

Synthesis of Cationic Flocculant by Radiation-Induced Copolymerization of Methyl Chloride Salt of *N,N*-Dimethylaminoethyl Methacrylate with Acrylamide in Aqueous Solution.

II. Copolymerization at Higher Monomer Concentration

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Synopsis

The radiation-induced copolymerization of methyl chloride salt of *N,N*-dimethylaminoethyl methacrylate with acrylamide was studied to prepare a polymer flocculant that can be handled as a solid. The product obtained in the presence of 5–20% water was a solid and could be ground to a powder without drying. In order to obtain a water-soluble polymer at a higher concentration, the effect of various additives on the copolymerization was investigated and found that alcohols bearing a hydrogen atom attached to the tertiary carbon atom effectively inhibit intermolecular crosslinking to give water-soluble polymer. It is suggested that the formation of water-insoluble polymer is predominantly attributable to the crosslinking of polymer chains rather than to the imidation of amide groups. Copolymerization in the presence of isopropyl alcohol as inhibitor of the crosslinking was also studied and compared with that reported previously, which was carried out at a lower monomer concentration without additives.

INTRODUCTION

The radiation-induced copolymerization of the methyl chloride salt of *N,N*-dimethylaminoethyl methacrylate with acrylamide in aqueous solution has been studied before.¹ It was found that the radiation process can easily provide a much higher-molecular-weight copolymer with a wide range of cationic strength as compared with the conventional process by free radical initiator. Although the molecular weight of copolymer increases with monomer concentration, intermolecular crosslinking tends to occur at a higher monomer concentration to form a water-insoluble copolymer that cannot be used as a flocculant. The monomer concentration above which intermolecular crosslinking occurs decreases with increasing mole fraction of acrylamide in monomer mixtures. In order to obtain water-soluble copolymer, copolymerization should be carried out using a relatively low monomer concentration.

It is well known that acrylamide gives a relatively high-molecular-weight polymer which becomes easily insoluble in water because of intermolecular crosslinking formed by imidation of two amide groups. Generally, nonionic and anionic polymer flocculants (polyacrylamide and copolymer of acrylamide-

sodium acrylate) are manufactured by using an aqueous solution with a relatively low monomer concentration of 30% at most or at a higher monomer concentration in the presence of additives to inhibit the intermolecular crosslinking. The polymerization at a lower monomer concentration requires much energy and complicated processes to obtain the powdery product.

The purpose of this study was to find useful additives inhibiting the formation of water-insoluble polymer at as high a monomer concentration as possible to obtain powdery product by crushing alone, without resorting to drying.

EXPERIMENTAL

Technical-grade methyl chloride salt of *N,N*-dimethylaminoethyl methacrylate (Mitsubishi Rayon Co. Ltd.) was purified by washing with acetone followed by drying in vacuo before use. Technical-grade acrylamide (Mitsubishi Chemical Industry Ltd.) was used without further purification. Other reagents were GR grade and were used as obtained.

An aqueous solution of the monomer was degassed by bubbling nitrogen gas for 15 min; additives were then added, followed by bubbling for 2 min. The ampoule thus obtained was subjected to γ -ray irradiation from ^{60}Co in a temperature-controlled bath. The dose rate was controlled by changing the distance between ampoule and the ^{60}Co source and was determined using cobalt glass dosimetry. After irradiation, the polymerization product was taken out off the glass ampoule at liquid nitrogen temperature. The product thus obtained was ground to a powder by using a crusher (Kyoritsu Riko SK-M2).

Polymer conversion was determined by measuring the residual monomer in the product. The amount of monomer was calculated from the double bond measured by the bromination titration method.

