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### Effect of Some Inorganic Salts on Methyl Methacrylate and Acrylonitrile in Dimethylformamide

Fred D. Williams<sup>a</sup>

<sup>a</sup> Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, Michigan

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## Effect of Some Inorganic Salts on Methyl Methacrylate and Acrylonitrile in Dimethylformamide\*

FRED D. WILLIAMS

*Department of Chemistry and Chemical Engineering  
Michigan Technological University  
Houghton, Michigan*

### SUMMARY

A polarometric titration was utilized to determine the extent to which the monomers methyl methacrylate and acrylonitrile complex with inorganic salts in dimethylformamide solution. No complexes were obtained with the nitrates of sodium, potassium, cesium, and lead. Evidence for 1:1 complexes between acrylonitrile and  $\text{LiCl}$ ,  $\text{LiNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{ZnCl}_2$  and between methyl methacrylate and  $\text{LiNO}_3$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{ZnCl}_2$  was obtained. A 1:2 (salt/monomer) complex was also indicated between acrylonitrile and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and between methyl methacrylate and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ . Although the presence of certain salts influenced the copolymerization of methyl methacrylate and acrylonitrile, particularly at high temperatures, the existence of a complex was not an a priori indication of unusual copolymerization behavior. Tacticities of all poly(methyl methacrylate) samples were determined by NMR spectroscopy and were found to be uninfluenced by the salts.

### INTRODUCTION

In a previous investigation we reported the initiation of polymerization by a unique electron transfer catalyst—the cathode of

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\*Work performed in part at Allis-Chalmers Manufacturing Company, Milwaukee, Wis.

an electrolytic cell [1]. To minimize the IR drop between the electrodes, a number of salts were dissolved in solutions of dimethylformamide and monomer. Although the sole purpose of each salt was to conduct electricity through the bulk of the solution, differences in copolymer compositions occurred. These differences were ascribed to the simultaneous occurrence of free radical and ionic polymerization, but no correlation with the only variable, the type of salt employed, was attempted at that time.

It has been demonstrated that inorganic salts influence almost every phase of vinyl polymerizations. The polymerization of acrylonitrile is induced by metal nitrates [2, 3]. The rate and molecular weight of free radically initiated acrylonitrile polymerization is increased by the presence of LiCl [4] but decreased by FeCl<sub>3</sub> [5]. CuCl<sub>2</sub> inhibited the polymerization of methyl methacrylate [6]. It has been reported that ZnCl<sub>2</sub> increased the rates of polymerization of methyl methacrylate and acrylonitrile by the formation of 1:1 salt/monomer complexes [7]. A 1:1 complex between MgBr<sub>2</sub> and methyl methacrylate increased the isotacticity of the Grignard-initiated polymer [8]. Rhodium salts have been shown to catalyze the stereospecific addition polymerization of butadiene in aqueous emulsions [9]. In this paper the results of a study on the effect of a number of inorganic salts on methyl methacrylate and acrylonitrile in dimethylformamide are reported.

## EXPERIMENTAL

Polarometric titrations were conducted in 120-cc cylindrical cells using a mercury pool as the anode. A Sargent Model XXI polarograph with a current scale calibration of 0.003  $\mu$ A/mm at maximum sensitivity was used in conjunction with a dropping mercury cathode operated from a height of 47 cm. In dimethylformamide at zero potential the capillary had a drop time of 9.29 sec and an  $m^{2/3}t^{1/6}$  value of 0.536  $\text{mg}^{2/3}/\text{sec}^{1/2}$ . At 1 V,  $t$  was 7.12 sec and  $m^{2/3}t^{1/6}$  was 0.529  $\text{mg}^{2/3}/\text{sec}^{1/2}$ .

For each experiment, approximately  $5 \times 10^{-4}$  mole of monomer in 50 ml of dimethylformamide saturated with tetramethyl ammonium bromide was titrated with salt solutions of known concentrations. The solution was vigorously bubbled with nitrogen before each experiment and after each addition of salt solution. Diffusion currents were determined and, after correcting for dilution effects, were plotted as a function of the amount of salt added.

Purifications and polymerizations were similar to those previously described [1].

