

Polymerization of Acrylamide in the Presence of Calcium Sulfate Dihydrate and Calcium Sulfate Hemihydrate

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SYNOPSIS

The homopolymerization of acrylamide in water alone and also in the presence of calcium sulfate dihydrate and of calcium sulfate hemihydrate has been studied. Polymerizing acrylamide with the redox pair potassium persulfate–sodium bisulfite, the rate increased steadily with increasing initiator concentration. In the presence of up to 25% dihydrate, the rate was like that of acrylamide alone. However, when adding the “reactive” hemihydrate that is hydrated to the dihydrate concurrently with the progressing polymerization, the rate is somewhat slower in comparison with the two other systems. For determination of the compositions of the various reaction products, a method combining DTA and XRD data has been developed.

INTRODUCTION

The addition of acrylic polymers and copolymers to building material, e.g., concrete¹ and gypsum, in order to improve their mechanical properties and also to reduce the water absorption, even in low concentration, is a well-established practice. This incorporation of the acrylic polymer can be achieved either directly by mixing the ready-made polymer with, e.g., calcium sulfate hemihydrate and the necessary amount of water² or by impregnation of the porous solid such as concrete, gypsum casts, etc., with a liquid monomer that is then polymerized *in situ*.^{3–6} Regarding the direct application of monomers, a number of studies on the free-radical-initiated polymerization of vinyl monomers in aqueous media in the presence of inorganic fillers, such as CaCO₃,⁷ CaSO₃ · H₂O,^{8,9} BaSO₄,¹⁰ CaSO₄ · $\frac{1}{2}$ H₂O,¹¹ CaSO₄ · 2H₂O,¹¹ various metal oxides,¹² and sand¹² have been reported. The vinyls include, especially,

methyl methacrylate,^{7,8,12} a copolymer of methyl methacrylate with methylacrylic acid,¹³ and vinyl acetate.¹⁴ As initiators, potassium persulfate and redox pairs, e.g., potassium persulfate–sodium bisulfite, are usually applied.

In the present paper, we report the solution polymerization of acrylamide in water alone and also in the presence of various amounts of (a) the inert calcium sulfate dihydrate and (b) the “reactive” calcium sulfate hemihydrate. Considering the possible practical application of the system monomer–calcium sulfate hemihydrate–water to form a composite of polymer–calcium sulfate dihydrate, the water-soluble acrylamide was chosen as monomer. The polymerizations were initiated by the redox pair potassium persulfate–sodium bisulfite.

EXPERIMENTAL

Materials

Acrylamide from various sources was purified by recrystallization from chloroform.¹⁵ *N,N*-Methylenebisacrylamide (Fluka, pract.) (*N,N*-mba), potassium persulfate (Merck, pro analysi), sodium bisulfite (Baker, anal. reagent), calcium sulfate dihydrate (“dihydrate”) (Analar), and calcium sul-

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Figure 1 DTA curves of a mixture of dihydrate (50%) and hemihydrate (50%).

fate hemihydrate ("hemihydrate") (BDH and Gesher Gypsum, Israel) were used.

Polymerization Procedures

- (a) Acrylamide without inorganic powder was polymerized in freshly boiled water with the redox couple $K_2S_2O_8$ — $NaHSO_3$ under nitrogen. The reactions were carried out in 250 mL flasks with constant stirring at $30 \pm 0.1^\circ\text{C}$. To follow up the rate of the polymerization, equally sized samples of the reaction mixture were taken at predetermined times and poured into methanol, where the polyacrylamide precipitated. After filtration and washing with methanol, the polymer samples were dried at 80°C under reduced pressure until constant weight was achieved.
- (b) The polymerizations of acrylamide in the presence of various amounts of dihydrate and of hemihydrate were carried out with the same redox couple under nitrogen, but in small reaction flasks (50 mL) placed in a thermostat ($30 \pm 0.1^\circ\text{C}$) fitted with a shaking device. For determination of the rate, the reaction flasks were successively taken out from the thermostat and their content was poured into methanol. The precipitate was filtered off, washed with methanol, and dried

under reduced pressure at 40°C (to prevent loss of water from the dihydrate) till constant weight. For the reactions with the dihydrate, there is no change of its weight during polymerization and therefore any additional weight was due to the polymer formed. Carrying out the reaction with the hemihydrate, there occurs concurrently with the polymerization hydration of the hemihydrate to dihydrate. Thus, the precipitates obtained in methanol may contain in addition to polyacrylamide hemihydrate and dihydrate. The composition of the precipitates of this series was determined quantitatively by combining DTA and XRD analyses.

Analytical Methods

DTA measurements were carried out on a "home-made" apparatus with a temperature range from room temperature up to 250°C , as necessary for measuring the endothermic reactions of both the dihydrate (at about 130 – 150°C) and the hemihydrate (at about 168 – 180°C) (Fig. 1). Based on a calibration curve, prepared from known mixtures of the two hydrates, the ratio of the areas of the peaks enabled the quantitative determination of the composition of the hydrates from the polymerization reactions.¹¹ Anhydrite, i.e., anhydrous calcium sulfate, was used as reference.