The reduced viscosity η_{sp}/c of the polymer at a concentration of 0.5 g/dl was measured in 1N NaNO_3 aqueous solution at 30°C, as reported previously.¹

RESULTS AND DISCUSSION

Effect of Water

As reported previously,¹ acrylamide (AAM) and methyl chloride salt of *N,N*-dimethylaminoethyl methacrylate (DMAEM-MC) can be easily copolymerized in aqueous solution to give a cationic polymer flocculant. In order to obtain a product that can be handled as a solid, it is advisable to carry out the polymerization at as a high monomer concentration as possible. In an extreme case, AAM can be easily polymerized in the solid state to give a solid polymer.²

Effects of water on the homopolymerizations of AAM and DMAEM-MC were studied. Figures 1 and 2 show the polymer yield-time curves at various amounts of water. The relationships between polymer yield at 1 hr and water concentration are shown in Figure 3. It can be seen that although the polymerization rate is extremely small, DMAEM-MC polymerizes as well as AAM even in the absence of water.

In the solid-state polymerization, polymer is formed by the successive reaction of active chain end with monomer molecule. Therefore, the polymerization rate

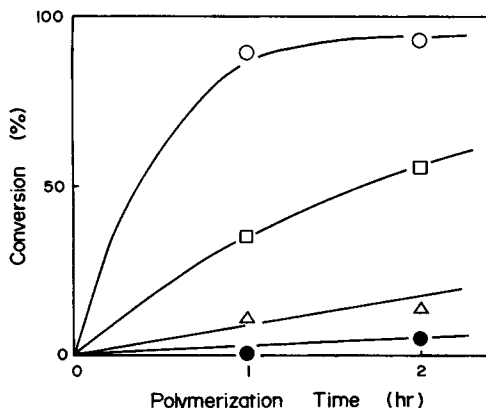


Fig. 1. Effect of water on polymerization of acrylamide (AAM). Dose rate, 5×10^3 rad/hr; polymerization temp., 30°C ; water conc.: (●) 0 mole %; (Δ) 17.2 mole % (5 wt %); (□) 30.5 mole % (10 wt %); (○) 49.7 mole % (20 wt %).

(polymer yield) is largely dependent on the mobility of monomer molecule. In the solid-state polymerization of AAM and trioxane, a maximum rate of polymerization was observed at a temperature slightly below the melting point of the monomer.³ This finding has been explained by the increase in mobility of monomer with increasing temperature. It is suggested that the mobility of DMAEM·MC is not large enough to polymerize at room temperature, because the melting point of DMAEM·MC is 184°C . However, both AAM and DMAEM·MC seem to become mobile on the addition of water since these monomers are hydrophilic and easily soluble in water. As shown in Figure 3, in fact, polymer yield (polymerization rate) was found to increase markedly with water concentration.

Figure 4 shows the logarithmic plots of polymerization rate against dose rate for DMAEM·MC. The dose rate exponent of the polymerization rate was found to be about 0.6. Since DMAEM·MC presumably polymerizes via radical mechanism, this result suggests that the termination reaction of two propagating

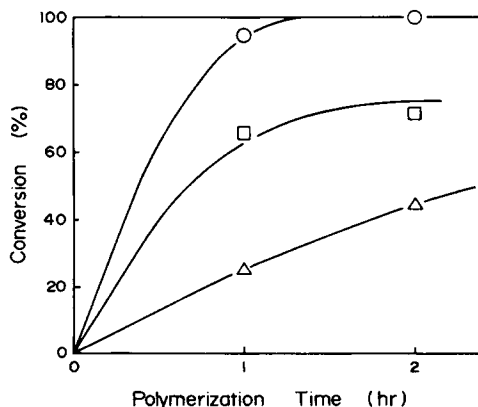


Fig. 2. Effect of water on polymerization of methyl chloride salt of *N,N*-dimethylaminoethyl methacrylate (DMAEM-MC). Dose rate, 5×10^3 rad/hr; polymerization temp., 30°C ; water conc.: (Δ) 37.8 mole % (5 wt %); (□) 56.2 mole % (10 wt %); (○) 67.1 mole % (15 wt %).

