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Cyclopentadienylation of PVC

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Summary

Cyclopentadienylation of PVC with alkaline (NaCPD, LiCPD) and acidic (Me_2CPDAl) cyclopentadienylating agents has been investigated. In terms of product quality (absence of discoloration, gelation) Me_2CPDAl was found to be a superior cyclopentadienylating agent than NaCPD and LiCPD.

Introduction

There is a dearth of information on the synthesis of polymers containing cyclopentadienyl(CPD) pendant groups. A Japanese patent claims CPD salts of alkali metals as cyclopentadienylating agents for chlorrine-containing polymers i.e., poly(vinyl chloride) (PVC), polyepichlorohydrin , polychloroprene (HARUMI and SHYUZO, 1973). Recently Me_2CPDAl was used as cyclopentadienylating agent with similar chlorinated polymers (KENNEDY and CASTNER, 1979). A U.S. patent describes the free radical copolymerization of CPD containing monomers with conventional monomers as a route to introduce CPD groups into polymer chains (TAKESHITA et al., 1974). In view of the high polymerization reactivity of substituted CPD, the latter method most likely will result in crosslinked, ill-defined products.

This note concerns comparison of cyclopentadienylations of chlorinated polymers, particularly PVC, by using alkaline (NaCPD, LiCPD) and acidic (Me_2CPDAl) cyclopentadienylating agents. In terms of product quality Me_2CPDAl was found to be superior to alkali salts of CPD as a cyclopentadienylating agent for PVC.

Experimental

Cyclopentadiene (CPD) was prepared by thermal cracking of dicyclopentadiene (Aldrich, Chem. Co.) in the presence of calcium hydride and subsequent

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distillation over CaH_2 before use. NaCPD was synthesized by adding dropwise stoichiometric amounts of freshly distilled CPD to a 10% by weight suspension of sodium in freshly distilled, water and peroxide free THF, under nitrogen. LiCPD was prepared by reacting stoichiometric amounts of butyllithium and CPD in n-hexane under nitrogen. The precipitated LiCPD was filtered, washed with n-hexane and dried under vacuum at room temperature. Me_2CPDAl was synthesized by the procedure for the preparation of diethylcyclopentadienylaluminum (GIANNI and CESCA, 1961).

A low molecular weight ($\overline{M}_n$ = 14,400) purified laboratory PVC sample (H14, from Borsod Chemical Factory, Hungary) was used.

All cyclopentadienylating agents were used within a few hours after synthesis. Reactions of cyclopentadienylating agents with PVC were carried out in solution (5% PVC by weight) for two hours of stirring in a stainless-steel enclosure under a dry nitrogen atmosphere. The solvent was dry methylene chloride with Me_2CPDAl and freshly purified THF with LiCPD and NaCPD.

To remove alkali and aluminum residues the modified PVC samples were repeatedly precipitated, dissolved in THF, centrifuged under nitrogen and finally dried at ambient temperature under vacuum.

UV-visible spectra were registered on a Carey 17 instrument. Freshly distilled, peroxide free THF was used as solvent and reference.

Results and Conclusions

PVC samples were cyclopentadienylated in solution under a variety of conditions with NaCPD, LiCPD and Me_2CPDAl and after thorough purification the products were analyzed. Results are summarized in Table I and Figure 1. Visual observation (Table I) showed conspicuous color differences between samples treated with alkali salts of CPD on the one hand (discolored products) and Me_2CPDAl on the other hand (unchanged, colorless products). The degree of discoloration from yellowish to red to brown upon NaCPD or LiCPD treatment reflects the intensity of reaction conditions employed, i.e., discoloration progresses with increasing salt concentration (CPD/monomer ratio) and temperature (from -30 to 25°C). A colorless sample was obtained

Table I. Color and UV-visible Spectra of PVC Samples Treated with Different Cyclopentadienylating Agents

Exp. No.	CPD agent	Temperature °C	CPD/monomer ratio·100	Color of treated samples	Remarks
1	Me_2AlCPD	-30	1	white	no absorption above 325 nm
4		-30	10	white	no absorption above 325 nm
6		25	1	white	no absorption above 325 nm
14		25	10	white	no absorption above 325 nm
15		25	25	white	no absorption above 325 nm
20*		-30 and 25*	5	white	no absorption above 325 nm
16	NaCPD	25	1	yellow	absorption above 300 nm
17		25	10	dark red brown	gelation, insoluble in THF
18		-30	1	yellowish	absorption above 300 nm
19		-30	10	brick red	absorption above 300 nm
21	LiCPD	25	1	yellowish	absorption above 300 nm
22		25	10	dark brown red	absorption above 300 nm
23		-30	1	white	absorption above 300 nm
24		-30	10	red brown	absorption above 300 nm