Because of the presence of polyacrylamide in the samples, an additional peak appeared quite near and partially congruent with that of the dihydrate (Fig. 2). Consequently, a second method, X-ray diffraction, was also applied, which enabled the determination of the crystalline dihydrate and hemihydrate without interference of the amorphous polyacrylamide.

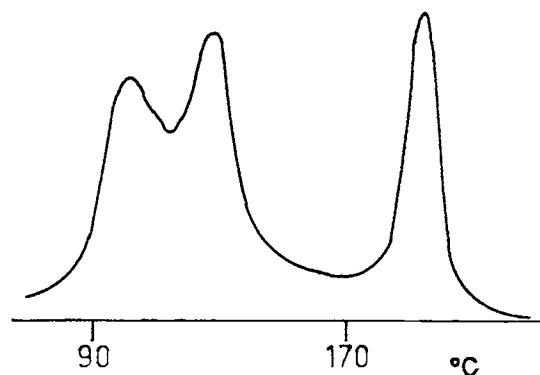


Figure 2 DTA curves of a mixture of dihydrate (25%), hemihydrate (25%), and polyacrylamide (50%).

XRD measurements were performed on a Philips powder diffractometer with $\text{CuK}\alpha$ (Ni) radiation. The scanning speeds in Θ were $1^\circ/\text{min}$ and $0.25^\circ/\text{min}$. The powdered samples were passed through a 150 micron sieve. Both hydrates have specific peaks that thus permitted their quantitative composition analysis, again based on a preprepared calibration curve. At a scanning speed of $0.25^\circ/\text{min}$, the peaks

chosen were in the range of $2\Theta = 20\text{--}21.5^\circ$ for the dihydrate and at $14\text{--}15.5^\circ$ for the hemihydrate (Fig. 3).¹³

The molecular weight of polyacrylamide was determined from viscosity measurements of the polymer in an aqueous solution of sodium nitrate [1 M] at $30 \pm 0.1^\circ\text{C}$ and by using the relationship $[\eta] = 3.73 \times 10^{-4} [M_w]^{0.66}$.¹⁶ To separate polyacrylamide

