Polymerization of Vinyl Monomers Initiated by Chromic Acid-Glycerol Redox System

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ABSTRACT

Polymerization of vinyl monomers initiated by chromic acid–
reducing agent (glycerol, sorbitol and mannitol) systems was
studied at 35-45°C in perchloric acid medium. Chromic acid
alone did not initiate polymerization. On the basis of the
experimental results embodying the dependences of various
variables on the rate of polymerization R_p and the rate of
chromium(VI) disappearance $-R_{Cr}$, a reasonable kinetic scheme
has been suggested. The order of the reactivity of different
polyhydroxy alcohols is: glycerol > sorbitol > mannitol.
The scheme is consistent with linear termination and the forma-
tion of a radical intermediate resulting from the oxidation of the
reducing agent by Cr(VI).

INTRODUCTION

The use of redox systems [1-4] for initiation of polymerization
has been frequently reported in literature, but reports of studies
involving chromic acid-reducing agent have been rather scanty [5].
Chromic acid is one of the most versatile oxidizing agents. E_0 for
the Cr(VI)-Cr(III) couple has been reported to be 1.33 V. On theoreti-
cal grounds, it was, therefore, expected that Cr(VI) should also effec-
tively initiate vinyl polymerization. Preliminary experiments [5]
with chromic acid-methyl acrylate(MA) or methyl methacrylate
(MMA) in acid media (HClO$_4$, HNO$_3$, H$_2$SO$_4$) have shown, however,
that no polymerization takes place, even though there is disappear-
ance of Cr(VI). One would, therefore, conclude that chromic acid
in acid medium oxidized MA (MMA) without affecting the polymeri-
zation of the latter. Probably the functional group and not the π-bond
of the monomer is involved in the oxidation. Such monomer oxidations
were observed as side reactions also with Co(III) [2] and Ce(IV) [7]
as initiators. With acrylonitrile, in the absence of the substrate,
there was no decrease in Cr(VI), and the polymerization of the
monomer also did not take place. In the presence of the substrate,
however, the redox system Cr(VI)-reducing agent was found to
initiate polymerization of acrylonitrile, though the yield was rather
poor. Reducing agents such as isopropyl alcohol, formaldehyde,
and tert-butyl alcohol gave only small amounts of the polymer (2%),
whereas n-butanol, isoamyl alcohol, ethylene glycol, cyclohexanone,
propionaldehyde, and benzaldehyde gave larger amounts of the
polymer (5%) without any induction period. These results warranted,
for a fuller understanding and correlation, more systematic studies
relating to the nature of the substrates which are effective in initiat-
ing polymerization and the mechanistic explanation.

The present paper reports our results on vinyl polymerization of
acrylonitrile initiated by Cr(VI)-polyhydroxy alcohols (glycerol,
sorbitol, and mannitol) systems.

EXPERIMENTAL

Materials

Acrylonitrile (American Cyanamide) was purified by standard
methods. Chromic acid solutions were prepared by dissolving
chromium trioxide (BDH, AnalaR) in conductivity water. Perchloric
acid (E. Merck, G. R., 60%) was used for maintaining the acidity of

reaction mixtures and for preparing other reagents. Sodium perchlorate (1.0 $\underline{M}$) was used for maintaining ionic strength. Other reagents, like ferrous ammonium sulfate, glycerol, sorbitol, and mannitol, were either BDH (AnalaR) or Merck (GR) products. Deaeration of the Cr(VI)-reducing agent-monomer system was done by passing nitrogen freed from oxygen (Fieser's solution) through the system.

Changes in Cr(VI) were determined by titrimetry. The unreacted Cr(VI) was quenched with an excess of ferrous ammonium sulfate, and the unreacted ferrous ammonium sulfate was titrated against standard solution of ceric ammonium sulfate (0.01 $\underline{M}$), ferroin being used as the indicator.

Polymerization Procedure

The reaction mixture containing the reducing agent, monomer, and acid was deaerated for 20-30 min in a vessel made up of a Pyrex tube fitted with standard joints. The temperature of the reaction mixture (35-45°C) was kept constant in a thermostat. Chromic acid solution, which was deaerated separately, was added to the reaction mixture. Polymerization took place without any induction period, and the steady state was attained within 60 min. The reaction was stopped by addition of excess ferrous ammonium solution; the precipitated polymer was filtered, washed with water, and dried to constant weight at 60°C in a vacuum oven. The rate of polymerization R_p was calculated from the initial slope of the plot of the time conversion curve. The slope was used to deduce R_p in mole/liter-sec.

$-R_{Cr}$ (the rate of oxidant consumption) was also calculated from the initial slope of a Cr(VI) consumption versus time plot.

