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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Boothe, Jerry E. , Flock, Howard G. and Hoover, M. Fred(1970) 'Some Homo- and Copolymerization Studies of Dimethyldiallylammonium Chloride', Journal of Macromolecular Science, Part A, 4: 6, 1419 – 1430

To link to this Article: DOI: 10.1080/00222337008081734

URL: <http://dx.doi.org/10.1080/00222337008081734>

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Some Homo- and Copolymerization Studies of Dimethyldiallylammonium Chloride

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SUMMARY

This paper summarizes some of the experimental procedures used for making homopolymers and copolymers of dimethyldiallylammonium chloride, along with a discussion of some of the experimental variables such as effects of catalyst ratio, monomer concentration, and impurities. Also discussed are some of the procedures used for evaluation of the polymers and copolymers in flocculation and sludge dewatering.

Quaternary ammonium polyelectrolytes offer a fertile area for research in developing more effective coagulants and flocculants for solids-liquid separation processes. The diallyl quaternary ammonium polymers, discovered by Dr. George Butler, constitute a new class of quaternary ammonium polyelectrolytes which have outstanding utility in many flocculation applications.

Figure 1 shows the monomer, dimethyldiallylammonium chloride (DMDAAC), and the mer unit of a typical polymer segment derived from free radical polymerization. Butler and Ingley [1] first disclosed the free radical polymerization of dimethyldiallylammonium bromide to yield a water-soluble polymer. Butler and Angelo [2] proposed and confirmed the intra-intermolecular cyclization polymerization mechanism. Butler's [3] further work showed that the chloride anion form of diallyl quaternary monomers gave polymers of significantly higher intrinsic viscosity than the previous bromide salts.

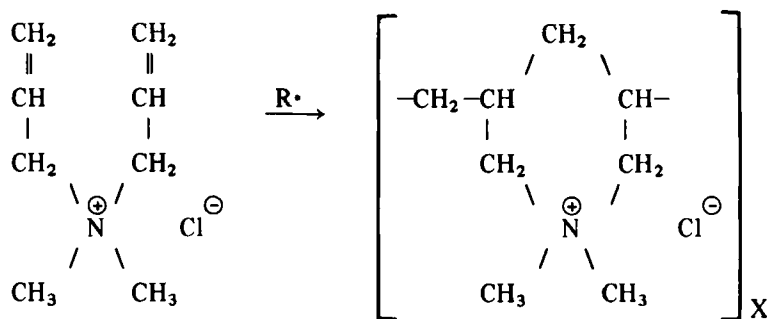


Fig. 1.

1. X% recrystallized monomer, Y%, Na₄EDTA, deionized water.
2. pH = 6.5.
3. N₂ purge, 80°C, 1 hr.
4. Addition of a solution of ammonium persulfate at a fixed rate expressed as:

$$\text{catalyst ratio} = \frac{\text{moles of catalyst}}{\text{moles of monomer, min}} = Z \times 10^{-5}$$

5. Total addition time, 100 min.
6. Dilute to 40% by weight.

Fig. 2. Polymerization procedure.

We would like to present some observations concerning the free radical polymerization of concentrated aqueous solutions of DMDAAC and the coagulation-flocculation characteristics of the homopolymers and copolymers of this monomer with acrylamide.

This work was undertaken in the course of developing effective cationic polyelectrolytes that could be used as primary coagulants in low solids water clarification and as conditioning agents for dewatering of digested sewage sludge. Various organic initiators such as azobisisobutyronitrile and t-butyl hydroperoxide were investigated in our preliminary work on the homopolymerization of DMDAAC; however, none of these initiators

produced polymers that were as effective as those produced by the system to be described and in addition required much longer conversion time. For these reasons we employed a catalyst system based on the thermal cleavage of persulfate ion. We also discovered that a small amount of ethylenediaminetetraacetic acid significantly improved the final viscosity and performance of the polymers obtained.