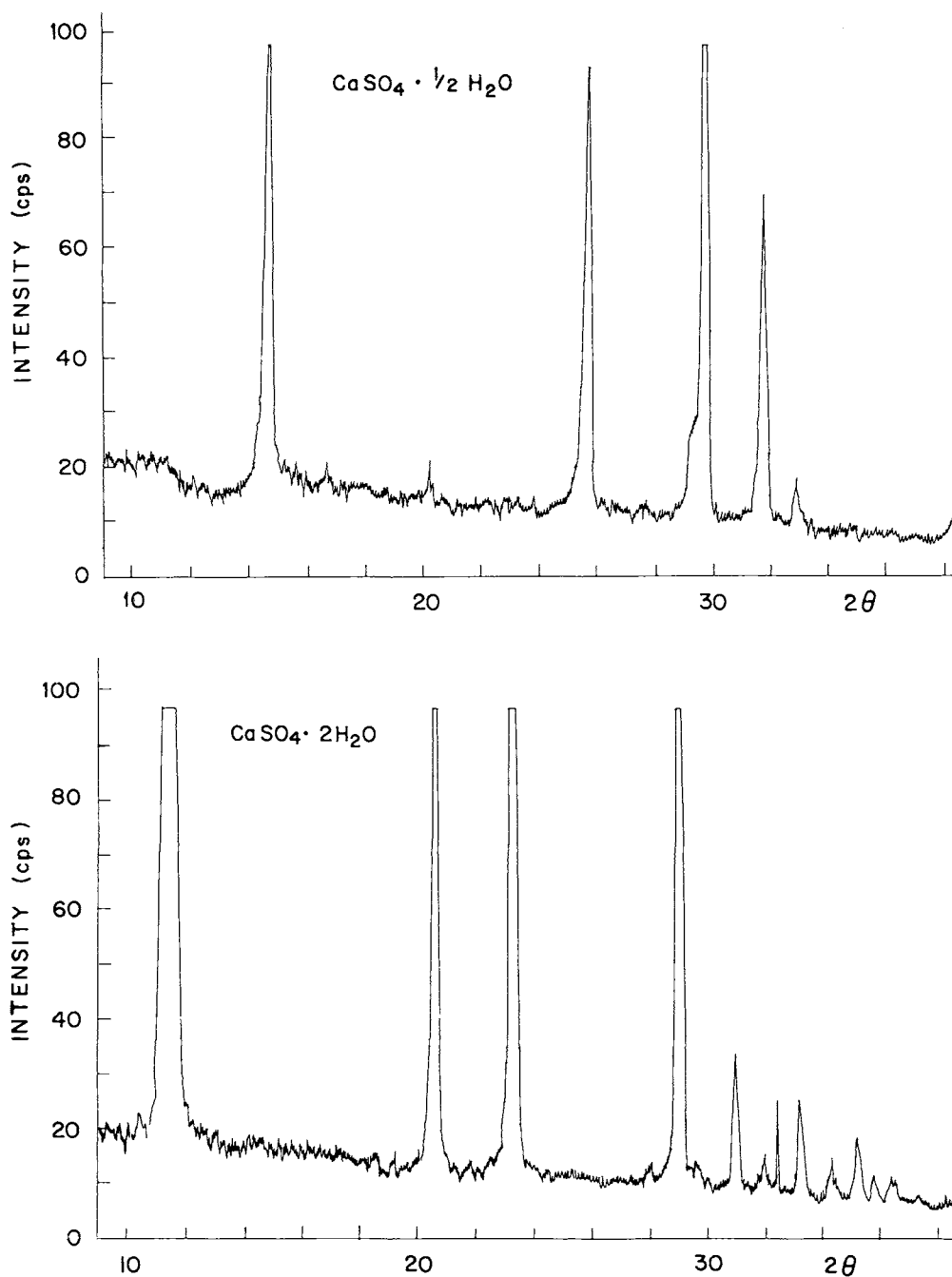


Figure 3 XRD curves of (a) calcium sulfate hemihydrate and (b) calcium sulfate dihydrate.

Table I Polymerization of Acrylamide in Water, Molar Composition of Reactants

Exp. No.	Reactants, Molar Composition		
	Acrylamide	K ₂ S ₂ O ₈	NaHSO ₃
1	0.7	0.75 · 10 ⁻³	0.75 · 10 ⁻³
2	0.7	1.0 · 10 ⁻³	1.0 · 10 ⁻³
3	0.7	1.5 · 10 ⁻³	1.5 · 10 ⁻³
4	0.7	2.0 · 10 ⁻³	2.0 · 10 ⁻³

from the reaction products, obtained when polymerizing acrylamide in the presence of hemihydrate, the solid composite was pulverized and extracted with water in a Soxhlet apparatus for about 18 h.

RESULTS AND DISCUSSION

Polymerization of Acrylamide

Working according to procedure (a), acrylamide was polymerized in water with the initiator couple K₂S₂O₈—NaHSO₃ at four concentrations, keeping their molar ratio equal (Table I and Fig. 4). Figure 4 shows the rise of the rate of conversion of acrylamide with increasing initiator concentration and the results are quite similar to those of Riggs and Rodriguez.¹⁷

Addition of a cross-linking agent *N,N*-mba (0.5, 1.0, and 2.0% of the acrylamide) to the reaction mixture, having the composition as in experiment 4, Table I, resulted in the formation of gels already

in the early steps of the reaction, yet the magnitude of the rates of conversion (Fig. 5) was quite similar to that without *N,N*-mba.

Polymerization of Acrylamide in the Presence of Calcium Sulfate Dihydrate

To determine the influence of the dihydrate on the rate of conversion of acrylamide, reaction mixtures, having the starting composition of experiment 4, Table I, were polymerized in the presence of four different quantities of dihydrate according to procedure (b). Comparing the rates of conversion of acrylamide in the presence of 5, 10, 20, and 25% dihydrate (Fig. 6) with the rates obtained with acrylamide alone (Fig. 4, experiment 4), one finds a nearly equal rate reduction in the presence of 5, 10, and 20% dihydrate, whereas with 25%, the rates are actually equal or even slightly higher than those of the corresponding polymerization of acrylamide in the absence of a solid phase.

Arai et al.⁹ found a similar behavior for the soap-less emulsion polymerization of methyl methacrylate in the presence of powdered calcium sulfite as the solid phase in comparison with the same system without the solid phase, i.e., without the powdered calcium sulfite, but with calcium sulfite below its saturated concentration as necessary for the initiating redox couple with potassium persulfate. No explanation for this suppression effect was given. Yet this behavior could possibly be explained by two opposing effects: The presence of solid surfaces in a free-radical-initiated polymerization enhances the

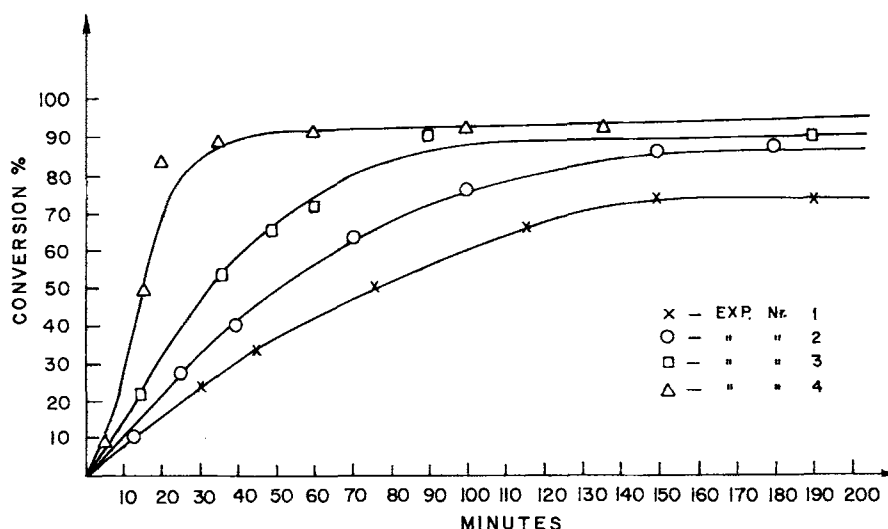


Figure 4 The effect of the redox initiator concentration on the time-conversion curve of acrylamide.

