

# Effect of Some Anions of Some Nickel Salts on the Aqueous Polymerization of Methyl Methacrylate

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## Synopsis

The aqueous polymerization of methyl methacrylate in the absence and in the presence of some anions of nickel salts was carried out at temperatures of 40°C, 50°C, and 60°C using sodium bisulfite as initiator. The nitrate anion ( $\text{NO}_3^-$ ) was found to have the highest catalytic effect and resulted in polymers having the least average molecular weights, while the sulfate anion ( $\text{SO}_4^{2-}$ ) was found to have the least catalytic effect and resulted in polymers having the highest average molecular weights. The apparent activation energy for the polymerization process was found to be 4.3, 3.6, 3.8, and  $4.8 \times 10^4$  J/mol in the absence and in the presence of  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{NiCl}_2$ , and  $\text{NiSO}_4$  containing the same amount of nickel (0.00587 g).  $^{13}\text{C}$ -NMR spectra for the polymers obtained in the absence and in the presence of different nickel anions were found to result in nearly the same tacticity.

## INTRODUCTION

The aqueous polymerization of methyl methacrylate was previously carried out in absence and in presence of inorganic substances such as sands,<sup>1</sup> sodalime glass,<sup>2-5</sup> metal oxides,<sup>6-8</sup> graphite,<sup>9</sup> silicon,<sup>10</sup> lead silicate,<sup>11</sup> and also in the presence of different cations and anions<sup>12</sup> and in the presence of copper metal powder and some of its salts.<sup>13</sup>

In this paper, we intend to find out the effect of some anions of nickel on the aqueous polymerization of methyl methacrylate without shaking.

## EXPERIMENTAL

The methyl methacrylate monomer was a product of Merck-Schuchardt, stabilized with 100 ppm hydroquinone, purified by washing with a small amount of sodium hydroxide solution (5%). The monomer was separated with a separating funnel, dried over anhydrous sodium sulfate, and then fractionated using a fractionating column of about 15 theoretical plates; the fraction boiled at 100–100.5°C was used. The nickel salts used were chemical pure reagents. Benzene and methanol were products of El-Nasr Pharmaceutical Chemical Co., ARE Laboratory Chemicals Division.

### Polymerization of Methyl Methacrylate

The polymerization of methyl methacrylate (2.9 g) in water (200 mL) was carried out using sodium bisulphite (0.10 mol/L) as initiator at 40°C, 50°C, and 60°C in nitrogen atmosphere without stirring for different periods of time. The reactions were carried out in absence and in presence of  $\text{Ni}(\text{NO}_3)_2$ ,

$\text{NiCl}_2$ , and  $\text{NiSO}_4$  salts containing the same amount of nickel metal. The polymerization system is homogeneous at the beginning of the polymerization. The prepared poly(methyl methacrylate) samples were filtered, washed with distilled water and methanol, and finally dried in an electric oven at  $105^\circ\text{C}$  till constant weight, as the polymer was found to be insoluble in the system. The conversion of monomer to polymer was determined.

### Polymer Purification and Precipitation

The poly(methyl methacrylate) was dissolved in benzene (thiophene-free) to obtain an approximately 2% polymer solution. The polymer was then precipitated by pouring the solution into a definite amount of methanol and stirring for a specified period of time. The precipitated polymer was then filtered and finally dried at  $105^\circ\text{C}$  till constant weight.

The  $^{13}\text{C}$ -NMR spectra were recorded on 10% w/v solutions in  $\text{CDCl}_3$  using a varian FT 20  $\times$  20 MH Fourier transform spectrometer operating at ambient probe temperature  $40^\circ\text{C}$ .

### Determination of Intrinsic Viscosity

The intrinsic viscosity  $[\eta]$  for each polymer was obtained by the usual method of extrapolation. The viscosity average molecular weight ( $\bar{M}_v$ ) for the respective polymers was calculated from the corresponding intrinsic viscosity values  $[\eta]$  by applying the following equation:

$$[\eta] = 0.94 \times 10^{-4} \cdot \bar{M}_v^{0.76}$$

The viscosity measurements were made in benzene (thiophene-free) at  $25^\circ\text{C}$ .<sup>14</sup>

## RESULTS AND DISCUSSION

Aqueous polymerization of methyl methacrylate was carried out in nitrogen atmosphere in the absence and in the presence of nickel salts containing the same weight equivalent of nickel, and the conversion time curves are represented in Figure 1.

