Suspension Polymerization of Vinyl Chloride with Peroxyester-Stannous Chloride Catalyst System

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SUMMARY

The suspension polymerization of vinyl chloride in the presence of t-butyl peroxyoctoate ($t_{\frac{1}{2}}$ = 133 hrs) and stannous chloride is effective at 50°C in the absence but not in the presence of acetic acid. The decomposition of the peroxyester in the presence of $SnCl_2$ and acetic acid in the monomer droplet is too rapid for effective polymerization. In the absence of acetic acid, the interaction between the monomer-insoluble $SnCl_2$ and the monomer-soluble peroxyester occurs at the water-monomer interface to generate radicals at a slow rate, presumably by a redox reaction.

INTRODUCTION

The suspension polymerization of vinyl chloride (VCM) is generally carried out at 40-60°C using a monomer-soluble free radical initiator having a 10 hr half life in this range, e.g. t-butyl peroxypivalate and di-isopropyl peroxydicarbonate. The use of peroxyesters having higher decomposition temperatures is not feasible due to the low molecular weight and poor stability of the polymer.

The reaction of diacyl peroxides and peroxyesters with stannous chloride in acid solution at room temperature or at a slightly elevated temperature is used in the quantitative analysis of the peroxygen compounds (JOHNSON and SIDDIQI 1970). The recommended procedure for the analysis of t-butylperoxyoctoate (POT) involves reaction with stannous chloride in acetic acid solution at room temperature for 10 min, followed by back-titra-

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tion of the unreacted stannous chloride (PENNWALT 1976).

The present contribution describes the results of an investigation of the use of stannous chloride in the suspension polymerization of VCM in the presence of POT at 50°C where the catalyst has a half life of 133 hrs.

EXPERIMENTAL

The suspension polymerization of VCM was carried out in a 4 oz glass bottle which was charged with the following suspension recipe:

> 21 ml distilled water (boiled)
> .1 ml 1% aqueous solution of Tween 60 (polyoxy-
>   ethylene sorbitan monostearate)
> 1 ml 1% aqueous solution of Span 60 (sorbitan
>   monostearate)
> 2 ml 1% aqueous solution of Methocel A15 (15 cps
>   viscosity grade methylcellulose)

Nitrogen was bubbled through the aqueous solution for 15 min. Gaseous VCM was purified by passage through 5% aqueous sodium hydroxide solution, dried by passage through a silica gel column and then condensed with the aid of a dry ice bath. After 10g liquid VCM and 0.052g (0.23 mmole) stannous chloride dihydrate were added to the suspension recipe, the bottle was closed with a screw cap containing a center hole and a self-sealing gasket. The addition of 0.055ml (0.23 mmole) POT (0.5% by weight of VCM) was made by injection through the gasket using a hypodermic syringe. The bottle was shaken for 13 hrs in a 50°C constant temperature bath. The bottle was removed from the bath and the residual VCM was released by inserting a needle into the gasket. The polymer was isolated by filtration, washed with water and methanol and dried in vacuo.

Suspension polymerizations were carried out in the same manner in the absence of stannous chloride dihydrate as well as in the presence of 2 ml glacial acetic acid.

RESULTS AND DISCUSSION

The reaction of the peroxyester with stannous chloride in the presence of acetic acid is apparently

rapid and complete enough at room temperature to serve as a quantitative assay method. However, there is no information as to the nature of the decomposition products, i.e. radical or ionic.

The attempted polymerization of VCM in the presence of 0.5 wt-% POT at 50°C, in the absence of stannous chloride dihydrate, failed to yield any polymer after 20 hrs at 50°C. This is consistent with the POT half life of 133 hrs at 50°C (10 hr half life 74°C).

The attempted suspension polymerization of VCM in the presence of 0.5 wt-% POT, stannous chloride dihydrate (POT/SnCl$_2$ mole ratio = 1) and glacial acetic acid resulted in a 5% yield of polymer after 13 hrs at 50°C. The low yield of PVC indicated that the POT-SnCl$_2$ interaction either yielded predominantly non-radical products or proceeded so rapidly in the VCM droplet as to preclude effective polymerization.