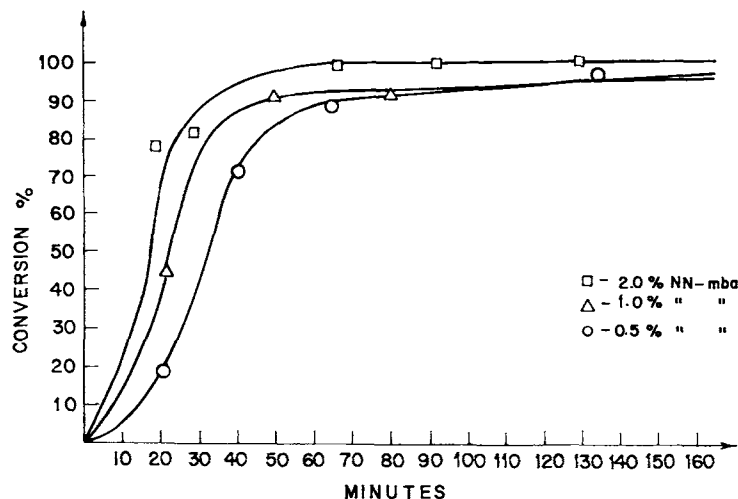


Figure 5 The effect of the addition of *N,N*-methylenebisacrylamide on the time-conversion curve of acrylamide. Conditions: Experiment 4, Table I.

destruction of free radicals. On the other hand, due to the solid powder phase, there is a rise of the viscosity of the reaction mixture, resulting in an autoacceleration-like effect. Up to about 20% solids, the two effects seem to be equal, whereas at the higher percentage of the powder, the second effect, the autoacceleration, seems to dominate.

Polymerization of Acrylamide in the Presence of Calcium Sulfate Hemihydrate

The reactions of this system were carried out as for the pair acrylamide-calcium sulfate dihydrate. The rates of polymerization of acrylamide (starting

composition as in experiment 4, Table I) and the concurrent hydration of the hemihydrate (starting concentrations: 5, 15, and 25%) to the dihydrate were calculated from both DTA and XRD determinations of the solid reaction products. As stated above, these double measurements were necessary, because the overlapping and consequent widening of the endotherms of the dihydrate and of the polyacrylamide in the lower temperature range did not permit a quantitative analysis of the products.

Thus, for the series with 5% hemihydrate (Fig. 7), the DTA curve 7(a-1) (after 15 min reaction time) shows the endothermic peak for the hemihydrate above 170°C and a wide very low curve between

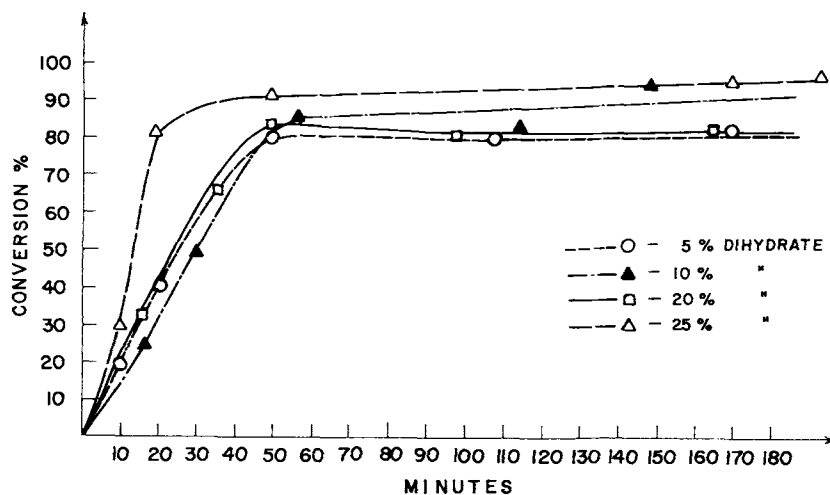


Figure 6 The effect of the amount of dihydrate on the time-conversion curve of acrylamide.