From Figure 1, it is observed that the polymerization reactions possess a considerable induction period in the absence and in the presence of nickel salts. The nickel salts were found to catalyze the polymerization reaction (Table I). From Table I, it is clear that nickel nitrate was found to have the highest catalytic effect, but nickel sulfate was found to have the least catalytic effect. The initial rate of polymerization was found to be  $1.85 \times 10^{-6}$ ,  $2.65 \times 10^{-6}$ ,  $2.43 \times 10^{-6}$ , and  $2.05 \times 10^{-6}$  ( $\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ ) at  $60^\circ\text{C}$  in the absence and in the presence of nickel nitrate, nickel chloride, and nickel sulfate, respectively.

### The Effect of Nickel Salts on the Viscosity Average Molecular Weights of the Obtained Poly(methyl Methacrylate)s

The effect of nickel salts containing the same weight of nickel metal on the viscosity average molecular weights of the poly(methyl methacrylates)

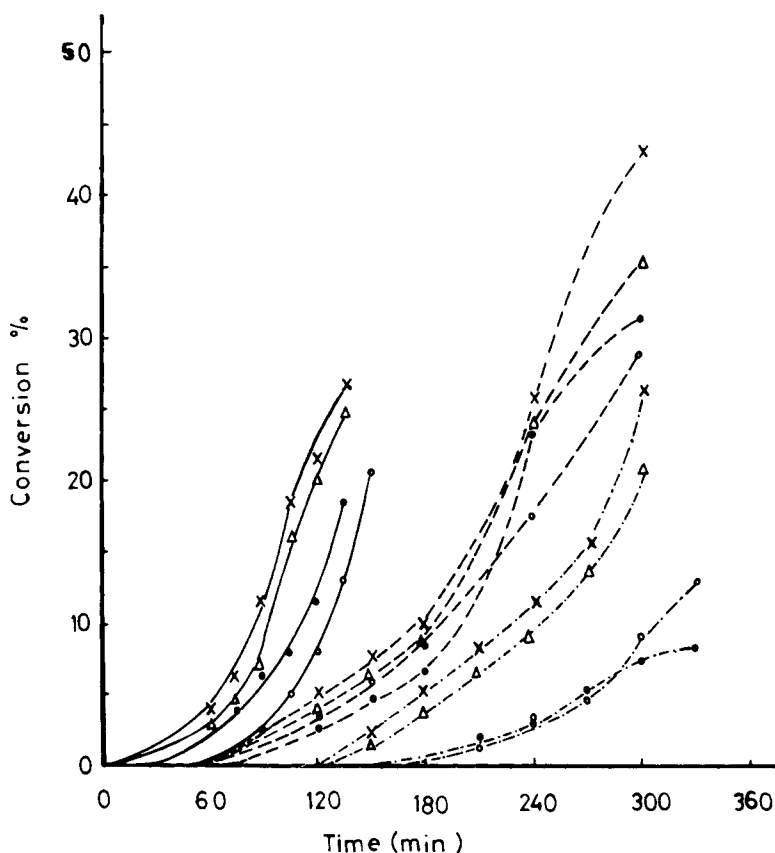


Fig. 1. Conversion time curves at different temperatures (°C): 60; (—) (---) 50; (- - -) 40; (○) in absence of salt; (x) in presence of Ni(NO<sub>3</sub>)<sub>2</sub>; (△) in presence of NiCl<sub>2</sub>; (●) in presence of NiSO<sub>4</sub>.

obtained in the polymerization reactions was studied and the data are given in Table II.

From Table II, it can be observed that the highest average molecular weights are those obtained in the presence of nickel sulfate and the least are those obtained in the presence of nickel nitrate.

TABLE I  
Initial Rates of Polymerization of Methyl Methacrylate (2.8 g) in Water (200 mL) Using Sodium Bisulfite (0.10 mol/L) as Initiator in Nitrogen Atmosphere in Absence and in Presence of Some Nickel Salts Containing the Same Amount of Nickel

Nickel salt	Initial rate of polymerization × 10 <sup>6</sup> (mol/L · s)		
	40°C	50°C	60°C
—	0.699	1.166	1.850
Nickel nitrate	1.033	1.390	2.650
Nickel chloride	0.926	1.280	2.430
Nickel sulfate	0.667	1.060	2.050

TABLE II  
 $\bar{M}_v$  Values of Poly(methyl Methacrylate) Obtained in Absence and in Presence of Nickel Salts at 50°C for a Period of 5 h

Nickel salt	Conversion (%)	$[\eta]$ (dL/g)	$\bar{M}_v \times 10^{-5}$
—	29.0	0.71	1.27
Nickel nitrate	43.2	0.45	0.70
Nickel chloride	35.4	0.5L	0.82
Nickel sulfate	31.0	0.95	1.86

### Apparent Activation Energy

The apparent activation energy ( $E_a$ ) for the aqueous polymerization of methyl methacrylate using sodium bisulfite as initiator at 40°C, 50°C, and 60°C in the absence and presence of nickel nitrate, nickel chloride, and nickel sulfate containing the same weight of nickel was calculated according to a previous publication,<sup>3</sup> and from Figure 2.