EXPERIMENTAL PROCEDURE

Figure 2 shows in outline form the experimental procedure that was used to evaluate the effect of 1) the catalyst ratio, 2) concentration of ethylenediaminetetraacetic acid (EDTA), 3) the initial monomer concentration, and 4) impurities on the viscosity and coagulation performance of the polymer.

The monomer solution was prepared by dissolving recrystallized monomer at the initial monomer concentration of interest in deionized water and then adding a predetermined amount of Na_4EDTA . The pH of the solution was adjusted to 6.5 and then purged with nitrogen for 1 hr at 80°C . After purging, a solution of ammonium persulfate was pumped in at a fixed rate expressed as moles of catalyst per mole of monomer per minute. This ratio was of the order of a constant times 10^{-5} ; total addition time was 100 min. Upon addition of catalyst, an immediate exothermic polymerization was obtained. Within 5 min the temperature rose from 80°C to around 110°C . The temperature remained greater than 95°C throughout the 100-min catalyst addition time. After the addition of catalyst was complete, the reaction mass was maintained at $90\text{--}100^\circ\text{C}$ for an additional 1/2 hr. After the hold period the contents were diluted to 40% and cooled to room temperature. Polymers made by this method were found to be stable and did not change with time. Polymer samples for intrinsic viscosity measurement were precipitated from a methanol-acetone mixture and dried over P_2O_5 . Intrinsic viscosities were measured in 1 N sodium chloride using a number 75-K866 Cannon-Ubbelohde tube.

Utilizing this technique we investigated the effect of catalyst ratio, EDTA concentration, initial monomer concentration, and impurities on the polymer's viscosity, residual monomer content, and flocculant performance.

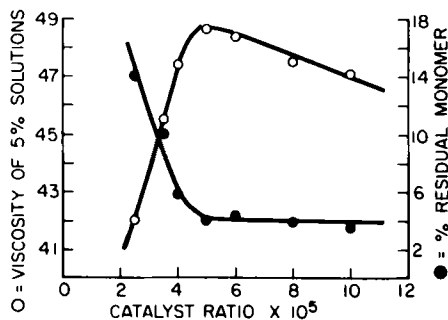


Fig. 3. Viscosity and residual monomer vs catalyst ratio $\times 10^5$.

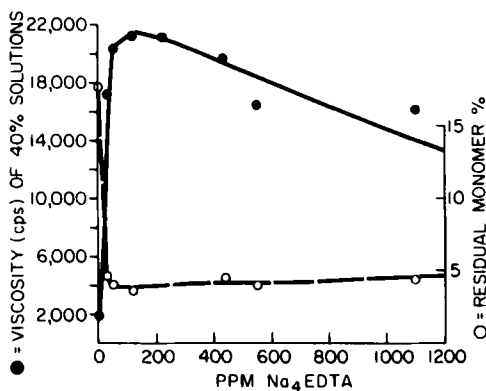


Fig. 4. Residual monomer and viscosity vs ppm Na_4EDTA .

EFFECT OF CATALYST RATIO

Figure 3 shows the effect of varying the catalyst ratio on the viscosity of 5% whole polymer solution and per cent residual monomer content. The polymerizations were performed at 65% initial monomer concentration with 200 ppm Na_4EDTA . The viscosity increases rapidly with increasing catalyst ratio up to 5×10^{-5} , then declines. The per cent residual monomer curve decreases from a maximum of 14% to a minimum of 4%.

Utilizing this data, 5×10^{-5} catalyst ratio was chosen because it gave the lowest per cent residual monomer and the highest viscosity.

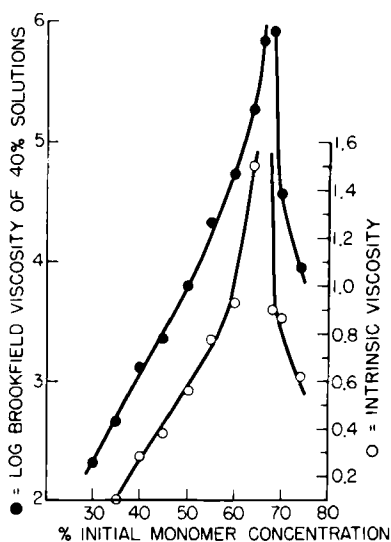


Fig. 5. Log Brookfield viscosity and intrinsic viscosity vs initial monomer concentration.

