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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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To cite this Article Sur, G. S. and Choi, S. K.(1981) 'Polymerization of Acrylamide with Cobaltous Chloride-N,N-Dimethylaniline Initiator', *Journal of Macromolecular Science, Part A*, 15: 4, 671 – 682

To link to this Article: DOI: 10.1080/00222338108056758

URL: <http://dx.doi.org/10.1080/00222338108056758>

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Polymerization of Acrylamide with Cobaltous Chloride-N,N-Dimethylaniline Initiator

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ABSTRACT

The pair of cobaltous chloride with N,N-dimethylaniline has been investigated as an initiator for the polymerization of acrylamide in aqueous media at 30, 40, and 50°C in a nitrogen atmosphere. The rate of polymerization was found to be proportional to the [monomer]^{1.08} over the range 0.5-2.0 × 10⁻² mol/L. The reaction order related to the cobaltous chloride concentration was 0.53, which indicates a bimolecular mechanism for the termination reaction in the range of 0.2-2.0 × 10⁻⁴ mol/L. The rate of polymerization and the maximum conversion fell as the temperature rose above 40°C. The apparent activation energy was 9.38 kcal/mol in the temperature range of 30-50°C. Methanol decreased the rate of polymerization, and polymerization was completely stopped when benzoquinone was added during an induction period. A reaction mechanism is proposed on the basis of the experimental data.

INTRODUCTION

N,N-Dimethylaniline (DMA) has been employed as a catalyst with benzoyl peroxide for the polymerization of vinyl monomers, and this has been interpreted in terms of the rapid formation of radicals from

the reaction between DMA and the peroxide involving a one-electron transfer mechanism [1, 2]. It was also shown that the polymerization was initiated by the benzoate radical and not by the DMA radical [3]. DMA in combination with acid chlorides [4], trichloroacetic acid [5], and O-benzoic sulfimide [6] has been used as an initiator for the polymerization of methyl methacrylate (MMA). It has been reported that DMA with copper sulfate formed a very efficient initiator for the graft polymerization of MMA onto viscous [7].

It has known that metal compounds can behave selectively with respect to the initiation of the polymerization of various monomers [8-10]. While a metal compound acts as an initiator for one monomer, it can be fully inactive for another one. This selectivity in the initiation of polymerization is known to be a specific interaction between metal compound and monomer [11]. This interaction results in the formation of an intermediate complex consisting of the metal compound and the monomer. The present investigation dealt with the kinetics of aqueous polymerization of acrylamide in a cobaltous chloride-DMA initiator system at 30, 40, and 50°C with a view to comparing the behavior of this pair with other redox systems. The effect of initiator system and monomer concentrations on the molecular weight of the polymer formed has also been investigated.

EXPERIMENTAL

Materials

Acrylamide was purified from methanol in several crystallizations and subsequently dried in vacuo (mp 84.5°C). Cobaltous chloride hexahydrate (Fischer Chemical Co.) was deprived of crystal water by drying for 24 h in vacuo at 40°C. DMA (Eastman Kodak Chemical Co.) was purified by fractional distillation (bp 210-211°C/736 mm). All solutions were prepared with double distilled water containing a small quantity of alkaline permanganate.

Procedure

A 0.2 M molar concentration of acrylamide solution was prepared. A freshly prepared solution of cobaltous chloride was used for each polymerization reaction. Cobaltous chloride and acrylamide solutions were placed in a 250-mL four-necked flask. The reaction mixture was freed from oxygen by passing dry and pure nitrogen gas. After 1 h DMA was added and the polymerization was carried out. After a certain time interval the sample drawn from the reaction mixture was introduced directly into an ice cold, standard, and known amount of brominating reagent [12]. The percentage of conversion was calculated by the formula used by Misra and Narain [13]:

$$\% \text{ conversion} = \frac{N(V_2 - V_1)M}{20W}$$

where W is the weight of acrylamide in the sample drawn for the estimation of the unchanged monomer, N is the normality of the sodium thiosulfate solution, V_1 is the volume of sodium thiosulfate used at zero time, V_2 is the volume of sodium thiosulfate used at different times, and M is the molecular weight of acrylamide. Every precaution was taken to bring the reproducibility within 3%.