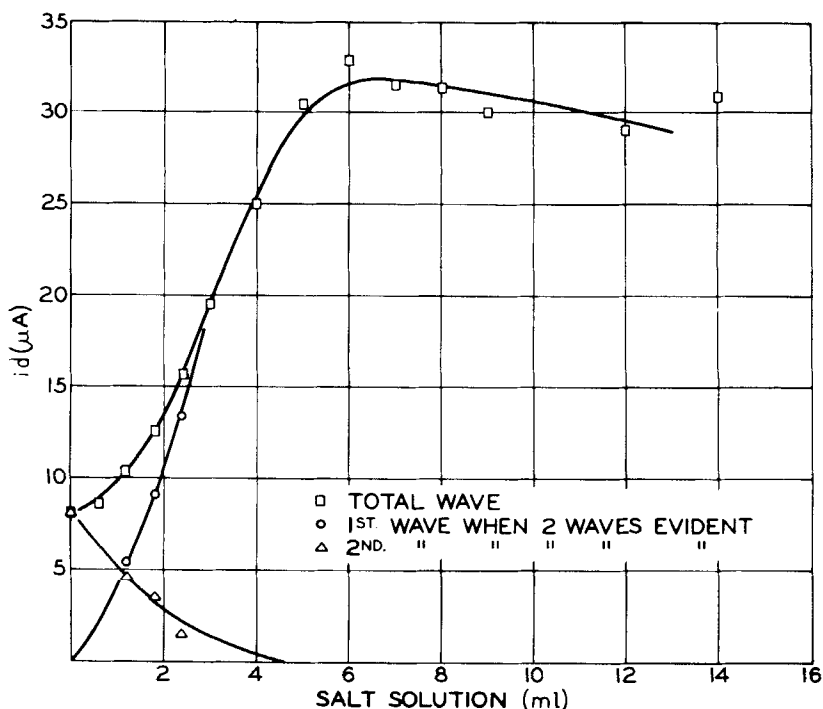
## RESULTS AND DISCUSSION

The diffusion currents for salts in the absence of monomer were directly proportional to their concentrations. In the range 0-0.01 molar and in the absence of salt, the diffusion current was essentially linear with monomer concentration. Because the complexes could not be isolated, it was impossible to prove diffusion control of current for these species directly. The precise correspondences between breaks in the diffusion current versus added salt solution curve with a stoichiometric end point when salt was incrementally added to monomer solution, however, strongly suggested that diffusion current was proportional to the concentration of complex in these cases.

A polarometric titration of monomer by salt solution was undertaken to determine the existence of complexes. The diffusion current for any electroreducible substance will vary according to the Ilkovic relationship, which under standardized conditions reduces to  $i_d = (\text{constant}) CD^{1/2}$  (C is the concentration of electroreducible substance and D is its diffusion coefficient). When the half-wave potential of the complex was sufficiently different from either monomer or cation, it was possible to follow the increase of complex concentration and the attendant decrease in monomer concentration. An example of this type of behavior is shown in Fig. 1 for the titration of methyl methacrylate with  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . Analogous results were obtained for  $\text{ZnCl}_2$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with both methyl methacrylate and acrylonitrile. In these examples the current due to complex increased to a limit which corresponded to complete conversion of monomer to complex.

When the reduction waves of monomer, salt, and complex are indistinguishable, the diffusion current is represented by the sum of the individual currents  $\bar{i}_d = k_m D_m^{1/2} C_m + k_x D_x^{1/2} C_x + K_s D_s^{1/2} C_s$ . The subscripts m, x, and s represent monomer, complex, and salt, respectively. If  $i_d$  is plotted as a function of added salt, there will be a sharp break in the curve at the end point due to loss of the monomer term and gain of a term due to excess salt. An example is shown in Fig. 2 for acrylonitrile and  $\text{LiCl}$ . Similar results were also obtained when acrylonitrile was titrated with  $\text{LiNO}_3$  and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution and for methyl methacrylate titrated with  $\text{LiNO}_3$  solution.