EFFECT OF Na₄EDTA

Figure 4 shows the effect of varying Na₄EDTA concentration on the Brookfield viscosity of 40% whole polymer solutions and the residual monomer content. The polymerizations in this series were run at 55% initial monomer concentration at 5×10^{-5} catalyst ratio. The viscosity curve rises sharply from 0% Na₄EDTA, reaches a maximum at 100-200 ppm, and then declines. The residual monomer content declines from a high of 17.7% to a plateau at 4%.

Whether the Na₄EDTA is participating in the initiation system or acting as a chelator for trace metals is unknown; however, all further experiments were run using 200 ppm Na₄EDTA.

EFFECT OF MONOMER CONCENTRATION

Figure 5 shows the effect of initial monomer concentration on log Brookfield viscosity of whole polymer samples at 40% and the intrinsic viscosity of precipitated monomer-free samples. These experiments were

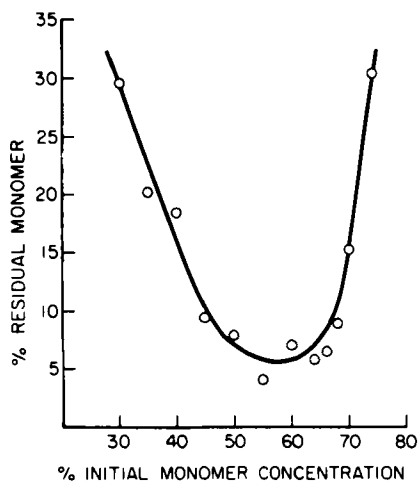


Fig. 6. % Residual monomer vs % initial monomer concentration.

run utilizing 200 ppm Na_4EDTA and 5×10^{-5} catalyst ratio. The plots of log Brookfield viscosity and intrinsic viscosity vs concentration are rather linear up to about 60%, then rise rapidly to a maximum at 66-68%, and then rapidly declines. Polymerizations conducted below this 66-68% concentration remained as clear viscose solutions throughout the reaction. Above this concentration, the polymer precipitated from solution as a waxy solid after about 5 min of catalyst addition. When this product was diluted with water the major portion redissolved; however, about 10% remained as hydrated gel. We have postulated that the observed behavior of the intrinsic viscosity vs monomer concentration curve may be caused by cross-linking of the polymer at high monomer concentrations but have not yet obtained the data necessary to resolve this question.

Figure 6 shows the relationship between the initial monomer concentration and the residual monomer in the polymer samples. The residual monomer content declines with increasing monomer concentration, reaching a minimum at 55 to 65%, and then increases rapidly between 65 to 70%.

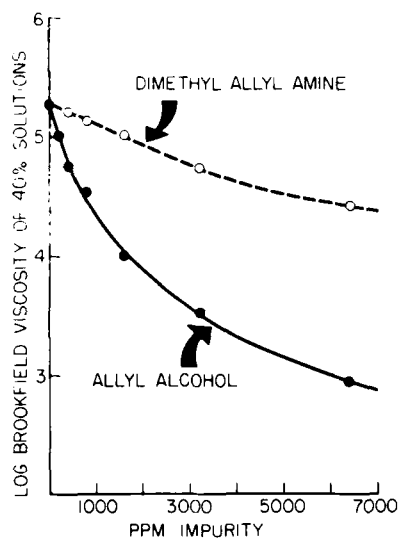


Fig. 7. Log Brookfield viscosity vs impurity concentration (ppm).