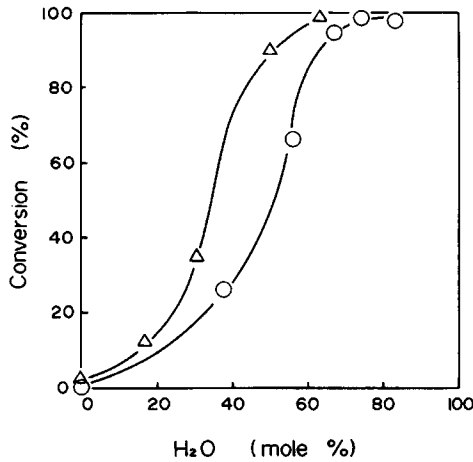


Fig. 3. Relationship between polymer conversion and water concentration for polymerization of AAm and DMAEM-MC. Dose rate, 5×10^3 rad/hr; polymerization time, 1 hr; polymerization temp., 30°C; (Δ) AAm; (O) DMAEM-MC. Polymer conversions at solid state (water conc., 0%) were 2.5 and 1.0% for AAm and DMAEM-MC, respectively.

polymer radicals is slightly depressed because of the decrease in their mobilities at a higher monomer concentration.

Although the solid-state polymerization of AAm and DMAEM-MC seems to be one of the most advantageous processes to produce solid product, the rates of polymerization were found to be too small to obtain polymer at 100% conversion. It was also found that the products at 100% polymer conversion obtained even in the presence of 5–20% water can be handled as a solid polymer and ground to a powder without drying, but unfortunately all products were not soluble in water because of the intermolecular crosslinking of the polymer.

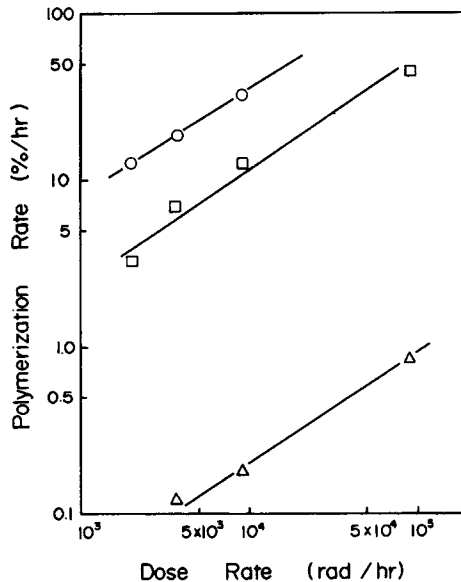
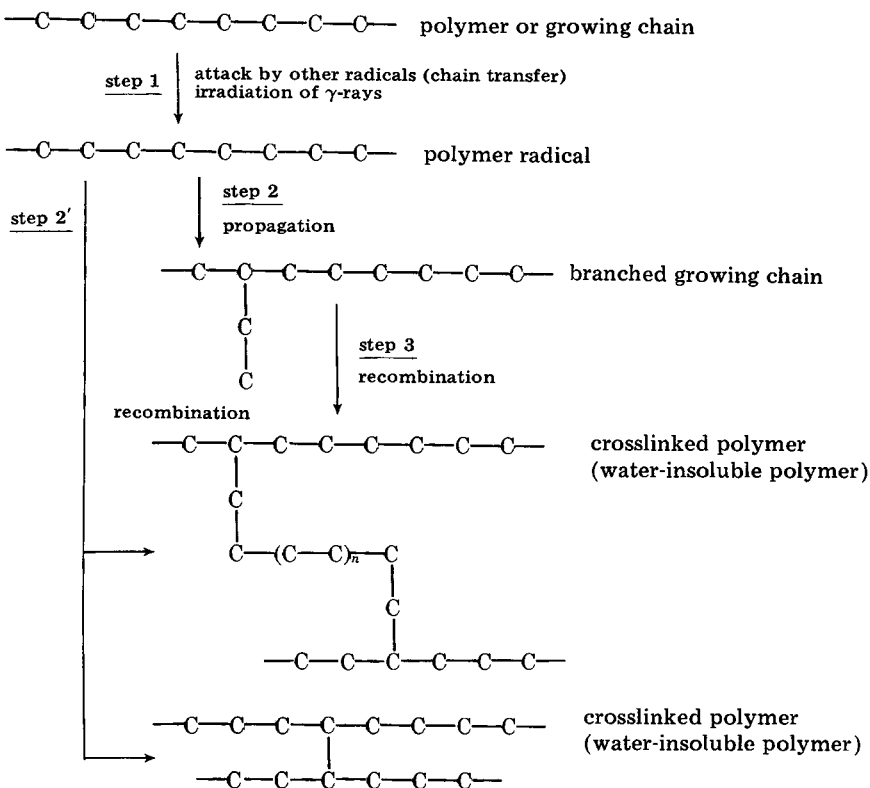