The nickel sulfate was found to result in the highest apparent activation energy ( $E_a$ ) for the polymerization processes. Nickel nitrate was found to have the least apparent activation energy value.

The  $E_a$  values obtained in the absence and in the presence of nickel nitrate, nickel chloride, and nickel sulfate were found to be  $4.3 \times 10^4$ ,  $3.6 \times 10^4$ ,  $3.8 \times 10^4$ , and  $4.8 \times 10^4$  (J/mol), respectively.

The  $^{13}\text{C}$  nuclear magnetic resonance spectra were very similar to those presented previously for poly(methyl methacrylates) prepared by similar

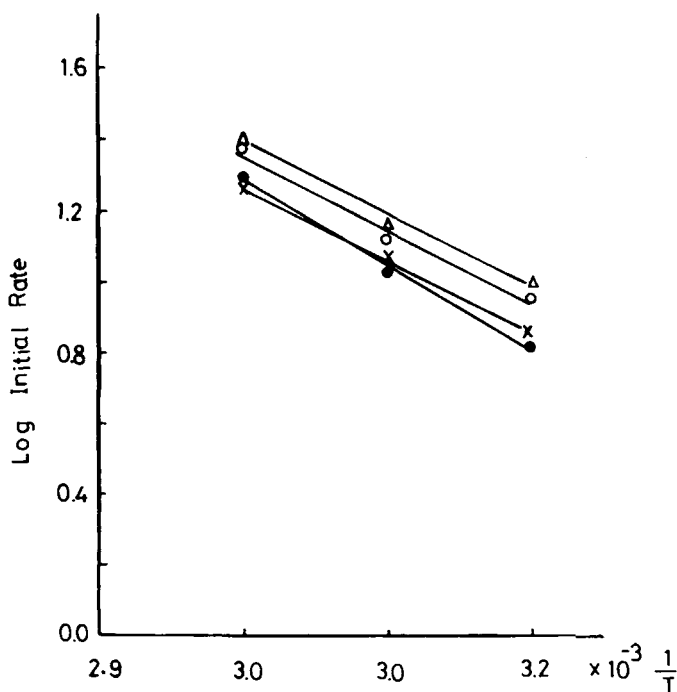


Fig. 2. Log initial rate vs.  $1/T$ .

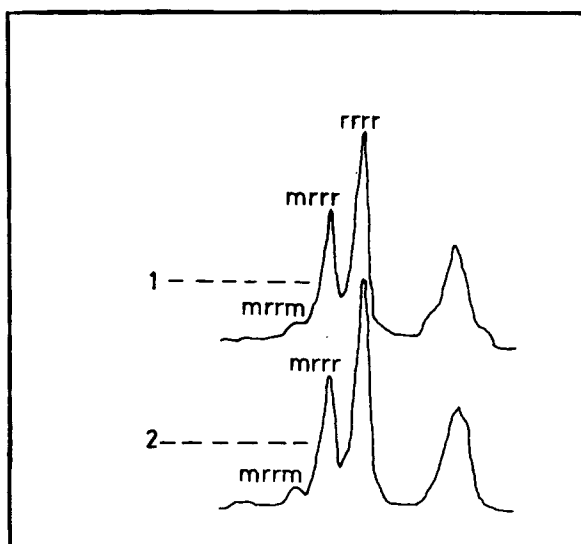


Fig. 3.  $^{13}\text{C}$ -NMR spectra of PMMA polymerized (1) in the absence and (2) in the presence of nickel nitrate.

methods.<sup>15</sup> The relative areas of the components of the carbonyl peaks indicated a ratio close to 5:34:61 for the relative concentration of isotactic (mrrm), heterotactic (mrrr  $\pm$  rrrm) and syndiotactic (rrrr) configurational pentads. This same ratio was obtained for the relative concentrations of the mm, mr, and rr triads measured from quaternary and  $\alpha$ -methyl signals (Fig. 3).

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