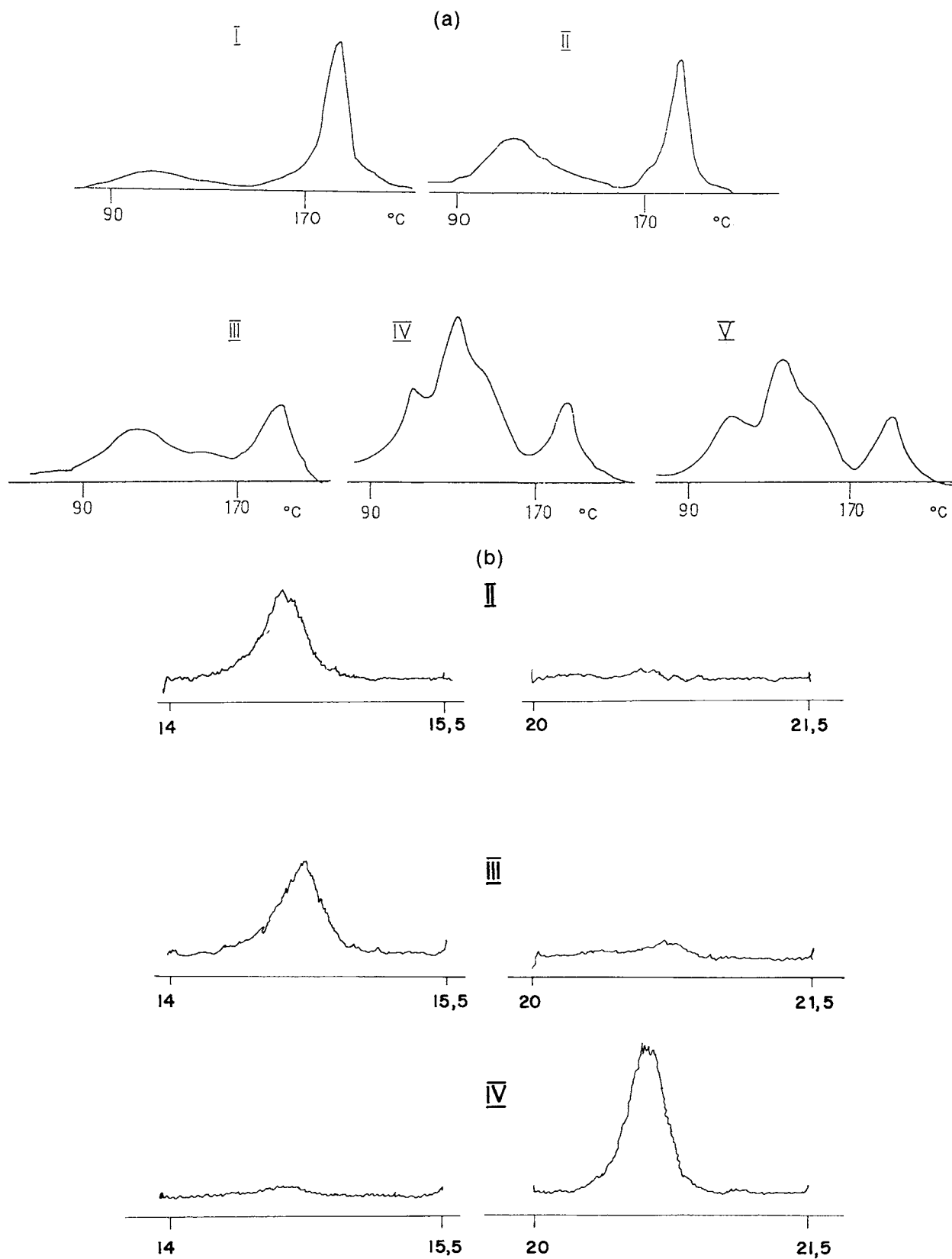


Figure 7 Polymerization of acrylamide in the presence of 5% hemihydrate: (a) DTA thermograms; (b) XRD spectra.

about 80 and 115°C, which is ascribed to the polyacrylamide. Curve 7(a-II) (after 30 min) shows, except for the peak of the hemihydrate, again a wide, but higher curve, starting at about 90°C. This is ascribed mainly to the polymer, as the XRD curve 7(b-II) shows only very little dihydrate. The composition of sample III, which shows the presence of both the hemihydrate and the dihydrate was calculated from the XRD spectrum 7(b-III). After 90 min, little hemihydrate is left according to the DTA [7(a-IV)] and XRD [7(b-IV)] spectra, whereas sample V consists, according to the DTA spectrum [7(a-V)], of polymer and dihydrate only. With 15% hemihydrate (Fig. 8), the DTA spectra of samples after 15 min [8(a-I)] and 30 min [8(a-II)] reaction time are quite similar to those with 5% hemihydrate

and, also, the XRD spectrum [8(b-III)] shows very little dihydrate. The compositions of samples III and IV, containing in addition to the polymer both hemihydrate and dihydrate were calculated from their XRD spectra [8(b-III) and (b-IV)], as these enable a more accurate determination than do the corresponding DTA curves. In the series with 25% hemihydrate (Fig. 9), the compositions of the first three samples, containing polyacrylamide, hemihydrate, and dihydrate, were calculated from the more accurate XRD data [9(b-I), (b-II), and (b-III)], whereas the compositions of samples IV and V were determined from their DTA curves [9(a-IV) and (a-V)].