Fig. 4. Logarithmic plots of polymerization rate vs. dose rate for polymerization of DMAEM-MC at various water concentrations. Polymerization temp., 20°C; water conc.: (Δ) 0 mole %; (\square) 56.1 mole % (10 wt %); (O) 74.2 mole % (20 wt %).

Effect of Additives

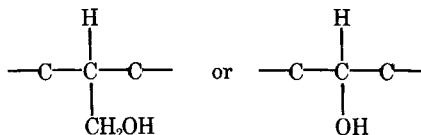
In order to obtain water-soluble polymer at a higher concentration, the effects of various additives on the copolymerization of DMAEM-MC and AAm were investigated. The formation of water-insoluble polymer is attributed not only to imidation of amide groups but also to recombination of the branched growing chains and polymer radicals. The mechanism of the intermolecular crosslinking attributable to the latter is presumed to be as follows:



Step 1 is the formation of polymer radicals, i.e., radicals may be formed on the terminated or growing main chains both by the chain transfer reaction of growing chain and the direct irradiation effect of γ -rays. In step 2, the polymer radicals thus formed react with monomers to produce the branched growing chains. Then the radicals of the branched growing chains recombine with each other to form the crosslinked polymer chains as shown in step 3. Some polymer radicals recombine directly with each other or with branched growing chains to form crosslinked polymer via step 2'.

The effects of various additives on the formation of water-insoluble polymer at a higher monomer concentration were studied. Amines and ureas were chosen as inhibitors for the imidation of amide groups and alcohols as chain transfer agents to depress the recombination of polymer radicals. In the copolymerization of DMAEM-MC with AAm, none of the amines and ureas, except ethylene diamine, was found to inhibit effectively the formation of water-insoluble polymer at a monomer concentration of 80 wt %. On the other hand, some al-

cohols, such as isopropyl alcohol, isobutyl alcohol, *sec*-butyl alcohol, 3-pentanol, propylene glycol, and glycerol, effectively inhibited the crosslinking to give the water-soluble polymer. All the alcohols that worked effectively to inhibit crosslinking were found to have at least one hydrogen atom attached to a tertiary carbon atom, which can be represented by



It is well known that the hydrogen atom attached to the tertiary carbon atom is more easily drawn out than those attached to the secondary and primary carbon atoms.⁴ These facts suggest that the formation of crosslinked (water-insoluble) polymer in the copolymerization of AAm with DMAEM-MC is predominantly one of recombination of branched growing chains and/or polymer radicals rather than of imidation of amide groups. It is reasonably concluded that the alcohols work as a chain transfer agent to depress mainly the recombination (steps 2' and 3) of polymer radicals.

Copolymerization in the Presence of Alcohols

The copolymerization of DMAEM-MC with AAm was investigated in detail in the presence of alcohols bearing a hydrogen atom attached to the tertiary carbon atom. The polymer yield-time curves obtained at various concentrations of isopropyl alcohol are shown in Figure 5. The polymerization rate was found to decrease slightly with increasing isopropyl alcohol. Figure 6 shows the rela-