Unambiguous conclusions could not result when the monomer current decreased with addition of salt solution and for which there was no auxiliary information. This behavior could occur when the reduction wave of the complex is unobservable. It is also possible that the loss of monomer is due to a secondary reaction which the reduced inorganic ion in the vicinity of the dropping mercury electrode. Polarometric curves with slowly decreasing monomer currents such as that shown by methyl methacrylate and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

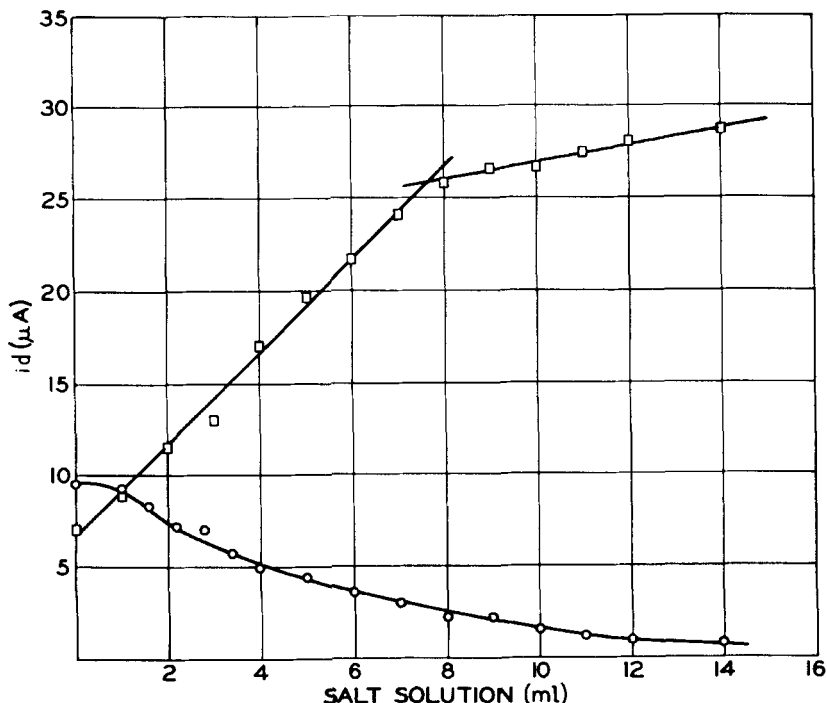


**Fig. 1.** Titration of  $4.67 \times 10^{-4}$  mole of MMA with  $\text{La}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $1.0 \times 10^{-4}$  mole/ml) in DMF solution.

in Fig. 2 may be the result of either phenomenon. For the purpose of this investigation, however, it was not considered as a definite indication of complexation.  $\text{Pb}(\text{NO}_3)_2$ -acrylonitrile and  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ -methyl methacrylate systems behaved similarly.

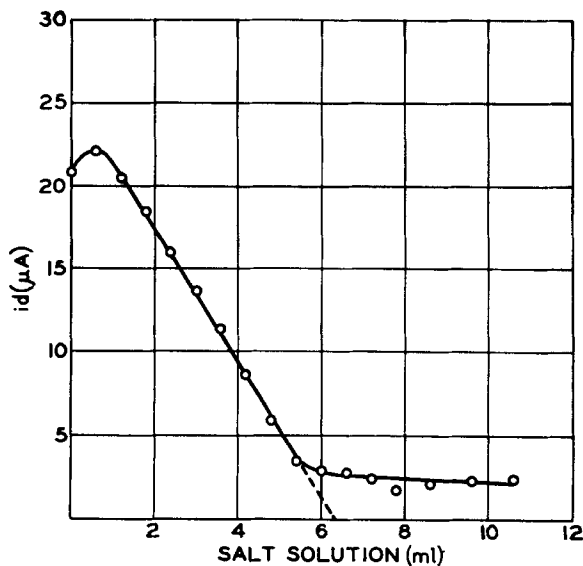
Sharp decreases in the monomer current curves were obtained with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ -methyl methacrylate (Fig. 3),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ -acrylonitrile, and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -acrylonitrile systems. Again, in these examples no current specifically due to complex could be discerned. Complex formation was arbitrarily concluded, however, since the monomer currents disappeared at the salt concentration which corresponded to a 1:1 complex.