EFFECT OF IMPURITIES

In producing DMDAAC by the reaction of allyl chloride, dimethyl amine, and caustic, an aqueous solution of DMDAAC is obtained which may be contaminated with dimethylallylamine and allyl alcohol. Both of these compounds are very active monoallylic chain-transfer agents. In order to determine the degree of monomer purity necessary to produce polymers with the performance we desired, we investigated the effects of adding these impurities to recrystallized monomer solutions.

Figure 7 shows the relationship between parts per million of impurity and log Brookfield viscosity of 40% whole polymer solutions. The polymerizations were run at 64% initial monomer concentration, 200 ppm Na_4EDTA , and 5×10^{-5} catalyst ratio. Conversion was 95 to 96% for all of these experiments and did not vary with impurity level. This data illustrates that both of these impurities are efficient chain-transfer agents. As little as 1500 ppm allyl alcohol reduces the viscosity by a factor of 10. Allyl alcohol is approximately eight times as effective as dimethylallylamine in reducing viscosity. This relationship clearly points out the necessity for extreme monomer purity if polymers of high intrinsic viscosity with the performance characteristics demonstrated are desired.

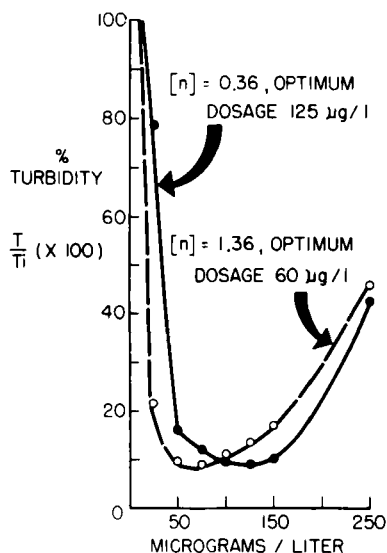


Fig. 8. % Residual turbidity vs poly-DMDAAC dosage.

FLOCCULATION EVALUATION

An important objective of this study was to correlate polymer synthesis variables with the polymer's performance as a coagulant. The laboratory method used to measure the coagulation characteristics was based on that developed by Vilaret and Black [4]. In this method a specially prepared kaolinite clay suspension is treated with varying concentrations of polymer, and measurements are made of the equilibrium residual turbidity. Figure 8 shows the results obtained with two polymers of different intrinsic viscosity. Residual turbidity is plotted as per cent of initial turbidity ($T/T_i \times 100$) against dosage in micrograms per liter. The turbidity decreases with increasing dosage, reaches a minimum, then increases because of redispersion caused by overtreatment. From these curves one obtains the optimum dosage for coagulation (in this system only) for a particular polymer sample. In the cases shown, the sample with an intrinsic viscosity of 1.36 has an optimum dosage of 60 $\mu\text{g}/\text{liter}$ and the sample with an intrinsic viscosity of 0.36 has an optimum dosage of 125 $\mu\text{g}/\text{liter}$.

Figure 9 shows the optimum dosage as determined by the Vilaret method plotted against the intrinsic viscosity of the polymer samples. As the

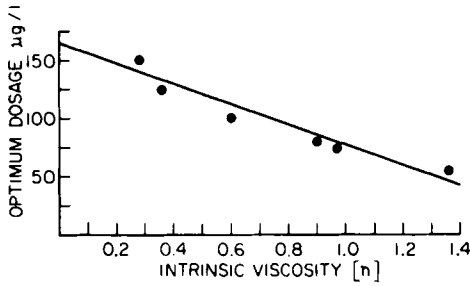


Fig. 9. Optimum Vilaret dosage vs intrinsic viscosity.

