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Effect of Vinyl Chloride Polymerization Conditions on Polymer Thermal Stability

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ABSTRACT

By appropriate modification of the reaction conditions in the polymerization of vinyl chloride, it is possible to prepare polymer with increased thermal stability. Two procedures are discussed: addition of a small amount of alkyl acrylate during radical polymerization and anion-radical polymerization by alkyllithium compounds.

My contribution concerns the effect of some conditions of polymerization of vinyl chloride on the thermal stability of the polymer.

If we take into consideration the fact that the rate of the degradative reaction doubles, or even trebles for each of 10°C increment, we can conclude that the improvement of stability of PVC to light or heat will exceed the lifetime of polymer severalfold. Such a life prolongation has the same result as an increase in polymer production with the simultaneous preservation of its original quality.

One of the methods for improving the general properties of PVC, including its thermal stability, is a process in which a small amount of another compound is added to the reaction mixture at the beginning or during polymerization. The added compounds fall into three groups:

first, monomers with higher polymerization activity than vinyl chloride; second, monomers with the same or lower polymerization activity; third, compounds which do not themselves polymerize but which are incorporated into the chain by interaction with the vinyl chloride.

It was useful to add compounds from the first group during polymerization in a controlled manner, either continuously or by gradual metering. If the copolymerization/reactivity ratios are equal, the second monomer does not need to be added gradually, but can be added at once before the polymerization starts. The purpose of this is to reduce the formation of labile sites along the poly(vinyl chloride) chain (i.e., the suggested presence of double bonds in the cis position) and also to shorten the length of the stereoregular sequences with just that amount of the second, or other suitable monomers or a combination, which will change the chemical and physical properties of the basic polymer only within the required limits.

According to the published data [1-4], the most stable structure results when there is one unit of the second monomer for each eight vinyl chloride units. However, such a copolymer would be completely different from PVC.

I will summarize some other cases published recently to illustrate the situation further. Thermal stability of suspension PVC was enhanced by the addition of fatty acids [5], for example, lauric acid, or by the addition of epoxidized cotton oil [6] or propylene cycloolefins and their various derivatives [7]. The vinyl chloride-vinyl fluoride, copolymer [8] exhibited increasing thermal stability with increasing content of vinyl fluoride.

We have been also interested in this problem. Several selected monomers were added continuously or by gradual metering during polymerization of vinyl chloride; for example, vinyl sulfate, styrene, alkyl methacrylates, alkyl acrylates, acrylonitrile, diphenylethylene. The amount added ranged from 1 to 5% relative to the initial monomer.

In the homologous series of acrylates, that is, methyl, ethyl, butyl, hexyl, and octyl acrylate, we investigated in more detail the effect of small additions of the second monomer on the changes in the chemical and physical properties of the product. We prepared samples of PVC incorporating about 0.5, 1.0, 3.0, and 5.0% alkyl acrylate. The chemical composition was determined by means of infrared spectra and the formation of sequences by NMR spectra, with other parameters obtained from measurements of viscosity, osmometry, light scattering, and GPC.

Figure 1 shows the relationship between molecular weight as determined by osmometry and the amount of methyl and octyl acrylate incorporated. The effect of the second monomer on this molecular parameter is not significant.

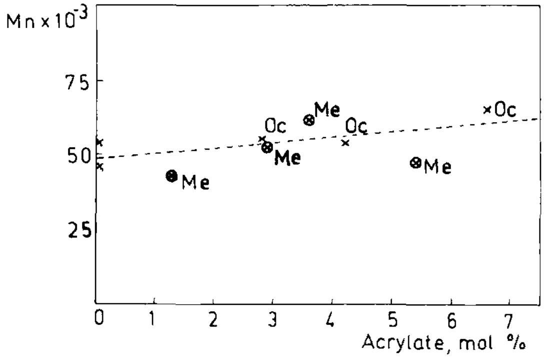


FIG. 1. Osmometrically determined $\overline{M}_n$ of vinyl chloride-methyl/octyl acrylate copolymers prepared under defined conditions with various amount of incorporated acrylate.