The results are summarized in Figures 10(a)–(c), showing the mutual influence of the two con-

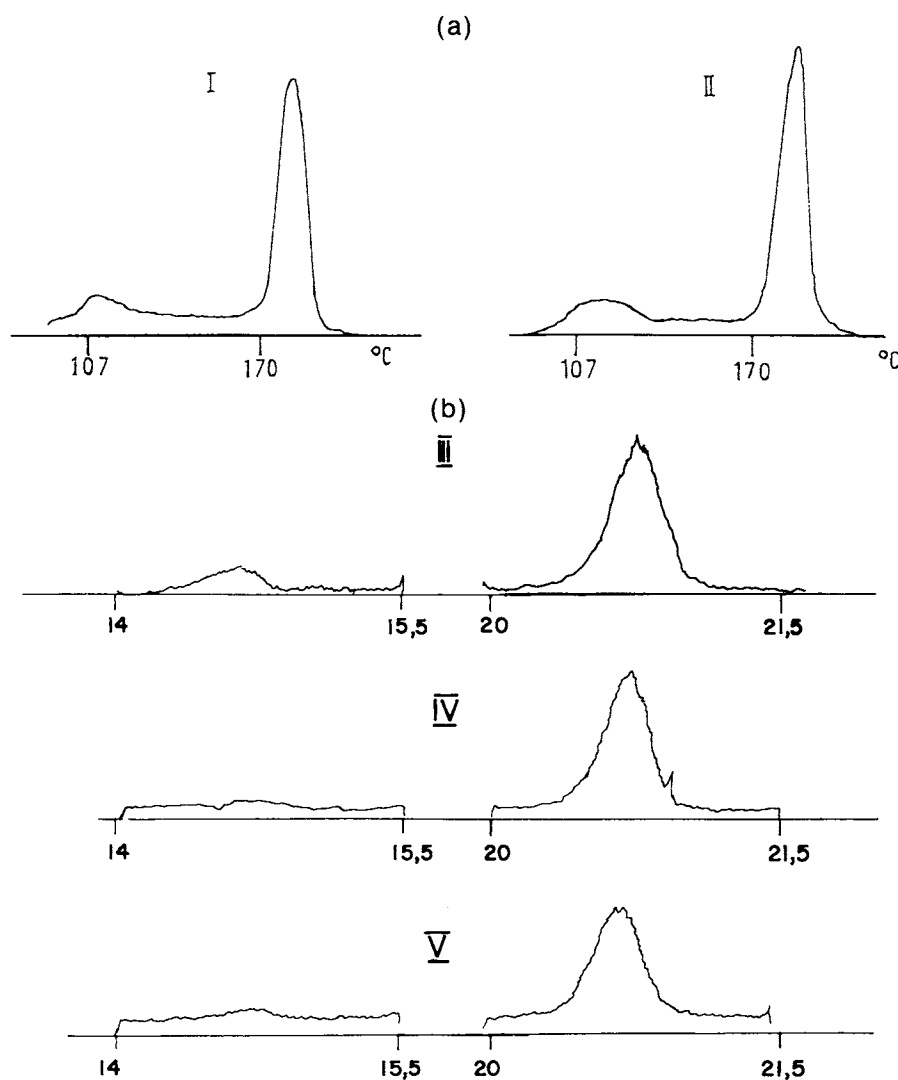


Figure 8 Polymerization of acrylamide in the presence of 15% hemihydrate: (a) DTA thermograms; (b) XRD spectra.