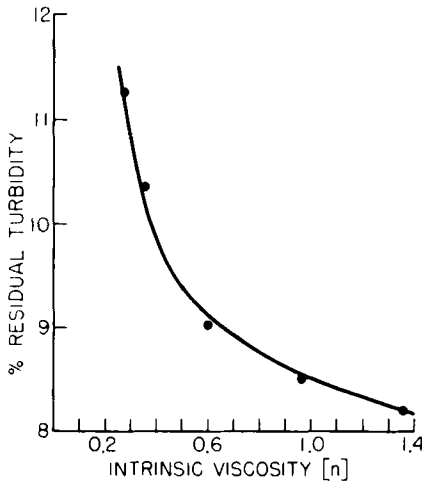


Fig. 10. % Residual turbidity (Vilaret) vs intrinsic viscosity.

intrinsic viscosity increases the optimum dosage decreases. Figure 10 shows the residual turbidity ratio at optimum dosage plotted against intrinsic viscosity. As intrinsic viscosity increases the minimum residual turbidity decreases. These evaluations have been checked utilizing natural water samples from throughout the U.S. and the trends demonstrated here have been confirmed. The results clearly show that as the intrinsic viscosity increases, the residual turbidity of a properly treated water and the dosage required decline.

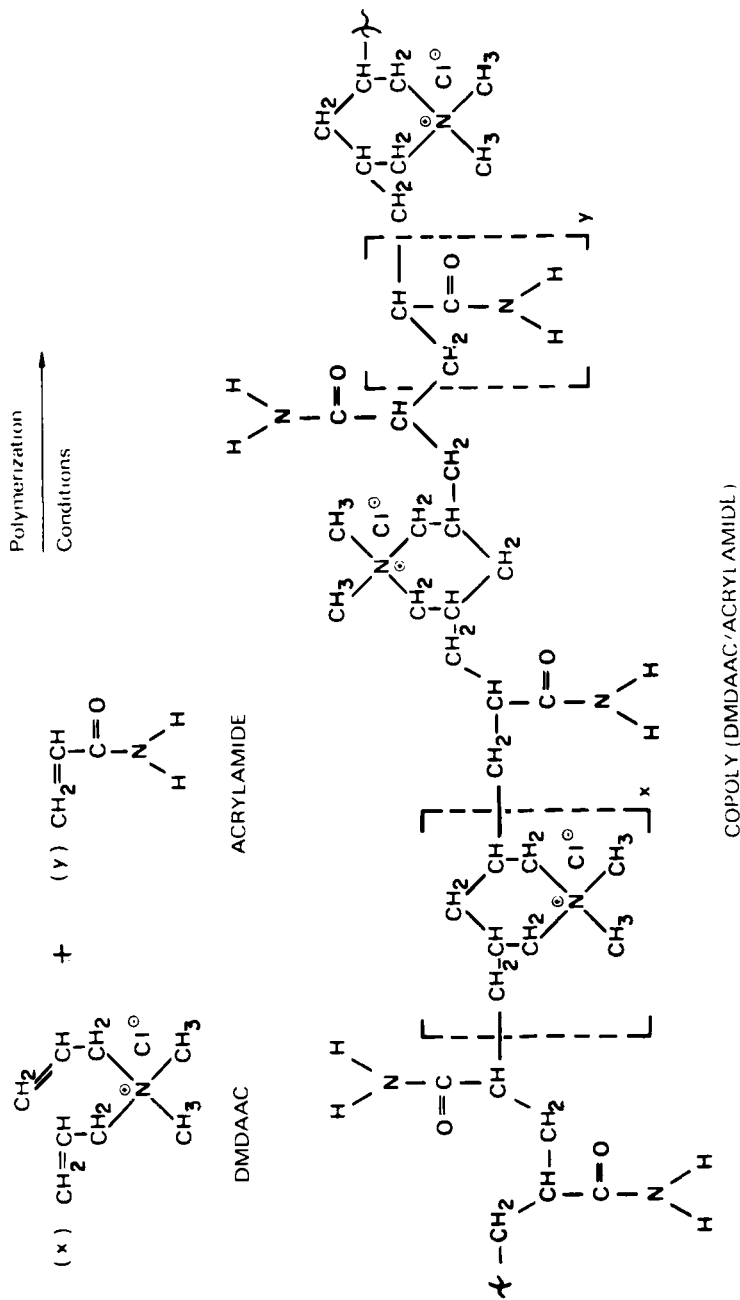


Fig. 11.