The intrinsic viscosity η of the polymers was measured in aqueous solution at 30°C by the use of an Ubbelohde viscometer. Molecular weights of polyacrylamide samples were calculated from the viscosity data by using [14]

$$[\eta] = 6.8 \times 10^{-4} M_n^{0.66}$$

RESULTS AND DISCUSSION

Effect on Cobaltous Chloride Concentration on Reaction Rate

The percentage of conversion data at varying concentrations of the CoCl_2 and at fixed concentrations of the DMA and monomers are shown in Figs. 1a and 1b. Within a certain concentration range of the CoCl_2 , the initial rate of polymerization and the maximum conversion increased ($0.2\text{--}1.5 \times 10^{-4}$ mol/L), and a decreasing trend was noticed beyond 1.5×10^{-4} mol/L. Such observations could be explained by considering the termination mechanism. When the concentration of the CoCl_2 became high, the metal compound participated in the termination reaction; hence the percentage of conversion decreased and low molecular weight polymers were formed. Another explanation is that by increasing the concentration of the CoCl_2 , the primary radicals were produced at a faster rate so that termination took place due to these radicals, hence decreasing the percentage of conversion. The order of reaction with respect to CoCl_2 concentration has been determined by plotting the logarithm of initial rate versus the logarithm of CoCl_2 concentration. Within the investigated range ($0.2\text{--}1.5 \times 10^{-4}$ mol/L CoCl_2), the reaction order of CoCl_2 is 0.53 (Fig. 2), which indicates a half-order dependence of the polymerization rate on CoCl_2 concentration. The dependence of the rate of polymerization on molecular weight when the CoCl_2 concentration was increased at a fixed concentration of the DMA and monomer is summarized in Table 1.

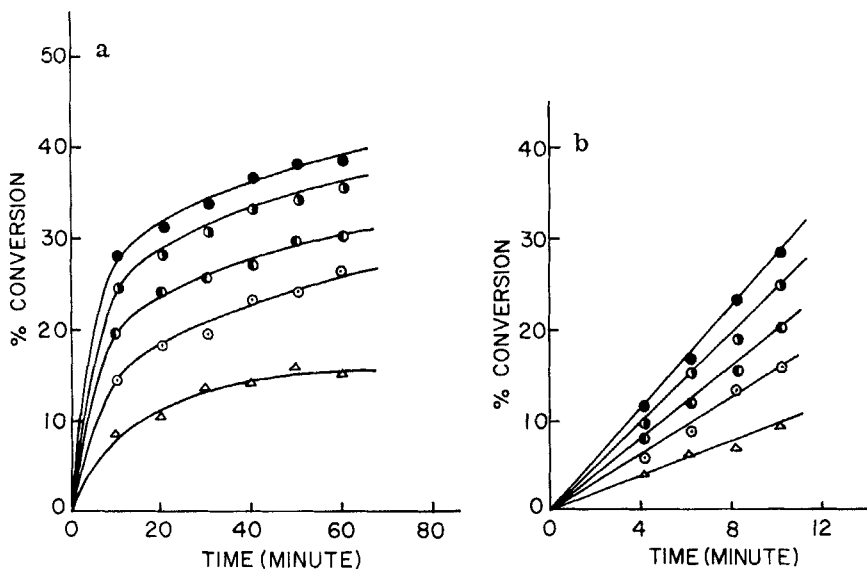


FIG. 1a. Time versus conversion curves for the aqueous polymerization of acrylamide with varying cobaltous chloride. $M = 2.0 \times 10^{-2}$ mol/L, $DMA = 1.5 \times 10^{-4}$ mol/L. Temperature = 40°C . CoCl_2 values: (\bullet) 1.5×10^{-4} ; (\circ) 1.2×10^{-4} ; (\circ) 0.8×10^{-4} ; (\circ) 0.5×10^{-4} ; (Δ) 0.2×10^{-4} .