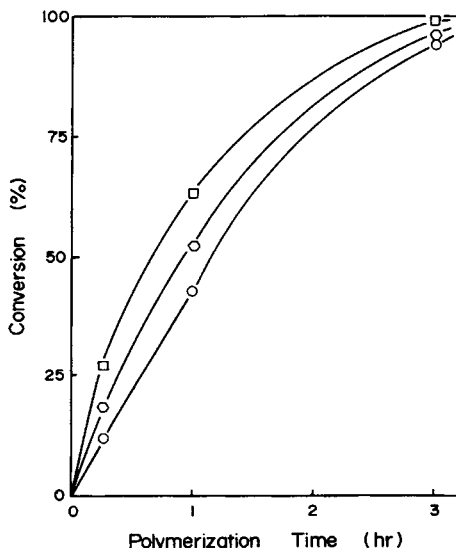


Fig. 5. Polymer yield-polymerization time curves at various isopropyl alcohol (IPA) concentrations. Monomer conc., 80 wt %; monomer composition, DMAEM-MC:AAM = 1:1 (in weight) = 25.5:74.5 (in moles); dose rate, 5×10^3 rad/hr; polymerization temp., 30°C; IPA conc.: (□) 1 wt %; (○) 4 wt %; (○) 8 wt %.

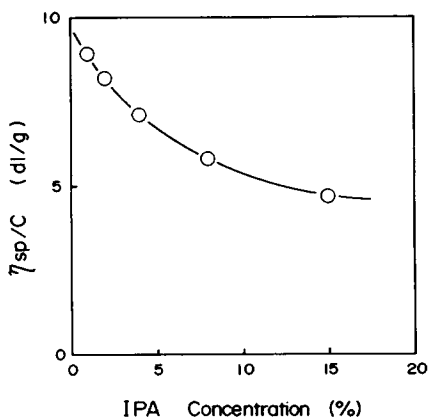


Fig. 6. Effect of concentration of isopropyl alcohol on η_{sp}/c of copolymer at a 100% polymer conversion. Reaction conditions are the same as in Fig. 5.

tionship between η_{sp}/c (at $c = 0.5$ g/dl) of the copolymer obtained at 100% conversion and concentration of isopropyl alcohol in the monomer solution. It can be seen that the molecular weight of copolymer decreases as isopropyl alcohol increases, i.e., isopropyl alcohol works as a chain transfer agent. Chain transfer constant of isopropyl alcohol determined in the polymerization of AAm is reported to be 1.9×10^5 (at 50°C).⁵ If the activity of the new radical formed by the chain transfer reaction is similar to that of the propagating radical, the transfer process would have no influence on the overall polymerization rate. In this copolymerization system, however, the low-molecular-weight radicals formed by the chain transfer reaction are assumed to be deactivated by mutual reaction before the propagation.

Figure 7 shows the η_{sp}/c of copolymer obtained with various alcohols in comparison with isopropyl alcohol. The η_{sp}/c of copolymer decreased with increasing alcohol concentration. Although the decrements in η_{sp}/c were similar, the value of η_{sp}/c at a given concentration of alcohols decreased in the order of propylene glycol > glycerol > isobutyl alcohol > isopropyl alcohol > *sec*-butyl alcohol.

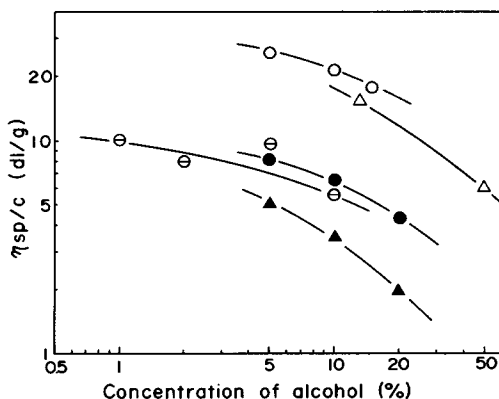


Fig. 7. Effect of concentration of various alcohols on η_{sp}/c of copolymer at a 100% polymer conversion. Reaction conditions are the same as in Fig. 5; (○) propylene glycol; (Δ) glycerol; (●) isobutyl alcohol; (⊖) isopropyl alcohol; (▲) *sec*-butyl alcohol.