DMDAAC-ACRYLAMIDE COPOLYMERS

Suen and Schiller [5] reported that DMDAAC copolymers with other monoethylenically unsaturated monomers, such as acrylamide, increased the settling rate of raw sewage and suggested that these copolymers may have utility in improving the filtration rate of the settled sludge. However, they did not report any data on this application. Figure 11 shows the proposed structure for these copolymers.

In order to evaluate the effect of charge density in polymers used for dewatering primary-digested sewage sludge, we prepared a series of copolymers of DMDAAC with acrylamide with various compositions having comparable intrinsic viscosities. The copolymers were prepared by dissolving recrystallized DMDAAC and acrylamide in deionized water in varying weight ratios at 30% total monomer concentration, purging with N_2 at 50°C for 1 hr and initiating the polymerization at 50°C with ammonium persulfate. The polymerization was terminated at less than 10% conversion by precipitation with methanol to isolate the copolymer formed at each monomer feed ratio. No attempt was made to optimize a catalyst system for each of these various copolymers.

SEWAGE SLUDGE DEWATERING EVALUATION

The method of evaluating these polymers was the standard Buchner Funnel Vacuum Filtration Test used in the sewage treatment field. In this test 100 ml of sewage sludge is mixed with the polyelectrolyte under investigation for 20-30 sec. The sample is transferred to a 9-cm Buchner funnel containing a #42 Whatman filter paper. A constant vacuum of 20 in. Hg is applied to the funnel and the volume of filtrate collected is measured against time. For a given polyelectrolyte sample an optimum dosage is determined from a series of such tests.

Figure 12 shows the dewatering curves for a series of DMDAAC-acrylamide copolymers. On the left, volume of filtrate in milliliters is plotted against time in seconds. On the right are the various weight ratios of DMDAAC to acrylamide in the monomer feed. The bottom curve is that obtained with 100% polyacrylamide, which gave identical results to that obtained with no treatment. The third curve from the bottom is that obtained with 100% poly-DMDAAC. Several mixtures of 100% polyacrylamide and poly-DMDAAC were evaluated and in no case were the results as good as that obtained from 100% poly-DMDAAC alone.

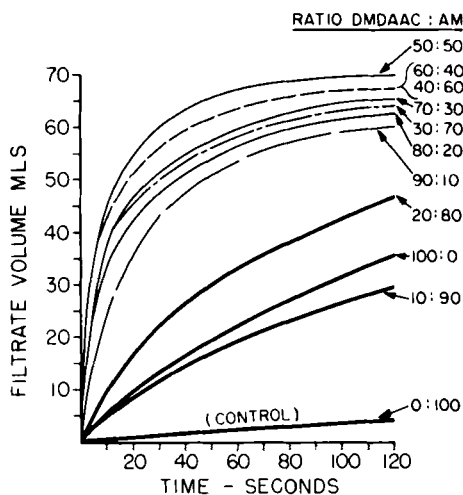


Fig. 12. Sewage sludge dewatering curves.

The dosage used to obtain these curves was the optimum for each sample and varied from 250 to 350 ppm. The dosage for the top three curves was 250 ppm, the next two 300, and the rest 350.

The curves clearly demonstrate that there is an optimum charge density for a polyelectrolyte used in dewatering digested sewage sludge. Unfortunately, since this optimum charge density is not the same for all digested sewage sludges, one is required to produce a variety of products of varying charge density in order to provide polymers that would work in most situations.

In summary, the effect of some variables in the persulfate catalyzed, aqueous homopolymerization of DMDAAC and the polymer's performance characteristics in low solids water clarification has been discussed. The effect of charge density on the dewatering rate of digested sewage sludge using cationic polyacrylamides has also been demonstrated.

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Accepted by editor November 21, 1969

Received for publication January 27, 1970