FIG. 1b. Conversion curve for first 10 min for the aqueous polymerization of acrylamide with varying cobaltous chloride. See Fig. 1a legend for conditions and symbols.

Effect of DMA Concentration on Reaction Rate

Figure 3 shows how the rate of polymerization and percentage conversion changed with respect to the concentration of DMA. It was observed that the initial rate of polymerization and the maximum conversion increased within the range of 0.2 – 1.5×10^{-4} mol/L. The conversion reached its maximum at a DMA concentration of 1.5×10^{-4} mol/L. This might be attributed to the fact that the increasing concentration of DMA produced an increased quantity of free radicals, whereby the maximum conversion was increased. The overall average molecular weight of the polymer was low due to an increase in the rate of chain initiation and termination. As the concentration of DMA was increased (2×10^{-4} mol/L), a considerable decrease in the initial rate as well as in the maximum conversion was observed.

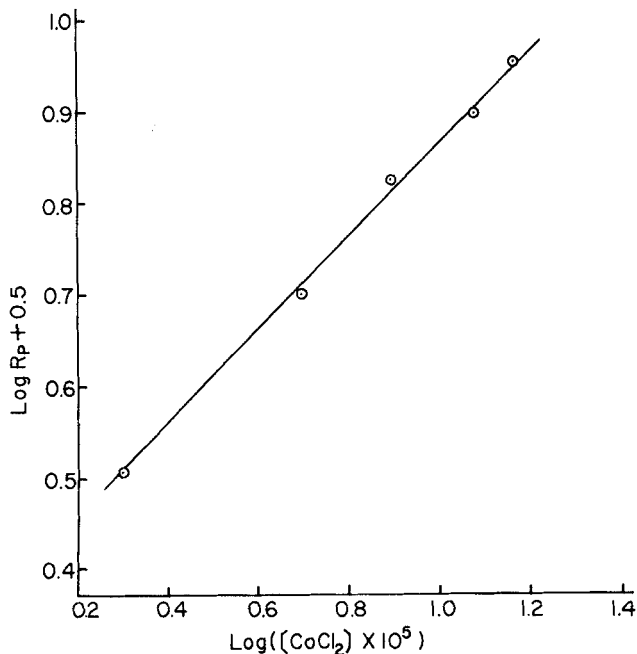


FIG. 2. Double logarithmic plot of initial rates of polymerization (in % conversion/10 min) versus CoCl_2 in moles/liter.

TABLE 1. Polymerization of Acrylamide in Aqueous Solution with Varying Concentrations of CoCl_2 and Fixed Concentrations of Acrylamide (2.0×10^{-2} mol/L) and DMA (1.5×10^{-4} mol/L) at 40°C .

Experi- ment no.	$\text{CoCl}_2 \times 10^4$	R_p % conversion/ 10 min	$M_n \times 10^{-4}$
1	0.2	9.80	7.53
2	0.5	15.93	4.69
3	0.8	20.43	3.65
4	1.2	25.33	3.05
5	1.5	28.51	2.61

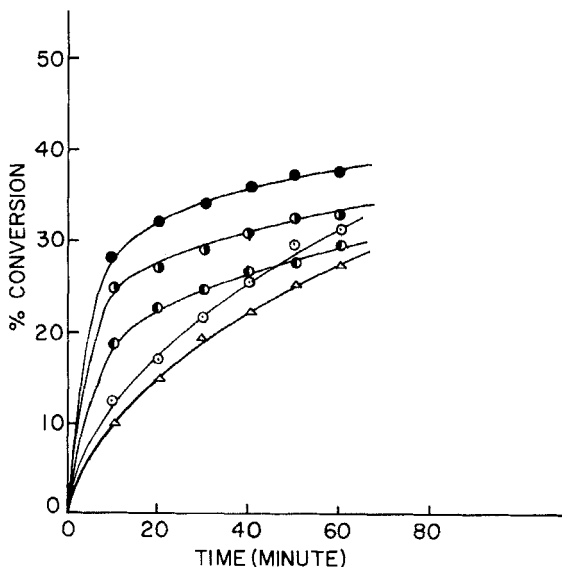


FIG. 3. Time versus conversion curves for the aqueous polymerization of acrylamide with varying DMA. $M = 2.0 \times 10^{-2}$ mol/L, $\text{CoCl}_2 = 1.5 \times 10^{-4}$ mol/L. Temperature = 40°C . DMA values: (\odot) 2.0×10^{-4} ; (\bullet) 1.5×10^{-4} ; (\circ) 1.2×10^{-4} ; (\ominus) 0.8×10^{-4} ; (\triangle) 0.2×10^{-4} .