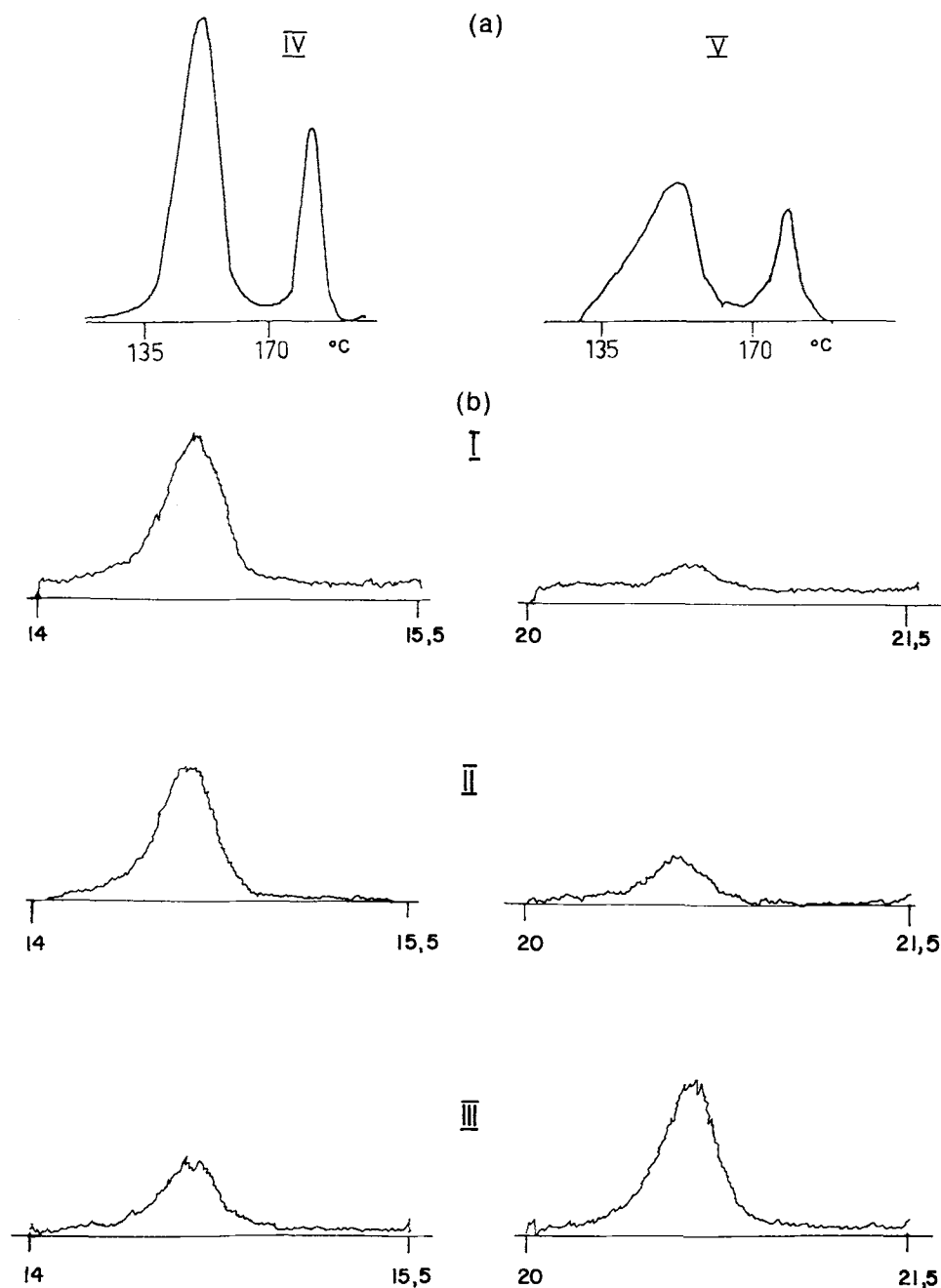


Figure 9 Polymerization of acrylamide in the presence of 25% hemihydrate: (a) DTA thermograms; (b) XRD spectra.

current reactions—polymerization of acrylamide and hydration of the hemihydrate. With 5% hemihydrate [Fig. 10(a)], the hydration of the hemihydrate is retarded for nearly 40 min and hydration was completed only after about 60 min later. For comparison, hydration of hemihydrate alone on contact with water starts after about 5 min and is completed after 10–15 min. Sherr and Roshal² reported the retarding effect of polyacrylamide above

0.02 wt % on the hydration of hemihydrate, which according to Kuntze¹⁸ is due to the absorption of the retarding compounds on the surface of the dihydrate, thus preventing its growth. With 15% hemihydrate [Fig. 10(b)], the retarding effect on the hydration of the hemihydrate is less, nearly 30 min, and with 25% hemihydrate [Fig. 10(c)], it is 10 min only. In both systems, nearly complete hydration was reached after about 30 min later.