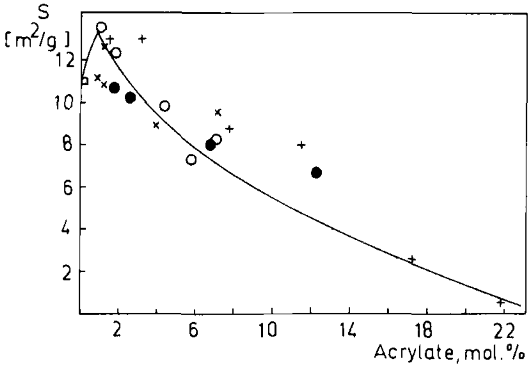


FIG. 2. Relationships between the specific surface area of VC-AA copolymers and the kind and amount of incorporated acrylate: (□) PVC; (×) MeA; (○) BuA; (●); (+) OCA.

The relationship between the specific surface area of vinyl chloride-alkyl acrylate copolymers and the type and amount of incorporated acrylate is demonstrated on Fig. 2. The specific surface area first increases up to about 2% alkyl acrylate incorporated and then decreases rapidly with increasing amount of alkyl acrylate.

As evident from Fig. 3, the glass-transition temperature T_g is

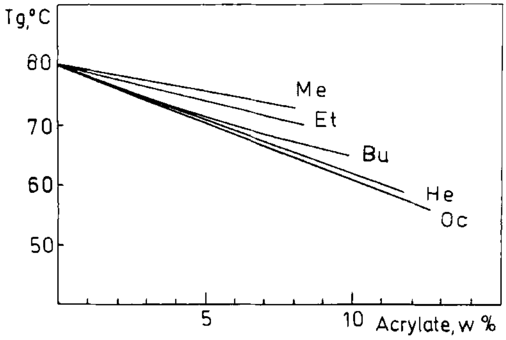


FIG. 3. Dependence of glass transition temperature on the amount of various alkyl acrylates incorporated in VCM-AA copolymers.

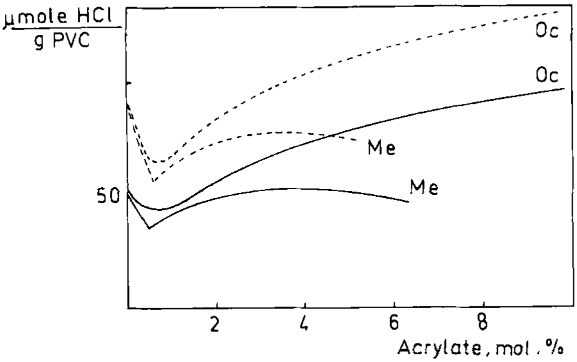


FIG. 4. Degrees of dehydrochlorination of VC-methyl/octyl acrylate copolymers at 180°C: (--) in air and (—) in nitrogen after 50 min as a function of amount of incorporated acrylate.

strongly reduced if 0.5-10% alkyl acrylate monomer is incorporated in the copolymer chain.

The thermal stability was characterized by dehydrochlorination analysis and by means of calendering tests. The results of the dehydrochlorination tests (Fig. 4) generally show that splitting off of HCl is reduced about 1% at relatively low amounts of incorporated acrylates. With increasing acrylate content it slowly increases, the

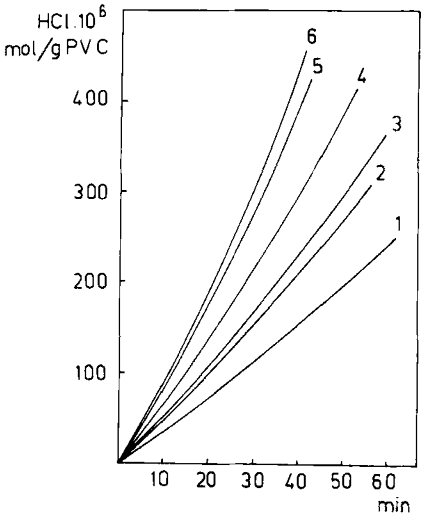


FIG. 5. Thermal dehydrochlorination of various VC-methyl acrylate (Covil) and VC-propylene copolymers (Airco) at 180° C in air: (1) Covil CAM3, 2.8% by weight; (2) Covil CAM3, 3.2%; (3) Airco 401, 2.5%; (4) Airco 405, 3.3%; (5) Airco 420, 4.7%; (6) Airco 470, 5.5%.

increase being higher the longer is the alkyl group of the acrylate monomer. Moreover, the dehydrochlorination reaction is reduced more markedly in nitrogen than in air.