Effect of Monomer Concentration on Reaction Rate

A typical plot of the conversion with time at different monomer concentrations is shown in Fig. 4. The initial rate of polymerization, as well as the maximum conversion, increased with a rise in the initial concentration of the monomer at fixed concentrations of CoCl_2 and DMA. It was seen that the results of polymerization increased linearly within a certain range of monomer concentrations (0.5 – 2×10^{-2} mol/L). The value of the monomer exponent was 1.08, thereby confirming the monomer concentration. The plot in Fig. 5 represents the results of varying the rate against the monomer concentration. Deviation from linearity was observed at higher concentrations of the monomer (2.0×10^{-2} mol/L). This might be due to the viscosity of the medium more than to the higher conversion of the monomer into polymer.

Dependence on Temperature

An increase in temperature caused an increase in initial rate of polymerization as well as maximum conversion up to 40°C . However,

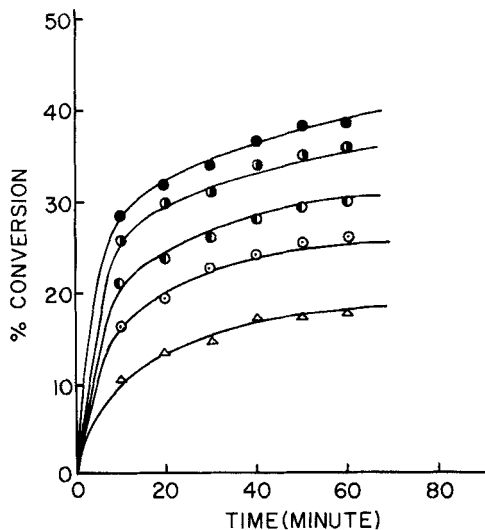


FIG. 4. Time versus conversion curves for the aqueous polymerization of acrylamide with varying monomer. $\text{DMA} = 1.5 \times 10^{-4}$ mol/L, $\text{CoCl}_2 = 1.5 \times 10^{-4}$ mol/L. Temperature = 40°C . Monomer values: (\bullet) 2.0×10^{-2} ; (\bullet) 1.8×10^{-2} ; (\circ) 1.6×10^{-2} ; (\circ) 1.2×10^{-2} ; (\triangle) 0.8×10^{-2} .

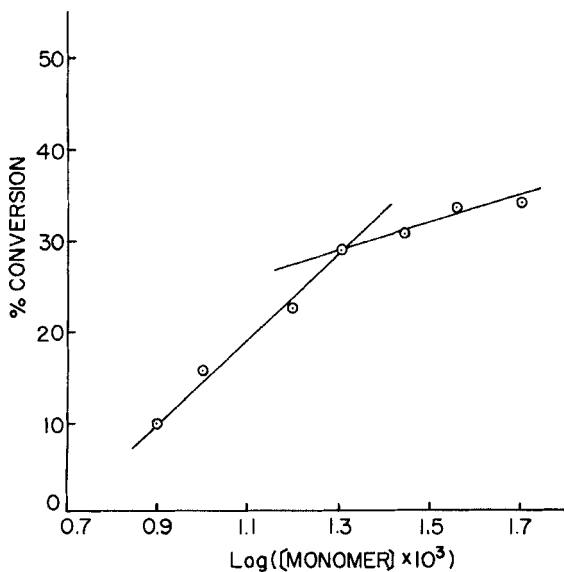


FIG. 5. Rate dependence on monomer concentration. $\text{DMA} = 1.5 \times 10^{-4}$ mol/L, $\text{CoCl}_2 = 1.5 \times 10^{-4}$ mol/L. Temperature = 40°C .