The reaction of an acyl peroxide or peroxyester with triethylaluminum results in practically instantaneous free radical generation. The polymerization of VCM in the presence of this catalyst system at low temperatures stops after 5-8% conversion, indicative of the inability of VCM to utilize the free radicals effectively (KOPP and MILOVSKAYA 1969, KOPP et al. 1972).

Although stannous chloride is insoluble in VCM, the presence of acetic acid increases its solubility in the VCM droplet which contains the VCM-soluble POT. The rapid POT-SnCl$_2$ reaction thus occurs in the homogeneous VCM phase.

When the suspension polymerization of VCM in the presence of 0.5 wt-% POT and VCM-insoluble stannous chloride dihydrate (POT/SnCl$_2$ mole ratio = 1) was conducted in the absence of acetic acid, the yield of PVC was 82% after 13 hrs at 50°C. This may be attributed to the interaction of the monomer-insoluble SnCl$_2$ or the hydrated ions thereof with the POT in the VCM at the water-monomer droplet interface to generate radicals at a slow useful rate.
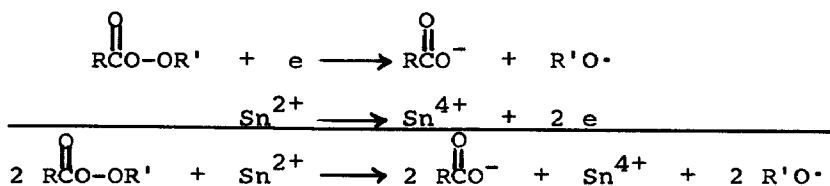
The effective polymerization of VCM in the presence of the POT-SnCl$_2$ catalyst system (GAYLORD 1981) confirms the generation of free radicals. This con-

trasts with the reported rapid decomposition of diacyl
peroxides in solution at room temperature in the pres-
ence of various metal halides, to non-radical species
through ionic intermediates. Thus, a polar carboxyl
inversion mechanism is proposed in the decomposition of
benzoyl peroxide and/or other diacyl peroxides in the
presence of aluminum chloride (EDWARD et al. 1962,
HUISGEN and EDL 1962, DENNEY et al. 1964, SIVARAM et
al. 1980), antimony pentachloride (DENNEY and DENNEY
1962, DENNEY et al. 1964, SIVARAM et al. 1980) and
boron trifluoride (HUISGEN and EDL 1962, SIVARAM et al.
1980).

However, radical generation has been confirmed in
the polymerization of various monomers in the presence
of a catalyst system consisting of an aluminum alkyl
and either a diacyl peroxide or a peroxyester, i.e.
peroxygen compounds containing carbonyl groups (KOPP
and MILOVSKAYA 1969, ZAMOISKAYA et al. 1971, KOPP et al.
1972). The proposed mechanism of decomposition invol-
ves complexation of the AlR_3 with the carbonyl group of
the peroxide as well as with the monomer, resulting in
an electron shift which weakens the peroxy linkage.

$$- \overset{\overset{\displaystyle O}{\|}}{C} - O - O -$$
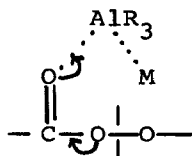
Although this mechanism may be operative to some
extent in the POT-$SnCl_2$ catalyst system, a redox mech-
anism analogous to that normally invoked in redox cat-
alyst systems containing peroxygen compounds probably
plays a major role.

$$R\overset{\overset{\displaystyle O}{\|}}{C}O{-}OR' \ + \ e \ \longrightarrow \ R\overset{\overset{\displaystyle O}{\|}}{C}O^- \ + \ R'O\cdot$$

$$\underline{\quad\quad\quad Sn^{2+} \ \longrightarrow \ Sn^{4+} \ + \ 2 \ e \quad\quad\quad}$$

$$2 \ R\overset{\overset{\displaystyle O}{\|}}{C}O{-}OR' \ + \ Sn^{2+} \ \longrightarrow \ 2 \ R\overset{\overset{\displaystyle O}{\|}}{C}O^- \ + \ Sn^{4+} \ + \ 2 \ R'O\cdot$$

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