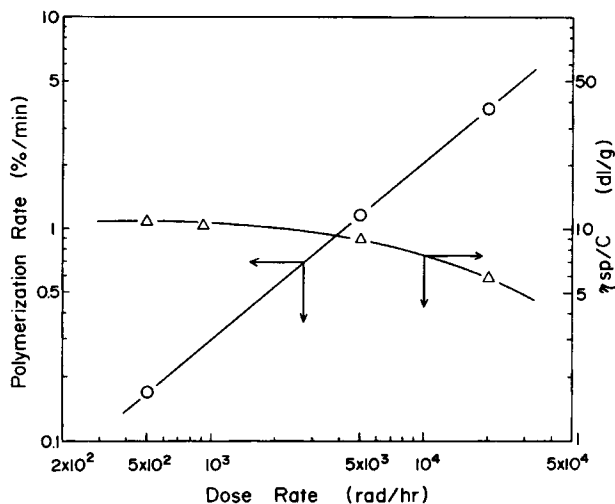


Fig. 8. Logarithmic plots of polymerization rate and η_{sp}/c of copolymer at a 100% polymer conversion vs. dose rate. Monomer conc., 80 wt %; monomer composition, DMAEM-MC:AAM = 1:1 (in weight) = 25.5:74.5 (in moles); IPA conc., 5 wt %; polymerization temp., 30°C.

Copolymerizations at various dose rates and a constant concentration of isopropyl alcohol, 5 wt %, were carried out, and it was found that polymer conversion increases with time and, at a dose rate more than 5×10^3 rad/hr, reaches a 100% value within 3 hr. The dose rate dependences of polymerization rate and η_{sp}/c of copolymer are shown in Figure 8. The dose rate exponent of the polymerization rate is about 0.8. This value agreed very closely with that reported previously for the copolymerization without chain transfer agent.¹ Although η_{sp}/c of copolymer was also found to decrease with increasing dose rate, its dose rate dependence was somewhat smaller than that found for the copolymerization system without alcohols.¹ In this system, the molecular weight of copolymer

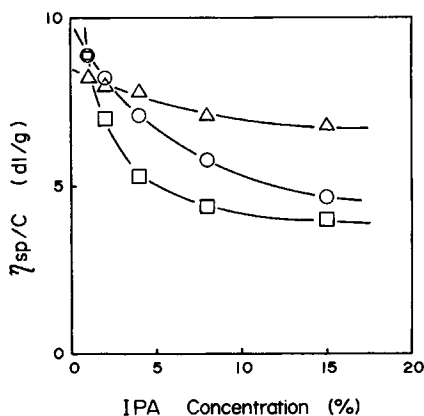


Fig. 9. Effect of isopropyl alcohol concentration on η_{sp}/c of copolymer at a 100% polymer conversion. Monomer conc., 80 wt %; dose rate, 5×10^3 rad/hr; polymerization temp., 30°C; polymerization time, 10 hr; monomer composition: (□) DMAEM-MC:AAM = 20:80 (in weight) = 7.9:92.1 (in moles); (○) DMAEM-MC:AAM = 50:50 (in weight) = 25.5:74.5 (in moles); (△) DMAEM-MC:AAM = 100:0.

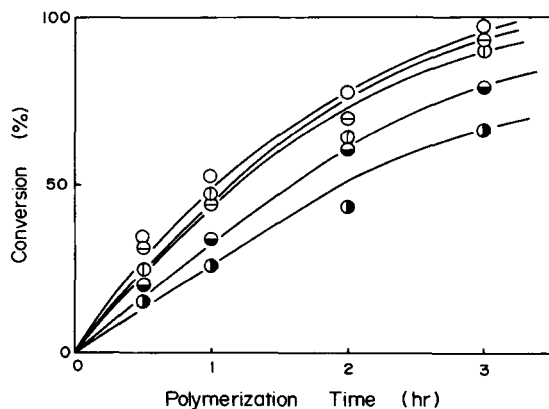


Fig. 10. Polymer yield-polymerization time curves at various monomer concentrations. Monomer composition, DMAEM-MC:AAM = 1:1 (in weight) = 25.5:74.5 (in moles); IPA conc., 5 wt %; dose rate, 5×10^3 rad/hr; polymerization temp., 30°C; monomer conc.: (●) 26 wt %; (●) 40 wt %; (○) 60 wt %; (○) 70 wt %; (○) 80 wt %.

is strongly dependent on the amount of isopropyl alcohol rather than on the dose rate.