An example of a polarograph with greater than normal detail and the resulting polarometric curve are shown for the titration of acrylonitrile with  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution in Figs. 4 and 5. Curves 1 and 2 in Fig. 4 represent the individual polarograms of acrylonitrile and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , respectively, whereas curve 3 resulted after they

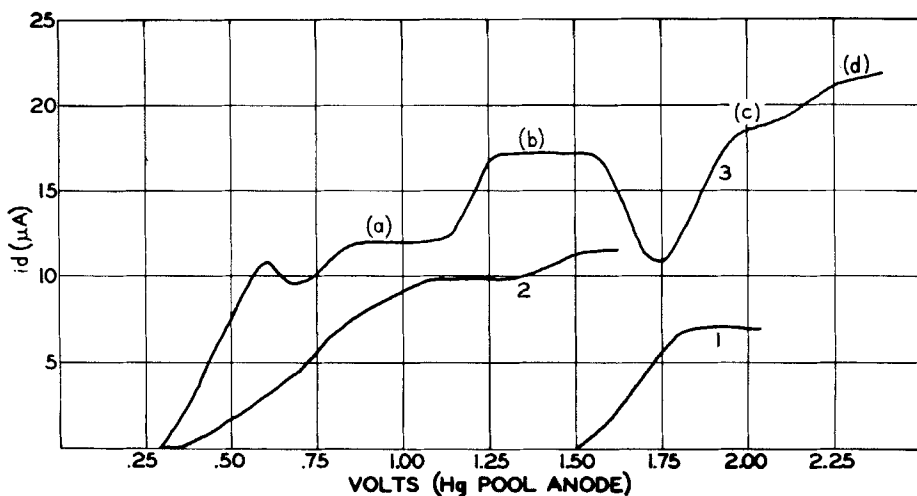


**Fig. 2.** □ Titration of  $7.50 \times 10^{-4}$  mole of AcN with LiCl ( $1.0 \times 10^{-4}$  mole/ml) in DMF solution. ○, Titration of  $4.67 \times 10^{-4}$  mole of MMA with  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $7.22 \times 10^{-5}$  mole/ml) in DMF solution.

were mixed at a comparable concentration. It was evident from the growth of a new wave (Fig. 4b) that interactions between  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and acrylonitrile occurred. A plot of the height of this new wave as a function of salt solution added (Fig. 5b) indicated that a 1:2 (salt/monomer) complex formed. A cursory examination of the monomer current (Fig. 5c) indicated that it initially increased with salt concentration. This anomaly was apparently a result of the nature of the polarogram. A very definite wave due to complex was followed by a rapid drop in current followed immediately by the acrylonitrile reduction wave. The diffusion current due to acrylonitrile was measured from the trough after the complex wave. It is quite possible that this does not represent a true equilibrium position. The disappearance of monomer current at approximately the position equivalent to a 1:1 end point was taken as equivocal proof of a 1:1 complex.



**Fig. 3.** Titration of  $9.34 \times 10^{-4}$  mole of MMA with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  ( $1.42 \times 10^{-4}$  mole/ml) in DMF solution.



**Fig. 4.** Polarograms of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and AcN in DMF solutions: (1)  $7.50 \times 10^{-4}$  mole of AcN in 50 ml of DMF; (2)  $2.17 \times 10^{-4}$  mole of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 53 ml of DMF; and (3)  $2.17 \times 10^{-4}$  mole of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $7.50 \times 10^{-4}$  mole of AcN mixed in 53 ml of DMF. In curve 3, a is wave due to  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , b is wave due to complex, and c and d are due to AcN.