RESULTS AND DISCUSSION

The polymerization of acrylonitrile initiated by the Cr(VI)-glycerol redox system shows characteristic features of heterogeneous polymerization. The conversion reaches only 20% within 1 hr in contrast to the larger percentage of conversion observed in redox systems involving Ce(IV) [4] and V(V) [3].
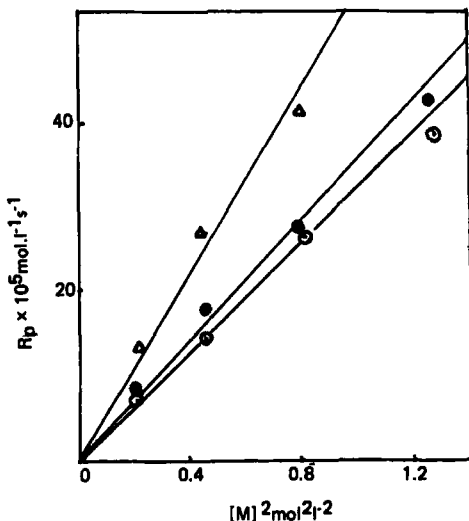
FIG. 1. Variation of R_p with $[M]^2$: ($\triangle$) 35°C; ($\bullet$) 40°C; ($\circ$) 45°C. $[Cr(VI)]$ = 0.005 mole/liter; $[R]$ = 0.35 mole/liter; $[H^+]$ = 0.585 mole/ liter; μ = 0.7 mole/liter.

Rate of Polymerization R_p:

The increase of monomer concentration increased R_p. The plot of R_p versus $[M]^2$ was found to be linear (Fig. 1). R_p values in case of methyl acrylate and methyl methacrylate are much less than that in case of acrylonitrile. This may be attributed to easier oxidation of the monomers, methyl acrylate and methyl methacrylate. When the concentration of glycerol (R) was varied from 0.4 to 2.0 M, R_p increased from 2.34 to 3.35 × 10^{-5} mole/liter-sec only. The evidence for linear termination with Cr(VI) was obtained from the inverse dependence of R_p on $[Cr(VI)]$. Plots of $1/R_p$ versus $[Cr(VI)]$ were linear (Fig. 2). The concentration of perchloric acid was varied over a wide range (0.29-2.34 M). The rate increased to 1.755 M of $HClO_4$ and then decreased. Previous studies on Cr(VI) polymerization [5] also reported similar observations. The order with respect to $[H^+]$ has been reported to be about two in the case of butanol, ethylene glycol, etc. In the present investigation, however,
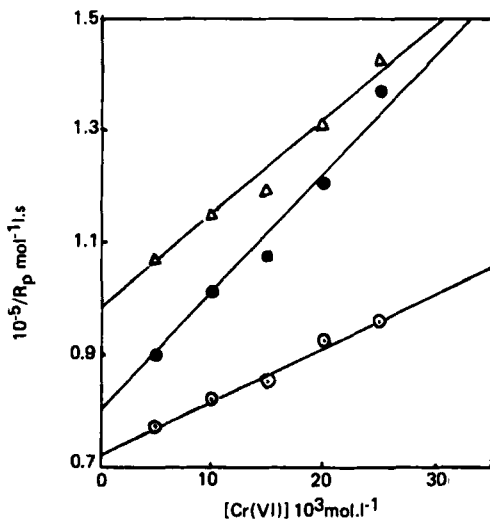
FIG. 2. Plots of $1/R_p$ versus $[Cr(VI)]$: ($\triangle$) 35°C; ($\bullet$) 40°C; ($\odot$) 45°C. $[R]$ = 0.05 mole/liter; $[H^+]$ = 0.585 mole/liter; μ = 0.7 mole/liter; $[M]$ = 0.7539 mole/liter.

as the experimental results indicate, protonation of chromic ester does not appear likely.

Rate of Disappearance of Chromium (VI) $(-R_{Cr})$

The rate of disappearance of Cr(VI) was dependent on the first power of $[Cr(VI)]$ and $[R]$ (Fig. 3); $-R_{Cr}$ was found to be independent of $[AN]$, showing that Cr(VI) was not directly involved in the initiation.

KINETIC SCHEME

The polymerization of acrylonitrile by the system Cr(VI)-glycerol in acid media must involve one of the following possible radical production steps for the initiation: Cr(VI) + R, Cr(V) + R, Cr(IV) + R. In the chromic acid oxidation of phenyl tert-butyl alcohol containing acrylonitrile in the system, polymerization of the latter, reported by
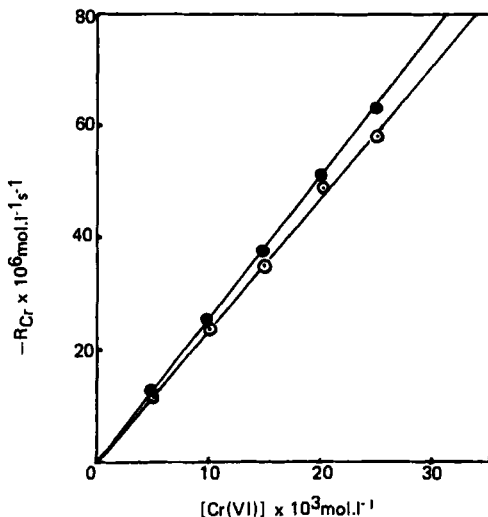
FIG. 3. Variation of $-R_{Cr}$ with $[Cr(VI)]$: ($\odot$) 35°C; ($\bullet$) 45°C.
$[R]$ = 0.05 mole/liter; $[H^+]$ = 0.585 mole/liter; μ = 0.7 mole/liter;
$[M]$ = 0.7539 mole/liter.

