

Thermal and Kinetic Study of Radical Polymerization I. Melt State Bulk Polymerization of Acrylamide by DSC

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ABSTRACT: Radical-initiated bulk polymerization of acrylamide in the presence of potassium persulfate in the melt phase has been investigated by differential scanning calorimetry (DSC). The method presented here has been carried out in isothermal condition. This not only saves energy and time but also has some less probable side effects. Side effects such as evaporation and imidization could affect the final yield and properties of the obtained product. Different temperatures have been examined for isothermal polymerization to find out the optimum temperature with

complete conversion of acrylamide to its corresponding polymer. During the polymerization process, high-molecular-weight polyacrylamide is being produced without any significant loss in total yield. The molecular weight was determined by inherent viscosity measurement. Also, no side reaction such as imidization resulting in partial insolubility or crosslinked product was being observed. It is noteworthy that we believe DSC studies show the existence of living radicals that has not been reported before. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2335–2340, 2003

INTRODUCTION

Acrylamide itself is by far the most important monomer of amides of acrylic and methacrylic acid groups. Acrylamide polymers and copolymers have found applications in a wide variety of fields, such as adhesives, dispersants, flocculants, printing plates, viscosity modifiers and thickeners, fiber dyeing and modification, leather, paper sizing, protective colloids in photographic emulsions, surface coatings, textile treatments, gels for electrophoresis, improvement of cements, water purification, paper treatment, soil stabilization, well drilling, boiler water treatment, hair sprays, ion-exchange resins, pigment binders, and polyester-binding resins.¹

Acrylamide, methacrylamide, and many of the simple non-fluorinated-related monomers are generally water-soluble. Usually they are also soluble in a large variety of organic solvents. Since they are amides, their solutions may be expected to have considerable compatibility or solvency for a variety of materials such as inorganic salts. Polyacrylamide, even when of high molecular weight, is readily dissolved in water. Under certain polymerization condition, imide formation may take place (Scheme 1).

Polymers that are partially imidized exhibit reduced water solubility. The intermolecular imide represents a thoroughly crosslinked polymer, which is quite insoluble, while the intramolecular imides may exhibit only partial insolubility.^{2,3}