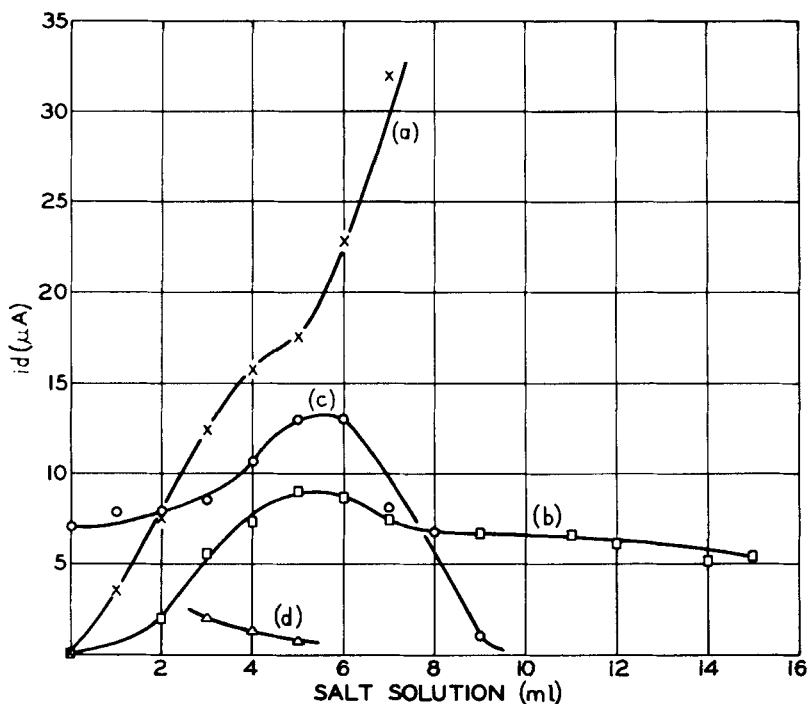


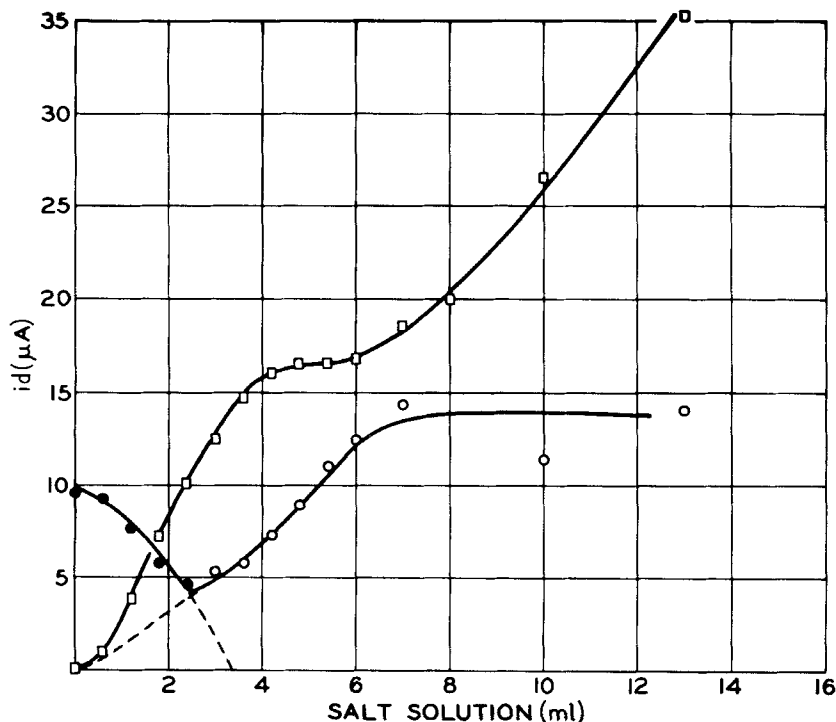
Fig. 5. Titration of  $7.50 \times 10^{-4}$  mole of AcN with  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $7.22 \times 10^{-5}$  mole/ml) in DMF solution. a, b, c, and d refer to the waves illustrated in Fig. 4.

The possibility of both a 1:2 and a 1:1 (salt/monomer) complex in the same system was indicated in several cases. Figure 6 illustrates the titration of methyl methacrylate with  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ . The rapid loss of monomer was indicative of a 1:2 complex, whereas a plateau on both a new curve and the  $\text{Mn}^{2+}$  curve was presumed due to a 1:1 complex. Evidence for 1:2 complexes was also found for acrylonitrile titrated with  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

The validity of the polarographic technique for the determination of monomer/salt complexes was confirmed by the titration of methyl methacrylate and acrylonitrile with a solution of  $\text{ZnCl}_2$ —a salt known to form complexes with these monomers [7]. Additional confidence in the method was obtained by the exact correspondences of breaks in the curves and the calculated positions for 1:1 complexes.