The dehydrochlorination of vinyl chloride-methyl acrylate copolymers with about 3% of acrylate is significantly lower than that of vinyl chloride-propylene copolymers (Fig. 5).

The results given in Fig. 6 show the effect of methyl acrylate on the particle size after 10 min heat treatment in air at 200° C. Octyl acrylate groups exhibit a similar effect (Fig. 7).

Another way to improve the thermal stability of PVC lies in choice of a suitable catalyst system. Chain transfer reactions are one of the sources of defective structures in radical polymerization. This effect is reduced to a minimum in anionic or ion-radical polymerization. Thus, the thermal stability of PVC is substantially enhanced if vinyl chloride is polymerized with an organometallic catalyst, for example, with alkylaluminum or alkyllithium compounds [9-12].

We investigated the vinyl chloride-alkyllithium system, using as

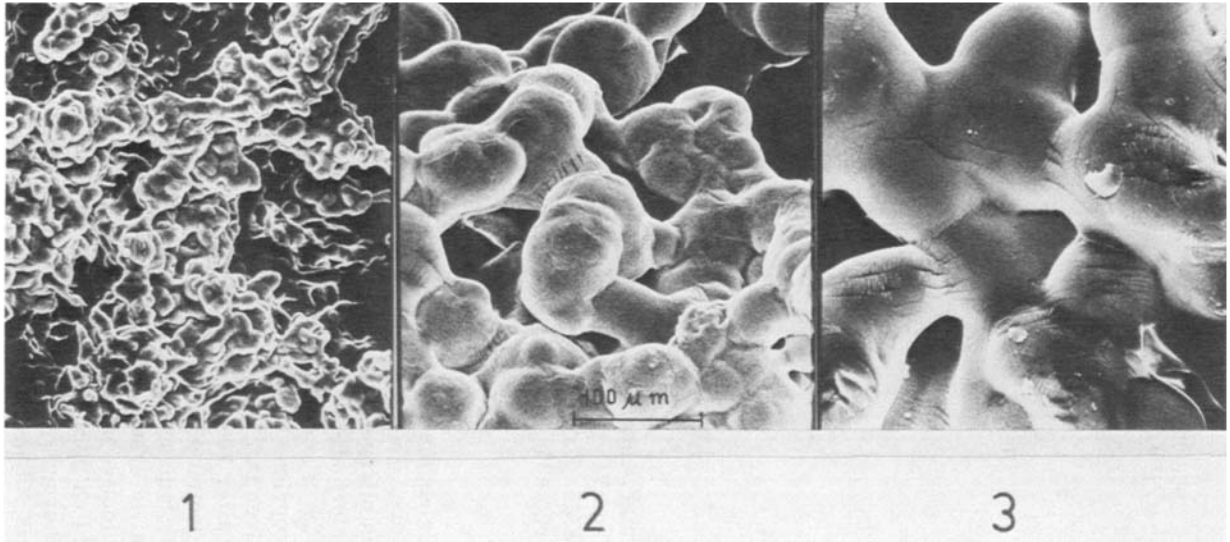


FIG. 6. Scanning electron micrographs (JEOL JSM-35) showing particle size of (1) PVC and VC-methyl acrylate copolymers with (2) 0.7 mole % and (3) 3.36 mole % of incorporated methyl acrylate after 10 min of treatment in air at 200°C.