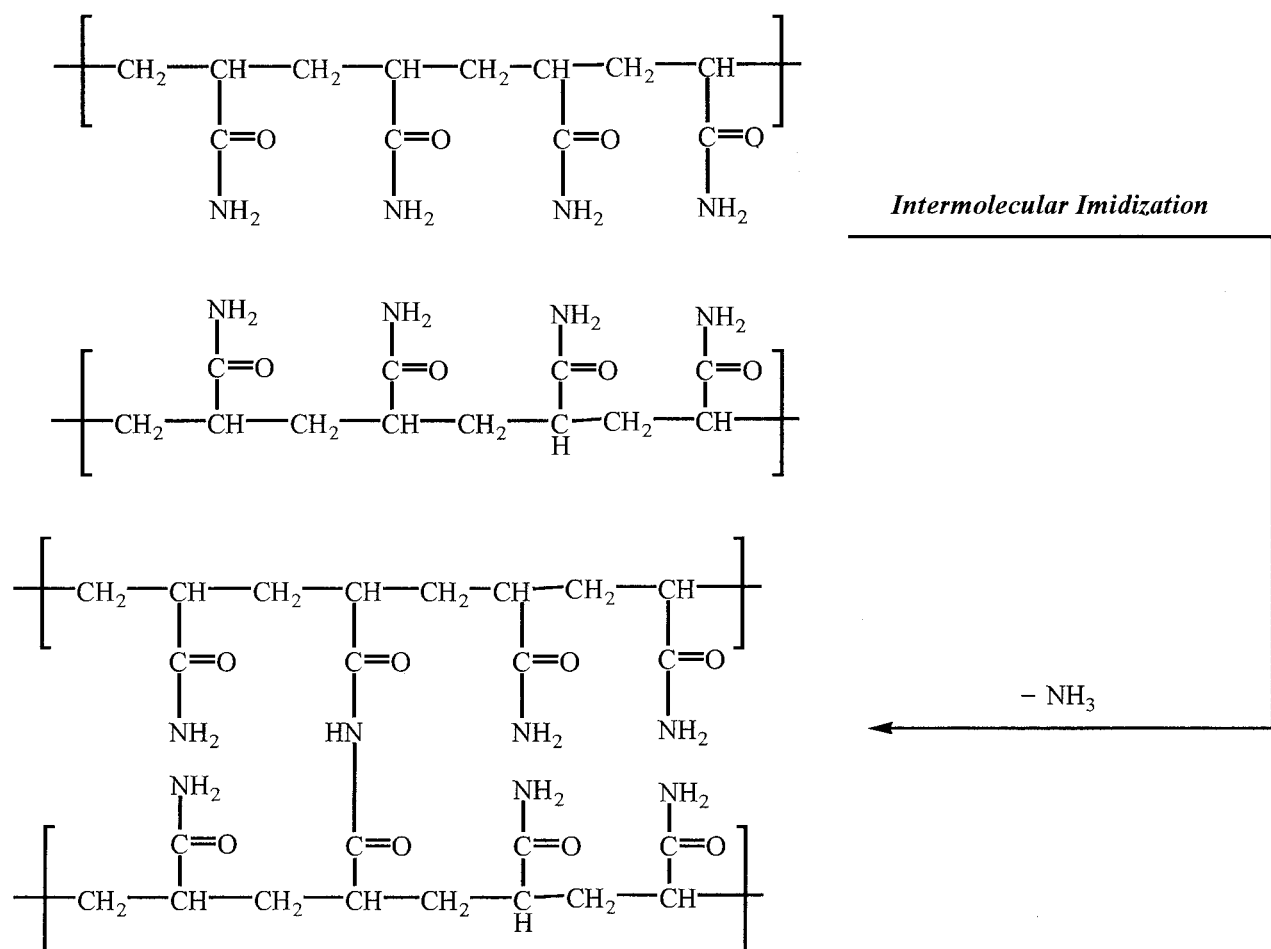
Few investigations have been performed on the polymerization of acrylamide without the use of solvent or a dispersing liquid. We could divide the bulk polymerization of acrylamide into the following subsections: catalytic and thermal polymerization^{4,5}; radiation-induced solid-state polymerization at normal pressure^{6–11}; and radiation-induced solid-state polymerization at high pressure.^{12–16}

The first reports on kinetic studies of bulk and radical polymerization of acrylamide by using differential scanning calorimetry (DSC) apparatus in isothermal condition have been presented by Horie et al.,^{17,18} after which the technique has been widely used. Several attempts have been performed on the kinetic study of thermal polymerization of acrylamide and its N-substituted derivatives. Unfortunately, these methods are not applicable for reasons discussed below.

Here we report a new method in radical polymerization of acrylamide at isothermal and bulk condition in the presence of potassium persulfate. This procedure not only saves energy and time during the polymerization reaction but also suppresses the probability of perturbing and side reaction. These undesired phenomena would be evaporation of acrylamide during thermal polymerization and also imidization. Total yield of the obtained product will decrease during evaporation and imidization, which causes partial

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Scheme 1

crosslinking and insolubility as a consequence. Hence, in spite of the simplicity of kinetic studies of bulk polymerization, these two problems make it more complicated and there is not enough information in the literature about these.

EXPERIMENTAL

Acrylamide and potassium persulfate were purchased from Merck Chemical. DSC thermograms were recorded on a DSC-PL instrument from England. The essential operations were carried out according to the manufacturer's instructions. The samples containing 4% (w/w) of initiator were weighed on a Shimadzu LIBRORE AEU-210 analytical electrobalance to an accuracy of 0.0001 g. Indium was used as a standard for calibrating the temperature axis and enthalpy output. The calibrations on the enthalpy measurements were based on the area measurements in the respective thermograms. All DSC scanning were repeated two or three times to confirm the obtained data. All of the reactions were performed under nitrogen atmosphere.

Inherent viscosity of the polymer was measured by an Ubbelohde viscometer at 25°C. FTIR spectrum was recorded on an FTIR BRUKER-IFS 48 spectrophotometer using KBr pellet.