The results of the polarometric titrations are summarized in





**Fig. 6.** Titration of  $4.67 \times 10^{-4}$  mole of MMA with  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  ( $8.38 \times 10^{-5}$  mole/ml) in DMF solution. ●, Current due to MMA; ○, current due to complex; and □, current due to  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ .

Table 1. The presence of salt/monomer complexes is indicated by a plus sign.

Since salts will not usually dissolve into the monomer, although complex formation has been shown to exist, it appears that the solvent is involved in a role more significant than simple solvation. Attempts to isolate and purify the complexes have met with limited success. Preliminary results indicated the presence of dimethylformamide.

The effect of salts on polymer tacticity was determined by free radically polymerizing 10 mole% solutions of methyl methacrylate in dimethylformamide. An equimolar quantity of salt was added to the methyl methacrylate prior to the introduction of initiator, 2, 2'-azobisisobutyronitrile. Polymerization results are shown in Table 2. The NMR analyses of all poly(methyl methacrylate) samples were

**Table 1.** Polarometrically Determined Complex Formation<sup>a</sup>

| Salt   | AcN complex<br>(salt/monomer) |     | MMA complex<br>(salt/monomer) |     |
|--|-------------------------------|-----|-------------------------------|-----|
|  | 1:2                           | 1:1 | 1:2                           | 1:1 |
| LiCl   | —                             | +   | Not determined                |     |
| LiNO <sub>3</sub>                                      | —                             | +   | —                             | +   |
| Mg(NO <sub>3</sub> ) <sub>2</sub> · H <sub>2</sub> O   | —                             | +   | —                             | —   |
| La (NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O | —                             | —   | —                             | +   |
| MnCl <sub>2</sub> · 4H <sub>2</sub> O                  | +                             | +   | +                             | +   |
| FeCl <sub>2</sub> · 4H <sub>2</sub> O                  | —                             | +   | —                             | —   |
| FeCl <sub>3</sub> · 6H <sub>2</sub> O                  | +                             | +   | —                             | +   |
| Co(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O  | +                             | +   | —                             | +   |
| Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O  | +                             | +   | —                             | —   |
| ZnCl <sub>2</sub>                                      | —                             | +   | —                             | +   |

<sup>a</sup>No complexes were indicated with the nitrates of Na, K, Cs, and Pb.

sensibly identical, indicating a 56% syndiotactic and 35% atactic configuration.

Except for the LiNO<sub>3</sub> and NaNO<sub>3</sub> systems, it was not possible to anionically initiate methyl methacrylate samples in dimethylformamide containing the various salts which had been polarographically examined.

The effect of monomer/salt complexes on the copolymerization of acrylonitrile and methyl methacrylate in dimethylformamide solutions was determined at 25 and 130°C by free radically initiating the monomers with 2, 2'-azobisisobutyronitrile in the presence of an equimolar quantity of salt. Copolymers did not form when FeCl<sub>2</sub> · 4H<sub>2</sub>O, FeCl<sub>3</sub> · 6H<sub>2</sub>O, and La(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O was present, although MnCl<sub>2</sub> · 4H<sub>2</sub>O, a salt which had inhibited methyl methacrylate homopolymerization, produced copolymers and 130°C (Table 2). As shown in Fig. 7a, an increase in temperature caused the copolymerization to approach ideality when no salts were present. A similar result was obtained when LiNO<sub>3</sub> was used, indicating no net effect due to complexation. In contrast to these, the Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O systems produced no major differences in copolymer composition when the reaction temperature was in-

