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## NOTE

# HIGH YIELD SYNTHESIS OF LOW MOLECULAR WEIGHT POLY(VINYL ACETATE) IN AQUEOUS ACIDIC MEDIA

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### INTRODUCTION

Polymerization of vinyl acetate continues to interest workers in the field as evidenced by recent publications [1-3]. However, little information is available concerning the synthesis of low molecular weight poly(vinyl acetate) (PVAc) despite its industrial importance.

Ceric salts have been used in vinyl polymerization in the presence of various organic reducing agents such as alcohols, acids, amides, amines, etc. [4-6]. McAuley [7] reported that oxidation of thiourea by ceric salts proceeds by a radical mechanism. The ceric salt-thiourea system has been extensively used by Pramanick and coworkers [8-10] for vinyl polymerization, and the low molecular weights of poly(methyl methacrylate) (PMMA) they obtained have encouraged us to use this system in conjunction with *t*-dodecylmercaptan (TDM) as the chain regulator in order to obtain low molecular weight PVAc in high yields.

### EXPERIMENTAL

Vinyl acetate (VAc) (BDH) was freshly distilled before use. A stock solution of 0.1 *M* ceric sulfate (BDH) was made in 1 *N* sulfuric acid (AR). Thiourea (AR) from SD Chemicals and TDM (Fluka) were used. Twice-distilled water was employed throughout.

The monomer charge (3 mL VAc in 200 mL water) was added to a conical flask placed in a thermostat (accuracy:  $\pm 0.05^\circ\text{C}$ ), deaerated, and its pH adjusted to 2.1. Initiator was then added, resulting in an immediate reaction. The turbidity of the reaction mixture increased with time until a milky white emulsion was obtained ( $\sim 0.5$  h). The polymerization was terminated by introducing 5 mL of 1% aqueous hydroquinone. Aqueous sodium sulfate was used to break the emulsion and precipitate the polymer, which was filtered, repeatedly washed with water, and dried at  $45^\circ\text{C}$  under vacuum. Further purification was done by reprecipitation from the benzene-hexane system followed by drying.

The products were characterized by intrinsic viscosity in benzene, at  $30 \pm 0.05^\circ\text{C}$ , determined with an Ubbelohde suspended-level dilution viscometer and by their number-average molecular weights ( $\bar{M}_n$ ) measured with a Knauer vapor-pressure osmometer at  $60^\circ\text{C}$  in toluene.

## RESULTS AND DISCUSSION

The studies were aimed at optimizing conditions to obtain low molecular weight PVAc in reasonably good yields. The effect of changing the thiourea (TU) and *t*-dodecylmercaptan (TDM) concentrations on the yield and  $\bar{M}_n$  of the resulting polymer is shown in Tables 1 and 2, respectively. It is clear from the results of Table 1 that, for a specific concentration of the initiator, an optimum range of thiourea concentration of 0.25–0.50 mmol/L was found to produce PVAc of  $\bar{M}_n$  4000–6000 in 83–86% yield. Polymer of lower  $\bar{M}_n$ , 1500–2000, could be obtained in 75% yield at lower [TU], viz., 0.125 mmol/L. However, at concentrations above 0.5 and below 0.125 mmol/L, a precipitous fall in the polymer yields was experienced.

At an optimum TU concentration of 0.50 mmol/L and 1.0 mmol/L of ceric sulfate, PVAc of  $\bar{M}_n$  in the range 2000–25 000 could be obtained in high yields, as shown in Table 2, by changing [TDM] in the range of 0 to 6.4 mmol/L. Higher [TDM] causes poor yields but a substantial increase in  $\bar{M}_n$ .

Varying the polymerization temperature from 30 to  $60^\circ\text{C}$  (Table 3) gave a variation in  $\bar{M}_n$  from 2600 to 12 400. That longer reaction times at lower temperature would lead to higher yields has been demonstrated in a scaled-up experiment with 40 mL VAc in 2 L water at  $35^\circ\text{C}$ , in which PVAc of  $\bar{M}_n$  6300 was obtained in 92% yield.

The infrared spectrum of a film obtained from a typical sample was almost identical with the reported [11] spectra.

TABLE 1. Effect of Variation of [TU] on the Yield and  $\bar{M}_n$  of PVAc<sup>a</sup>

[TU], mmol/L	Yield, %	$[\eta]$ , dL/g	$\bar{M}_n$ (VPO)
1.5	4.4	—	—
1.0	51.7	0.35	28 200
0.5	83.3	0.18	5 800
0.25	85.8	0.16	4 300
0.125	75.0	0.09	2 740
0.10	22.8	0.08	2 600
—	23.9	0.09	2 500

<sup>a</sup>[VAc] = 162 mmol/L, [Ce(SO<sub>4</sub>)<sub>2</sub>] = 1.0 mmol/L, [TDM] = 4.24 mmol/L, temperature = 40°C, pH = 2.1, time = 0.5 h.

TABLE 2. Effect of Variation of [TDM] on the Yield and  $\bar{M}_n$  of PVAc<sup>a</sup>

[TDM], mmol/L	Yield, %	$[\eta]$ , dL/g	$\bar{M}_n$ (VPO)
—	91.3	0.37	24 500
2.12	84.3	0.28	14 100
4.24	83.3	0.17	5 300
5.31	82.3	0.17	4 500
6.37	81.9	0.08	2 400
10.61	33.1	0.19	6 170

<sup>a</sup>[VAc] = 162 mmol/L, [Ce(SO<sub>4</sub>)<sub>2</sub>] = 1 mmol/L, [TU] = 0.50 mmol/L, temperature = 40°C, pH = 2.1, time = 0.5 h.

TABLE 3. Effect of Temperature on Yield and  $\bar{M}_n$  of PVAc<sup>a</sup>

Temperature, °C	Yield, %	$[\eta]$ , dL/g	$\bar{M}_n$ (VPO)
30	47.3	0.25	12 400
40	82.30	0.17	4 500
60	72.8	0.12	3 000

<sup>a</sup>[VAc] = 162 mmol/L, [Ce(SO<sub>4</sub>)<sub>2</sub>] = 1.0 mmol/L, [TU] = 0.5 mmol/L, [TDM] = 5.30 mmol/L, pH = 2.10, time = 0.5 h.

In conclusion, PVAc of  $\bar{M}_n$  2 000-25 000 could be obtained in high yields in aqueous acidic media at 30-40°C by changing just the TDM concentration at a fixed concentration of the ceric sulfate-thiourea system.

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