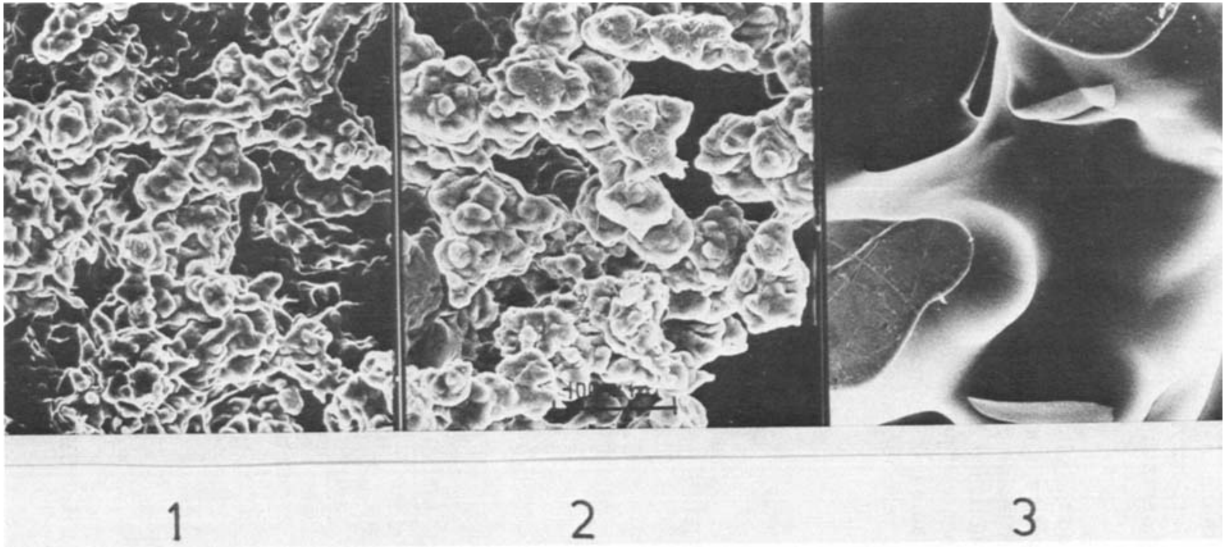


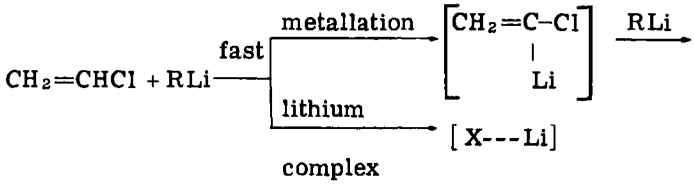
FIG. 7. Scanning electron micrographs (JEOL JSM-35) showing particle size of (1) PVC and VCM-octyl acrylate copolymers with (2) 0.5 mole % and (3) 2.8 mole % of incorporated octyl acrylate after 10 min of treatment in air at 200°C.

catalysts ethyllithium, n-butyllithium and tert-butyllithium. Of these, the last-named, tert-butyllithium, was tried for the first time for initiation of polymerization of vinyl chloride and has been found to be the best catalyst of all the alkyllithium compounds used for this purpose [13-15].

We followed up the effects of temperature, monomer concentration, solvent concentration, and concentration of catalyst on the conversion and properties of the polymer. The results obtained [13] agreed with the previously published data [9-12] for vinyl chloride and acrylonitrile, and a kinetic scheme of polymerization was proposed.

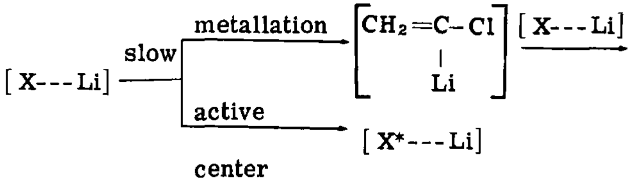
For the mechanism of the polymerization of vinyl chloride with alkyllithium, the reaction scheme shown in Eqs. (1)-(3) is suggested.

Initiation:



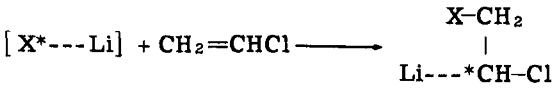
$$CLi{\equiv}CLi + LiCl + RH \qquad (1a)$$

(final products)



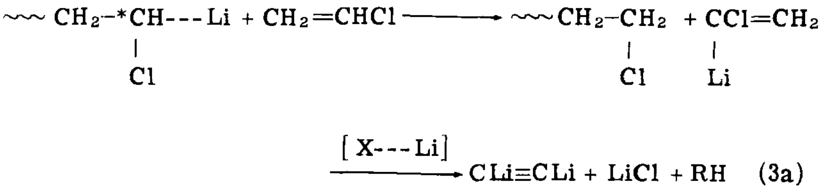
$$CLi{\equiv}CLi + LiCl + RH \qquad (1b)$$

Propagation:



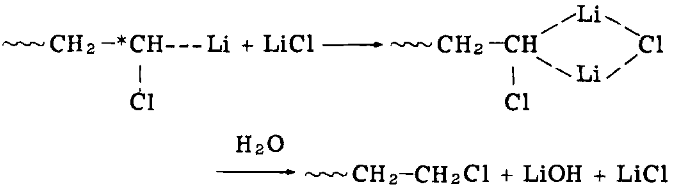
$$[X^*{-}{-}{-}Li] + CH_2{=}CHCl \longrightarrow \begin{array}{c} X{-}CH_2 \\ | \\ Li{-}{-}{-}^*CH{-}Cl \end{array} \qquad (2)$$

Termination by transfer to monomer:



$$\sim\!\sim\!\sim CH_2\text{-}{*}\underset{\displaystyle Cl}{CH}\text{---}Li + CH_2{=}CHCl \longrightarrow \sim\!\sim\!\sim CH_2\text{-}\underset{\displaystyle Cl}{CH_2} + \underset{\displaystyle Li}{CCl}{=}CH_2 \xrightarrow{[X\text{---}Li]} CLi{\equiv}CLi + LiCl + RH \qquad (3a)$$

Termination by formation of the complex with LiCl:



(3b)

Initiation occurs without an inhibition period. A complex of alkyllithium with vinyl chloride is rapidly formed, and a substantial number of growth centers appear (parallel to the simultaneously occurring metallation reaction) after dissociation or rearrangement of the lithium complex formed. The addition of a further molecule of vinyl chloride to the growth center starts the propagation of the polymer. The increase of the total amount of alkyls in the polymer during polymerization proves the gradual formation of initiation centers. The initiation with a partly metallated monomer is less probable, since the reactivity of the organolithium compounds with lithium attached to the carbon atom from which the double bond starts is very weak in the polymerization of vinyl compounds.

The relationships between the molecular weight and the initiator, monomer concentrations can be explained by several simultaneous termination steps, most probably by transfer to monomer and by formation of a complex between the growing end and lithium chloride formed in the metallation reaction.

The termination by transfer is actually a metallation with polymeric organolithium compound. In the polymerization with alkyllithium in the presence of lithium chloride, a decrease in the yield and molecular weight of the polymers is observed, which seems to indicate a termination due to the formation of stable complexes with lithium chloride.

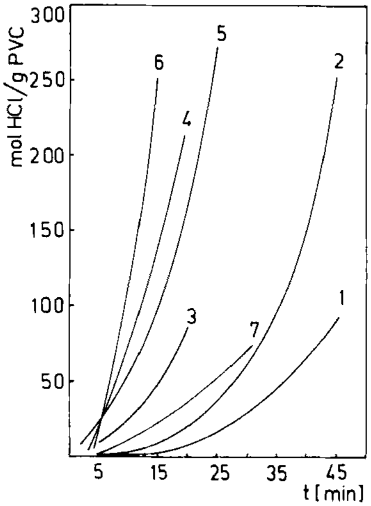


FIG. 8. Thermal dehydrochlorination of various poly(vinyl chloride) samples at 215°C in air: (1) Thervil 216, $P_n = 2500$, $K_w = 105$; (2) Thervil 209, $P_n = 1400$, $K_w = 85$; (3) Thervil 206, $P_n = 1000$, $K_w = 76$; (4) Geon 111, $P_n = 1500$, $K_w = 86$; (5) Geon 121, $P_n = 1000$, $K_w = 75$; (6) Geon 131, $P_n = 800$, $K_w = 68$; (7) Hostalit C270, $P_n = 900$, $K_w = 69$.

The termination by splitting off the lithium chloride from the growing polymer end has not been proved, since no other grouping has been found, even in a polymer having a molecular weight of 3000.

Under optimum conditions, polymer with molecular weight up to $\overline{M}_n = 160{,}000$ may be formed [16]. The product from polymerization of vinyl chloride by tert-butyllithium is a polymer which does not differ from polymers prepared by a radical polymerization in the ratio of the isotactic and syndiotactic components. The characteristic property of this polymer is the suppression of anomalous structures, accompanied by a marked increase of thermostability.

In Fig. 8 are presented dehydrochlorination curves of several thermally stable PVC samples in comparison with the described type of polymer. The first three samples (Thervil) were prepared in our laboratory, the second three were obtained from the Geon Company, and the last one was of German origin (Hostalit).

The methods I have mentioned do not exhaust all possibilities for improvement of the thermal stability of PVC. Thermal stability can be further improved, for example, by additional chlorination, by crosslinking with various crosslinking agents, or by grafting with other components.

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