Mosher and Driscoll [8], was attributed to initial cleavage of phenyl
tert-butyl alcohol to give benzaldehyde and tert-butyl alcohol and
the resulting reduction of Cr(VI) to Cr(IV). Cr(IV) thus formed then
reacts with benzaldehyde to give the radical intermediate, which
initiates the polymerization. Similar observations have also been
reported in the system Cr(VI)-2-propanol-benzaldehyde containing
acrylonitrile. In the absence of benzaldehyde, little or no polymeri-
zation took place. In the presence of benzaldehyde alone (without
2-propanol), polymerization occurred but it was delayed. On the
basis of the above findings, we suggest that glycerol is first oxidized
by Cr(VI) which is, in turn, itself reduced to Cr(IV). Cr(IV) thus
formed in the oxidation then reacts with the oxidation product of the
substrate, giving rise to the radical intermediate which initiates
polymerization.

Rocek and Radkowsky [9] have also reported that Cr(IV) and not
Cr(V) is involved in the oxidation of cyclobutanol. It has been now
generally established that the chromium species involved in radical
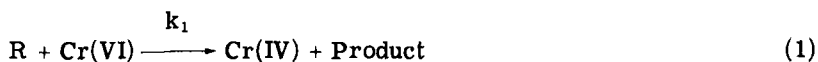production is Cr(IV).

The possibility of Cr(IV) reacting with the substrate itself to give
the initiating radical is not ruled out in view of the findings of Waters

et al. [10]. This has been taken into consideration in the formulation of the reaction scheme but it has been found that this reaction does not affect the final rate expression.
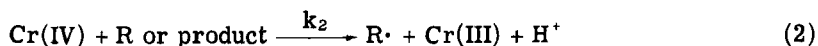
Reaction Scheme

Of the possible reaction schemes examined, that involving initiation by R· and termination by Cr(VI) best explained the experimental results.
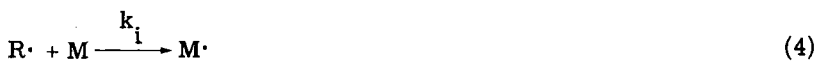Reaction of Cr(VI) with glycerol (R):

$$R + Cr(VI) \xrightarrow{k_1} Cr(IV) + Product \tag{1}$$

Formation of radical:

$$Cr(IV) + R \text{ or product} \xrightarrow{k_2} R· + Cr(III) + H^+ \tag{2}$$

Reaction of primary radical with Cr(VI):

$$R· + Cr(VI) \xrightarrow{k_0} Cr(III) + Product \tag{3}$$

Initiation:

$$R· + M \xrightarrow{k_i} M· \tag{4}$$

Propagation:

$$M· + M \xrightarrow{k_p} M_2·$$
$$\vdots$$
$$M_{n-1}· + M \xrightarrow{k_p} M_n· \tag{5}$$

Termination by Cr(VI):

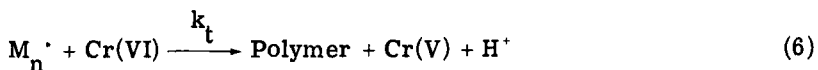$$M_n· + Cr(VI) \xrightarrow{k_t} Polymer + Cr(V) + H^+ \tag{6}$$

TABLE 1. Polymerization of Acrylonitrile Initiated by Cr(VI)-
Poly(hydroxy alcohols) Systems

Alcohol	Concentration (mole/liter)	$R_p \times 10^5$ (mole/liter-sec)
Glycerol	0.1	1.58
Sorbitol	0.1	0.61
Mannitol	0.1	0.6

Making the usual steady-state assumptions for free radicals and
unstable intermediates, we have

$$R_p = \frac{k_i k_1 k_2 k_p [R][M]^2}{k_t (k_0 [Cr(VI)] + k_i [M])} \tag{7}$$

$$-R_{Cr} = (2k_1 k_2) [Cr(VI)][R]$$

$$= k'[Cr(VI)][R] \tag{8}$$

The proportionalities between the experimental rates and various
variables were satisfactory.

Reactivity Order

The sequence of reactivity with respect to the three poly(hydroxy
alcohols) can be seen from the data given in Table 1. According to
the R_p values, glycerol seems to react faster than either sorbitol
and mannitol. The absence of any perceptible sequence of reactivity
of the substrates with regard to polymerization rate may be attributed
to the fact that Cr(VI) is a much more vigorous oxidizing agent than
Ce(IV) and V(V) and the powerful oxidizing nature of Cr(VI) irons out
the subtle difference between the reactivity of the substrates towards
polymerization. Another possible reason may lie in the nearly equal
stability constants of the complexes of Cr(VI) and the substrates.
Since the complexes play a significant role in the polymerization,

little or no difference will be observed in the polymerization rate as a consequence.

ACKNOWLEDGMENT

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