# NOTES

# Synthesis of High-Molecular-Weight Polymer of Methyl Chloride Salt of N,N-Dimethylaminoethyl Methacrylate by Radiation-Induced Polymerization at High Pressure

## INTRODUCTION

Polymer of the methyl chloride salt of N,N-dimethylaminoethyl methacrylate and its copolymer with acrylamide are used as cationic flocculants for the treatment of waste water containing organic suspensions. As we have reported, radiation-induced polymerization is one of the most convenient methods because of its temperature independence of initiation and extremely large G-value.<sup>1,2</sup> In general, a flocculant with higher molecular weight has larger flocculation effects. The high-molecular-weight products were prepared in high monomer concentration and at low dose rate.<sup>1</sup>

This note concerns the polymerization and copolymerization of methyl chloride salt of N,Ndimethylaminoethyl methacrylate at high pressure, up to 7000 kg/cm<sup>2</sup>, providing high-molecularweight cationic flocculants.

#### EXPERIMENTAL

Technical-grade methyl chloride salt of N,N-dimethylaminoethyl methacrylate (Mitsubishi Rayon Co. Ltd.) was purified by washing with acetone followed by drying under vacuum before use. Technical-grade acrylamide (Mitsubishi Chemical Industries Ltd.) was used without further purification.

An aqueous solution of the monomers in a collapsible polyethylene capsule of 20 ml was deaerated by bubbling with nitrogen. The application of pressure to the capsule was carried out hydrostatically by using a high-pressure apparatus.<sup>3</sup> Polymerization was carried out at 20°C with <sup>60</sup>Co  $\gamma$  rays at a dose rate of 7 × 10<sup>3</sup> rad/hr for methyl chloride salt of *N*,*N*-dimethylaminoethyl methacrylate of 0.5 mole/l. aqueous solution and mixed aqueous solution of acrylamide of 0.35 mole/l. and methyl chloride salt of *N*,*N*-dimethylaminoethyl methacrylate of 0.15 mole/l. The reduced viscosity of the polymer at a concentration of 0.5 g/dl was measured in 1*N* NaNO<sub>3</sub> aqueous solution at 30°C.



Fig. 1. Effects of pressure on polymerization rate (O) and reduced viscosity ( $\bullet$ ) of the polymer for the methyl chloride salt of N,N-dimethylaminoethyl methacrylate. Temperature 20°C, dose rate  $7 \times 10^3$  rad/hr.

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Fig. 2. Effects of pressure on polymerization rate (O) and reduced viscosity ( $\bullet$ ) of the polymer for the copolymerization of the methyl chloride salt of N,N-dimethylaminoethyl methacrylate with acrylamide. Temperature 20°C, dose rate 7 × 10<sup>3</sup> rad/hr.

#### **RESULTS AND DISCUSSION**

Figure 1 shows the results for polymerization of the methyl chloride salt of N,N-dimethylaminoethyl methacrylate at various pressues up to 7000 kg/cm<sup>2</sup>. Both yield and reduced viscosity of the polymer increase with pressure. The polymer formed at 7000 kg/cm<sup>2</sup> is insoluble in water because of crosslinking structure and high molecular weight.

Similar pressure effects are observed in Figure 2 for the copolymerization of the methyl chloride salt of N,N-dimethylaminoethyl methacrylate with acrylamide.

For both polymerization and copolymerization, the increase in polymerization rate and polymer molecular weight with pressure is due to the increase in the rate of chain growth. The overall activation volume is calculated from the Van't Hoff equation to be -13.3 and -7.9 ml/mole for the present polymerization and copolymerization, respectively. These values mainly reflect the growing step of polymerization in case of radiation-induced polymerization and are comparable with the case of sodium allylsulfonate, which also contains an electrolytic group.<sup>3</sup>

In conclusion, it was found that a high-molecular-weight polymer can be prepared by the highpressure polymerization of the methyl chloride salt of *N*,*N*-dimethylaminoethyl methacrylate induced by radiation.

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