The effect of isopropyl alcohol on η_{sp}/c for the various monomer compositions is shown in Figure 9. It was also found that the higher the mole fraction of AAm in the monomer composition, the larger the decrease in η_{sp}/c of copolymer. That is, as shown in Figure 9, η_{sp}/c of copolymer obtained at a higher AAm fraction decreased rapidly as the concentration of isopropyl alcohol increased. In the copolymerization of DMAEM-MC with AAm, it was reported previously that the molecular weight of copolymer increases with mole fraction of AAm.¹ Inversely, at a concentration of isopropyl alcohol more than 3%, η_{sp}/c of copolymer decreased as AAm content increased. This result suggests that polymer radical with AAm chain end transfers easier than that with DMAEM-MC chain end.

The polymer yield-polymerization time curves at various monomer concen-

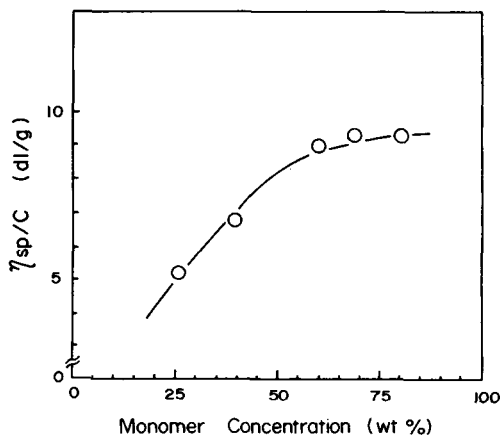


Fig. 11. Effect of monomer concentration on η_{sp}/c of copolymer at a 100% polymer conversion. Polymerization conditions are the same as in Fig. 10.

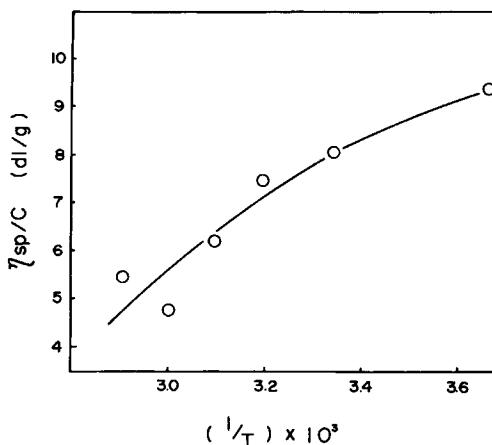


Fig. 12. Effect of polymerization temperature on η_{sp}/c of copolymer at a 100% polymer conversion. Monomer conc., 80 wt %; monomer composition, DMAEM·MC:AAM = 1:1 (in weight) = 25.5:74.5 (in moles); IPA conc., 5 wt %; dose rate, 5×10^3 rad/hr.

trations and a constant monomer composition are shown in Figure 10. The initial rate of polymerization increased with monomer concentration and reached a maximum value at a concentration of 60%. At a monomer concentration more than 60%, the polymerization rate seems to be depressed because of the decrease in the mobilities of propagating radicals and monomers. As shown in Figure 11, η_{sp}/c of polymer increased with monomer concentration and leveled off at a concentration higher than 60%. It was also found that the product polymerized at a monomer concentration above 70% can be handled as a solid polymer, i.e., the product containing less than 30% water, as polymerized, can be ground to a powder without any further process for drying.

For this copolymerization system, the overall activation energy estimated from the Arrhenius plots is about 2.6 kcal/mole. This value is similar to that for the copolymerization without isopropyl alcohol (2.0 kcal/mole).¹ The η_{sp}/c of copolymer was found to decrease as polymerization temperature increased, as shown in Figure 12. This is also a reasonable result, indicating that the temperature dependence of the chain transfer and termination reactions are larger than that of the propagation.

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