RESULTS AND DISCUSSION

Polymerization Process

In this work, we have investigated bulk and radical polymerization of acrylamide in the presence of potassium persulfate as an initiator in the isothermal condition. Several temperatures were experienced for this purpose and 89°C was designated as the optimum temperature with 100% conversion. Temperature of the DSC probe including the sample was raised from 25 to 60°C with heating rate of 20°C/min. Acrylamide is a hygroscopic compound. In order to be sure about its dryness, the sample was maintained in the DSC oven at 60°C for 10 min. DSC thermogram of Figure 1 shows an exothermic transition in the first 5-min interval. This confirms the evolution of adsorbed humidity at this condition. Then the temperature was

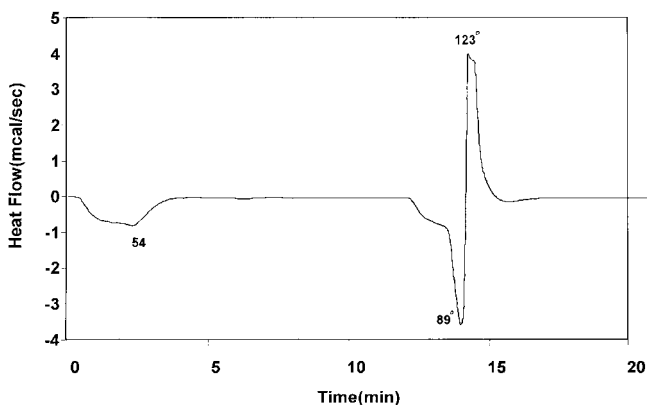


Figure 1 DSC thermogram related to the polymerization reaction of acrylamide at 89°C.

raised from 60 to 89°C with the heating rate of 20°C/min and stayed at this temperature for 15 min.

It is obvious that melting of the sample started at 80°C and complete melting occurs at 86°C (Fig. 1). Simultaneously, the polymerization reaction began and we observed a sudden increase in the evolved heat. The exotherm transition just beside the endotherm one (due to the melting process) owes to the exothermic polymerization reaction. This severe exotherm process exceeds the temperature of the system up to 123°C. No other transition was found during 15-min maintenance at isothermal temperature (89°C).

This observation was checked in another trial at the same condition and in the absence of initiator (Fig. 2). The first transition is due to the loss of the absorbed water and the second one is in accordance with the melting process of acrylamide monomer and no other transition appeared.

DSC thermogram of the obtained polymer (Fig. 3) shows that there is no sign of the unreacted monomer and the polymerization reaction has been proceeded up to 100% conversion. T_g of the resulting polyacrylamide is 189°C with heating rate of 20°C/min in N_2 atmosphere, which is in conformance with the data existing in literature.¹⁹

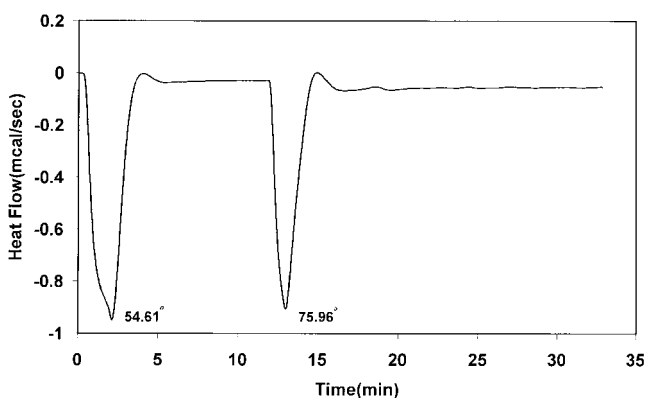


Figure 2 Thermal behavior of acrylamide at 89°C.

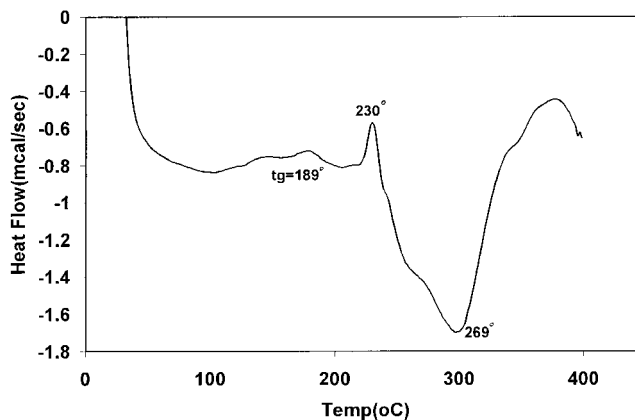


Figure 3 DSC thermogram of the obtained polyacrylamide.

