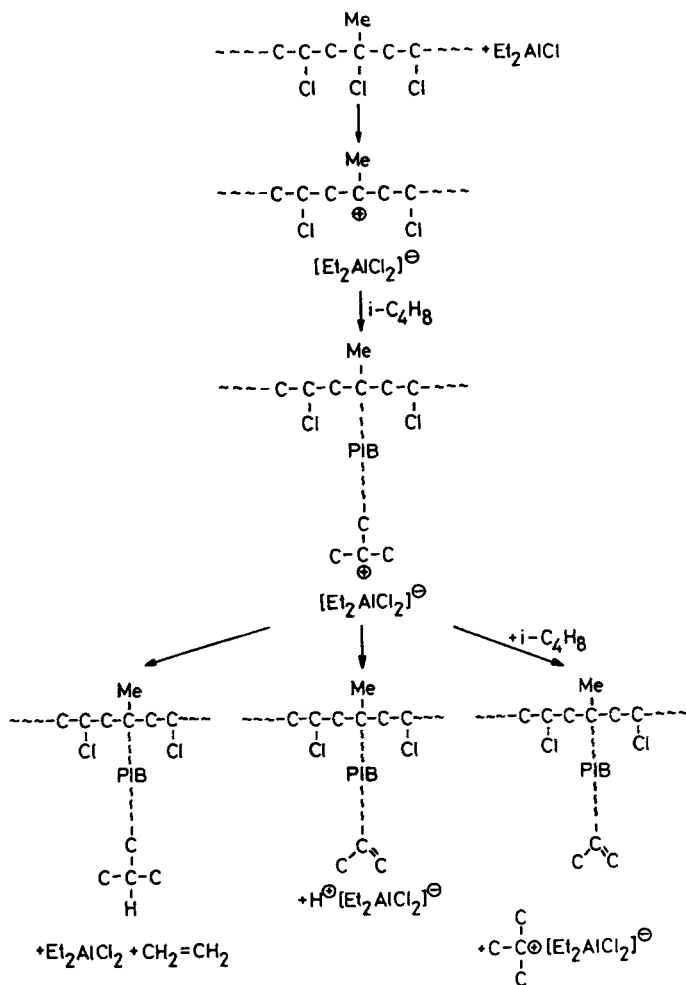


FIG. 10. Extent of HCl loss for VC/2-CP (Sample 4 of Table 1) and the corresponding VC/2-CP-Cp (Sample 4-Cp) during thermal (N₂) and thermo-oxidative (O₂) degradation (180°C).



SCHEME 2. Grafting of isobutylene from VC/2-CP copolymer using Et_2AlCl cointiator.

TABLE 3. Synthesis of VC/2-CP-g-PIB's

VC/2-CP sample ^a	m ^a	i-C ₄ H ₈ yield (%)	GE (%)	PIB homopolymer		VC/2-CP- g-PIB ($\bar{M}_n \times 10^{-3}$)	PIB in the graft (%)	b — B
				$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n			
2	0.78	8	58	101	1.9	180	59	1.05
3	1.42	14	61	111	1.8	188	68	1.16
4	3.45	16	68	98	2.2	285	81	2.36
5	6.46	23	71	139	1.9	400	89	2.65

^aFrom Table 1.

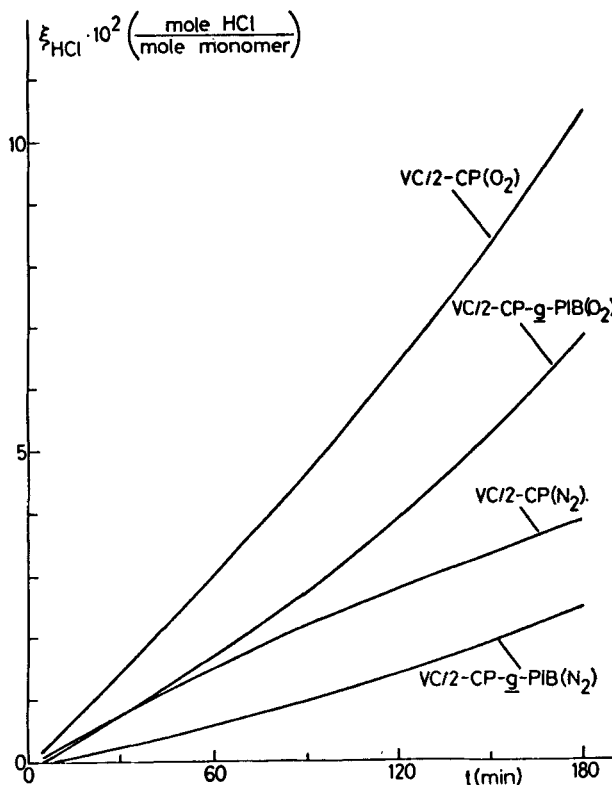


FIG. 11. Extent of HCl loss for VC/2-CP (Sample 3 of Table 1) and the corresponding VC/2-CP-g-PIB during thermal (N₂) and thermo-oxidative (O₂) degradation (180°C).

markedly upon Me₂CpAl treatment. This may be attributed to the introduction of highly oxidizable Cp groups into the resin. In line with the preceding part on degradation, fast oxidation of Cp groups leading to peroxy radicals would result in the initiation of subsequent HCl loss and thus would accelerate dehydrochlorination.

Grafting of Isobutylene from VC/2-CP's Using Et₂AlCl Coinitiator

Since tertiary chlorines in conjunction with certain organoaluminums are known to be effective initiators [23] in cationic polymerization of olefins, we decided to prepare poly[(vinyl chloride-co-2-chloroprene)-g-isobutylene] graft copolymers (VC/2-CP-g-PIB)

by using the VC/2-CP copolymer in conjunction with Et_2AlCl to initiate the grafting of isobutylene. Scheme 2 helps to visualize the formation of a polyisobutylene (PIB) branch. According to earlier investigations [24], chain breaking in this system may occur by termination (mainly hydridation) and/or by chain transfer to monomer. According to the data in Table 3, grafting efficiency GE [i.e., PIB in the graft/(PIB in the graft + PIB homopolymer)] increases with increasing tertiary chlorine concentration m in VC/2-CP. However, the effect is very small and may be within experimental variation. PIB yield also increases with m .

Branch frequencies (i.e., b/B , PIB branch/backbone, calculated from \bar{M}_n 's and assuming that the \bar{M}_n of the PIB branch and that of the extracted PIB homopolymer are identical) are relatively low and increase with m . Similar phenomena have been observed for the chlorinated ethylene-propylene copolymer/ Et_2AlCl and PVC/ Et_2AlCl graft systems [25].

Figure 11 shows the extent of HCl loss, ξ_{HCl} , as a function of time for VC/2-CP (Sample 3 of Table 1) and for the corresponding VC/2-CP-g-PIB during thermal (N_2) and thermo-oxidative (O_2) degradation. Evidently both thermal and thermo-oxidative stability significantly increase upon grafting which is due to the replacement of labile tertiary chlorines by stable PIB branches.

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