TABLE 2. Effect of Temperature^a

Experiment no.	Temperature (°C)	% Conversion with reaction time (min)					
		10	20	30	40	50	60
1	30	9.72	20.81	21.35	27.54	27.81	28.15
2	35	12.68	25.10	28.47	30.15	31.74	32.11
3	40	28.51	31.92	36.41	36.92	37.04	37.41
4	45	19.86	25.12	27.43	28.47	28.91	29.40
5	50	24.92	29.21	32.54	32.98	33.25	33.38

^aMonomer = 2.0×10^{-2} mol/L, DMA = 1.5×10^{-4} mol/L, CoCl_2 = 1.5×10^{-2} mol/L.

a marked decreased in the maximum conversion was noticed above 40°C (Table 2). This might be due to the following reason. As the temperature was increased, the case effect became less pronounced and the primary radicals could increasingly take part in termination reactions, thus reducing the overall reaction rate as well as the maximum conversion with an increase of temperature. The overall energy of activation calculated by an Arrhenius plot was 9.38 kcal/mole-deg in the temperature range 30-50°C (Fig. 6).

Effect of the Additives

The addition of organic solvents such as methanol or ethanol to the system was found to depress the initial rate of polymerization as well as the maximum conversion (Fig. 7). Similar results have been reported by other workers [15]. The time-conversion relationships are shown in Fig. 7, where they are compared with the polymerization of acrylamide without radical scavenger. Clearly, DPPH inhibited the polymerization of acrylamide. It is concluded that the polymerization proceeds through a radical mechanism.

Probable Mechanism

The spectra of CoCl_2 -DMA and CoCl_2 -DMA-acrylamide in H_2O at room temperature are shown in Fig. 8. Cobaltous(II) chloride in aqueous solution forms the hexacoordinated Co^{2+} complex ion. The spectra exhibited λ_{max} 537 nm. On adding DMA in this system, λ_{max} was the same. The lack of change in λ_{max} indicated that neither a

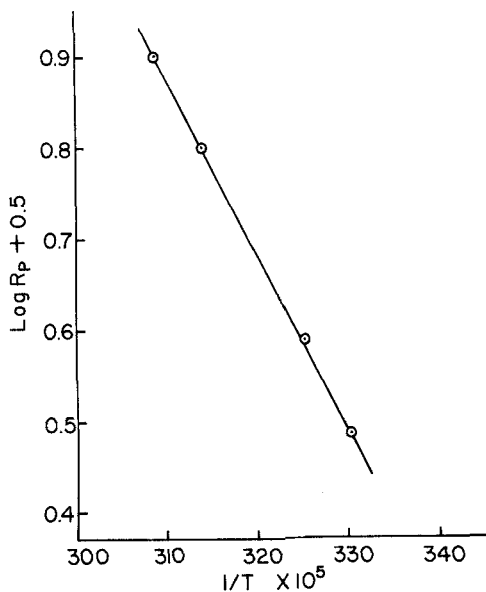


FIG. 6. Logarithmic plot of rate of polymerization (in % conversion/10 min) versus $1/T \times 10^5$ (in K).

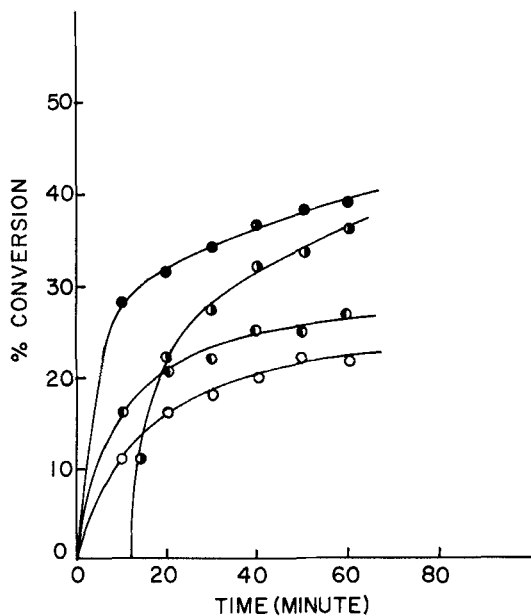


FIG. 7. Effect of organic compounds on rate of polymerization of acrylamide. Monomer = 2.0×10^{-2} mol/L, DMA = 1.5×10^{-4} mol/L, CoCl_2 = 1.5×10^{-4} mol/L. Temperature = 40°C . (●) No additive; (◐) DPPH = 10^{-4} mol/L; (●) 5 mL MeOH; (○) 5 mL EtOH.