*Treated 5 hrs at -30°C and subsequently 72 hrs at 25°C

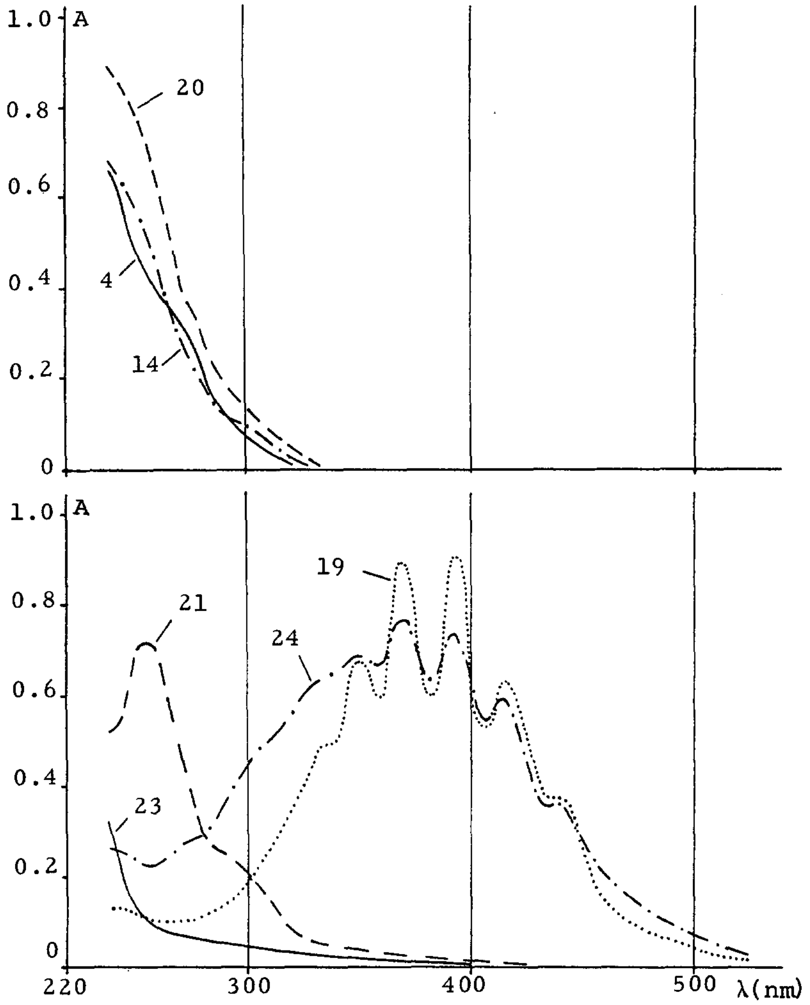

Figure 1. UV-visible spectra of THF solution of PVC treated with different cyclopentadienylating agents; numbers correspond to Exp. No. in Table I. Concentrations: (4), (14) and (20) 2 g/l, (19) and (24) 0.2 g/l, (21) 0.1 g/l and (23) 1 g/l

with LiCPD only in one experiment (Expt. No. 23, lowest salt concentration and temperature) however, according to spectroscopic analysis, the degree of cyclopentadienylation is very low, if at all present in this instance. In contrast, all cyclopentadienylated products prepared with Me_2CPDAl were colorless, white, even after relatively aggressive conditions (highest CPD/monomer ratio, temperature).

Subsequently UV-visible spectra of cyclopentadienylated samples were analyzed. According to the results shown in Figure 1 (numbering in the figure corresponds to Expt. No. in Table I), samples treated with NaCPD or LiCPD indicate the presence of long polyene sequences (strong, characteristic absorptions above 300 nm). These spectra are similar to those obtained by chemical dehydrochlorination of PVC with alcoholic KOH (BENGOUGH and VARMA, 1966; SHINDO and HIRAI, 1972; WIRSÉN and FLODIN, 1978) and by thermal degradation (for a review see DAVID, 1975). The colorless sample obtained with LiCPD under mildest conditions (Expt. No. 23) shows very little absorption throughout the range investigated and in this resembles virgin PVC. In contrast, the Me_2CPDAl-treated samples are transparent above ~325 nm. Significantly, absorption in the 200-300 nm range indicates the presence of pendant cyclopentadienyl groups in PVC (KENNEDY and CASTNER, 1979).

The long polyene sequences in the NaCPD and LiCPD treated samples indicate severe dehydrochlorination. This finding is not surprising in view of the well known alkali-sensitivity of PVC (MARVEL et al., 1939; WIRSÉN and FLODIN, 1978). Evidently, dehydrochlorination is less prone to occur in the presence of acidic Me_2CPDAl, rather the active chlorines in PVC are substituted by cyclopentadienylation and/or methylation. Model experiments with $\underline{t}$-BuCl/Me_2CPDAl have indicated (KENNEDY and CASTNER, 1979) preferential cyclopentadienylation, minor methylation and essentially no dehydrochlorination under conditions comparable to those employed in this study.

In conclusion, under acidic conditions cyclopentadienylation probably by S_N1 mechanism is faster than E1 elimination, whereas under basic conditions preferential elimination occurs by E2 or E1cB mechanisms and produces unacceptable resins under the conditions investigated. Studies are continuing in this field and will be reported.

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