**Table 2.** MMA Homopolymerization and MMA-AcN Copolymerization in the Presence of Equimolar Concentrations of Salt

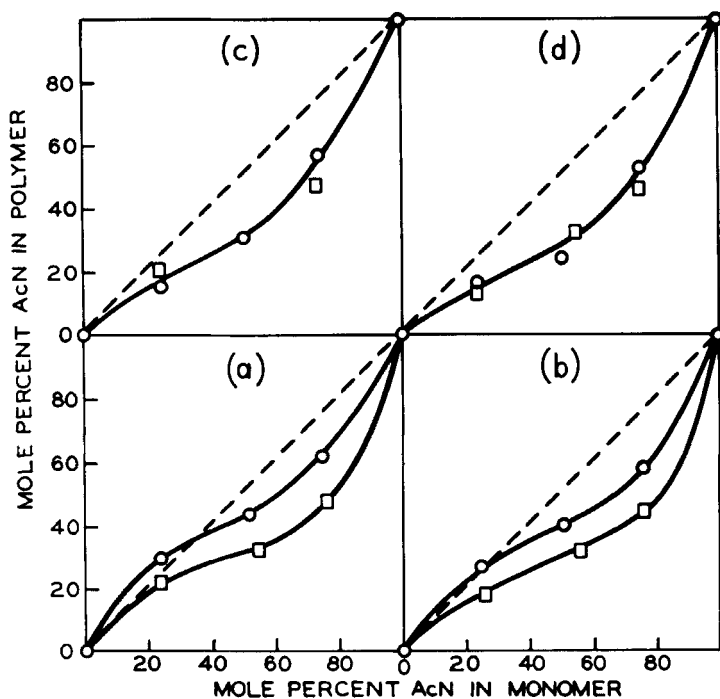
| Salt  | Homopolymerization<br>of MMA at 25°C | Copolymerization<br>of MMA-AcN |       |
|---|--------------------------------------|--------------------------------|-------|
|   |                                      | 25°C                           | 130°C |
| LiNO <sub>3</sub>                                     | +                                    | +                              | +     |
| Mg(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O | +                                    | +                              | +     |
| La(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O | +                                    | —                              | —     |
| MnCl <sub>2</sub> · 4H <sub>2</sub> O                 | —                                    | —                              | +     |
| FeCl <sub>2</sub> · 4H <sub>2</sub> O                 | —                                    | —                              | —     |
| FeCl <sub>3</sub> · 6H <sub>2</sub> O                 | —                                    | —                              | —     |
| Co(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O | +                                    | +                              | +     |
| Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O | +                                    | +                              | +     |
| ZnCl <sub>2</sub>                                     | +                                    | +                              | +     |
| NaNO <sub>3</sub>                                     | +                                    | +                              | +     |
| No salt   | +                                    | +                              | +     |

creased 105°C (Fig. 5c and d). The copolymerization results obtained at 25°C when Mg(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, ZnCl<sub>2</sub>, and MnCl<sub>2</sub> were employed were similar to those shown in Fig. 5a-d. Copolymers found at 130°C in the presence of these salts were intermediate in composition between the extremes of Fig. 5a and c.

Copolymerizations at 25°C in which the mole ratio of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O to monomer was varied from 0:1 to 2:1 did not produce significant variations in copolymer composition.

## CONCLUSIONS

The existence of complexes between the monomers, methyl methacrylate and acrylonitrile, and salts was much more common than had been anticipated. The presence of a complex, however, was not an a priori indication of unusual or even consistent polymerization phenomena. For example, in some copolymerizations an increase in temperature caused the reaction to approach ideality, whereas in others no noticeable effect occurred. A similar inconsistency has been shown by Bamford, who demonstrated that the rate of free



**Fig. 7.** Copolymerization of MMA and AcN in the presence of equimolar amounts of salt: □, at 25°C; ○, at 130°C. (a) No salt, (b)  $\text{LiNO}_3$ , (c)  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and (d)  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

radical polymerization may be either increased or decreased by the addition of certain salts [5, 6]. In the case of rate enhancement, a complex between the growing radical and the salt was considered sufficient to explain the results. In the light of the present investigation, however, it appears that an increased rate of polymerization is, at least in part, due to reactions of the complexed monomer.

Free radical and anionic homopolymerization of complexed methyl methacrylate did not produce any change in the tactic configuration of the polymers examined.

The results presented above give definite evidence that salt/monomer complexes occur. If, as it appears, the interest in electrolytically initiated polymerizations continues [10], the extent of supporting electrolyte/monomer interactions must be determined before detailed mechanisms can be formulated.

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