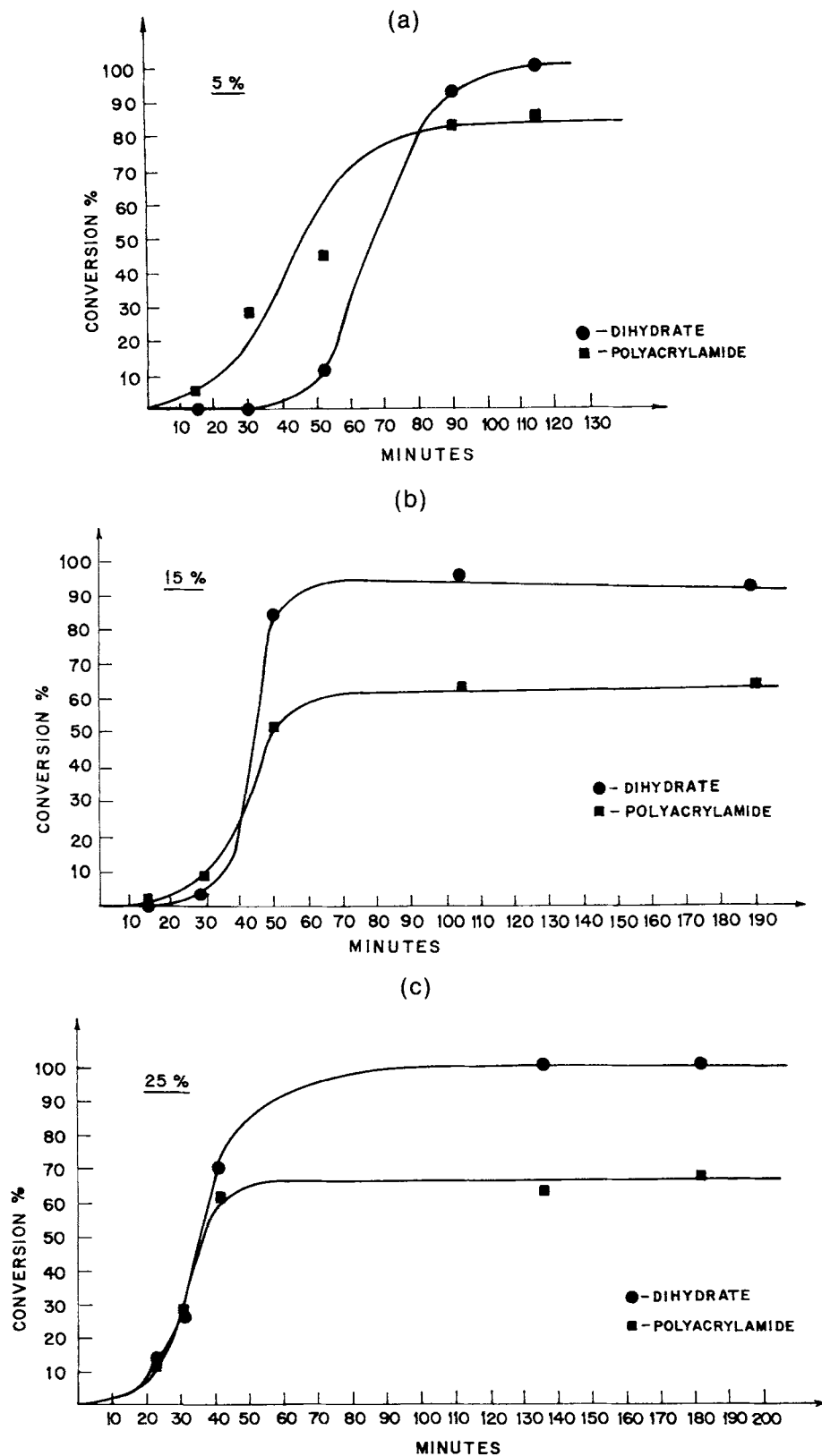


Figure 10 Polymerization of acrylamide in the presence of 5, 15, and 25% hemihydrate. Time dependence of the formation of polyacrylamide and dihydrate. Conditions: Experiment 4, Table I.

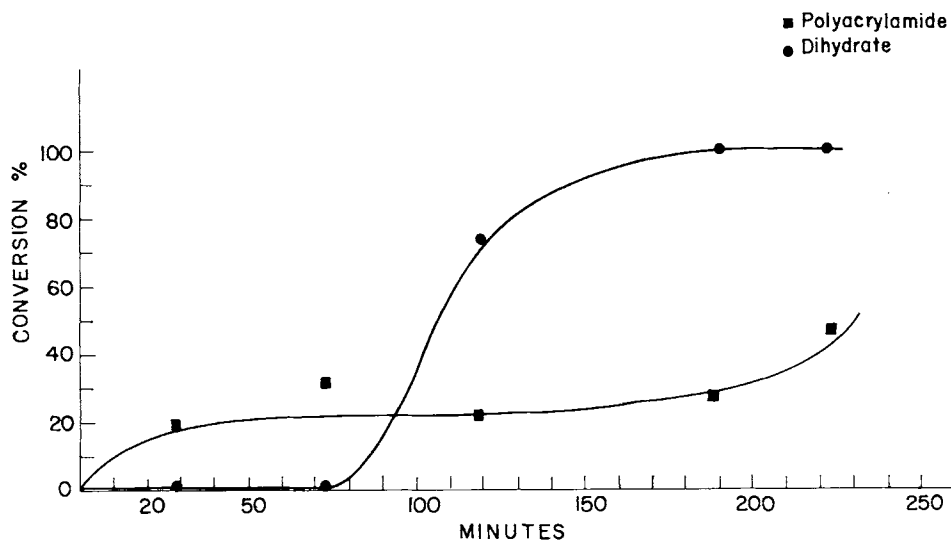


Figure 11 The effect of oxygen (air) on the time-conversion curve of acrylamide and of hemihydrate (25%).

Regarding the rates of conversion of acrylamide in the presence of hemihydrate [Fig. 10(a)–(c)], those are definitely lower than the corresponding runs, without any inorganic powder (Fig. 4) and also with various amounts of dihydrate (Fig. 6). Further, with 15 and 25% hemihydrate, the maximal conversions were only about 60% after 40–50 min, possibly due to the solidification of the reaction mixture, as at the same time the hydration of the hemihydrate to the dihydrate was nearly complete.

Molecular Weight

The molecular weight of the polymer from the reaction with 25% hemihydrate ($[\eta] = 0.36$; M_w : 3.3×10^4), determined by viscosity measurement after its extraction from the solid product, was about one magnitude lower than that of the corresponding polymer made without an inorganic solid ($[\eta] = 1.04$; M_w : 1.6×10^5). This reduction of the molecular weight may be ascribed to the destruction of the radicals of the growing polymer chains due to the large surface of the inorganic phase.

Effect of the Presence of Oxygen

When acrylamide was homopolymerized at the conditions of experiment 4, Table I, but with unboiled water and in normal atmosphere, instead of in the presence of nitrogen, as expected, no reaction occurred even after 4 h. Yet, when this polymerization with unboiled water and in air was carried out in

the presence of 25% hemihydrate, polymerization did occur (Fig. 11), although at a much slower rate than when it was done under inert conditions [Fig. 10(c)]. This interesting effect warrants a more thorough investigation.

CONCLUSIONS

The results of the present study clearly indicate the feasibility of the polymerization of acrylamide with the concurrent hydration of calcium sulfate hemihydrate to calcium sulfate dihydrate. The practical application of this process to produce a gypsum-polymer composite will be reported separately.

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