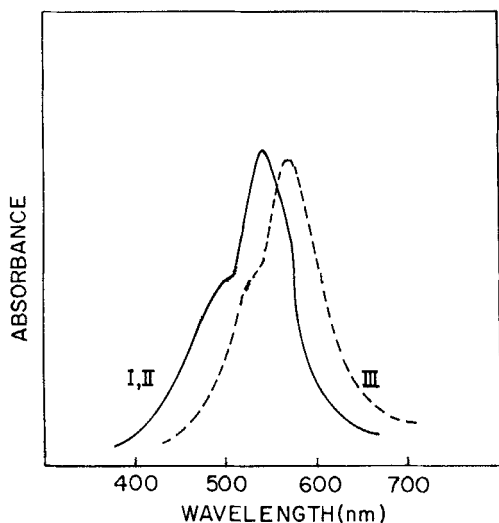
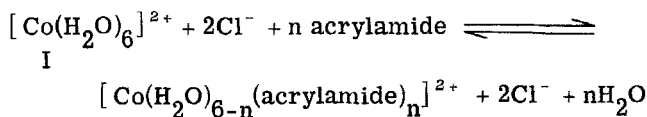


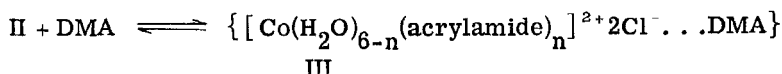
FIG. 8. Spectra of the systems CoCl_2 -DMA- H_2O and CoCl_2 -DMA-monomer- H_2O . (I) $\text{CoCl}_2 = 1.5 \times 10^{-4}$ mol/L; (II) $\text{CoCl}_2 = 1.5 \times 10^{-4}$ mol/L, DMA = 1.5×10^{-4} mol/L; (III) $\text{CoCl}_2 = 1.5 \times 10^{-4}$ mol/L, monomer = 2.0×10^{-2} mol/L.

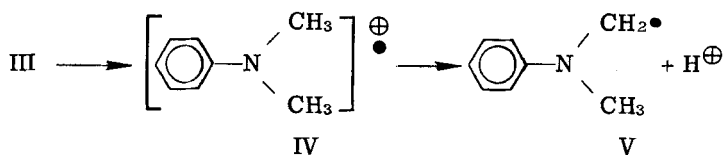
chemical reaction nor a formation of the complex CoCl_2 -DMA took place. In the system CoCl_2 -acrylamide in H_2O , the spectra exhibited a characteristic maximum absorption band at 564 nm. Such observation could be explained by considering the formation of the complex. On adding acrylamide, the H_2O molecules were substituted for by acrylamide molecules in the internal sphere of the complex Co^{2+} ion. The substitution of acrylamide molecules for H_2O resulted in an increase in electron-accepter properties so that this complex reacted with DMA.

On the basis of the results of spectral analysis of the system CoCl_2 -DMA-acrylamide- H_2O and with the results from the kinetics of polymerization, it may be assumed that the following mechanism occurs:

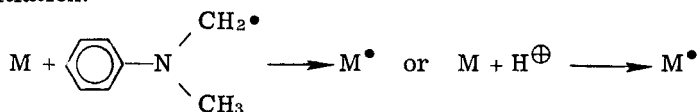


II

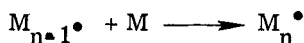




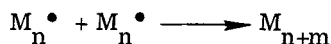
Initiation:



Propagation:



Termination



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Accepted by editor February 4, 1980

Received for publication March 5, 1980