Also, its FTIR spectrum confirms well with the reported one.²⁰ Inherent viscosity of the obtained polymer via this method in water at 25°C is 1.53 dl/g ($C = 0.3680$ g/dl). The area measurement of the thermogram relating to the polymerization reaction reveals that the enthalpy of this exothermic process is 8.01 kcal mol⁻¹.

The graphs of reacted or polymerized fraction, which shows the amount of conversion, versus time (Fig. 4) and also versus temperature (Fig. 5) were generated from the polymerization thermogram (Fig. 1) by segmental area measurements. The amount of polymerized fraction at any time and temperature was calculated according to eq. (2) below. From Figure 4, it could be concluded that after about 60 s, the conversion of about 100% is attainable and this would be categorized as one of the fastest polymerization reactions reported in the literature. Also, Figure 5 reveals that the reaction temperature reaches its maximum value (123°C) at about 25% of conversion.

Mechanistic Studies

The present study on acrylamide polymerization represents a typical thermal bulk polymerization in the

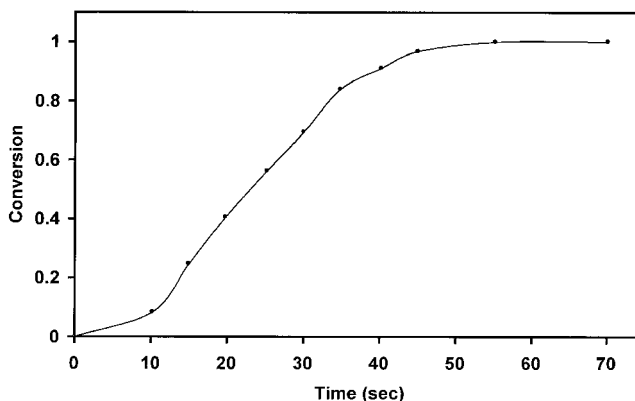


Figure 4 Time dependence of conversion of acrylamide to the corresponding polymer at 89°C.

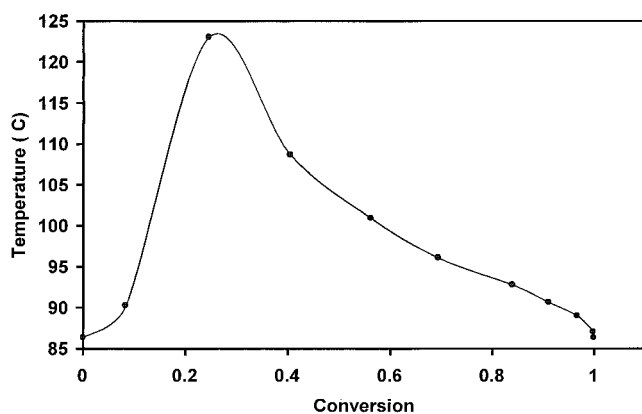


Figure 5 Variation of temperature versus conversion during the polymerization reaction of acrylamide.

presence of initiator, where the polymerization occurs in a heterogeneous medium since the polymer is insoluble in the molten monomer. Free-radical vinyl polymerization in a precipitating medium (for the polymer) exhibits an accelerating rate from the start of reaction up to high conversion. These kinds of reactions could be divided in two categories: those without any catalyst (simple reactions) and those in the presence of initiator (autocatalytic reactions). The research presented here is an autocatalyzed one. In autocatalysis, reaction rate gradually decreases due to the consumption of monomer and is also different from the typical gel effect observed in the viscose polymer solutions at relatively high conversions. The precipitating polymers, as formed, have higher molecular weight than could be attained by homogeneous polymerization under similar conditions. It should be noted that precipitation polymerization may be useful commercially in making it possible to obtain polymers with high reaction rates and high molecular weights.

There are two well-organized theories on precipitation polymerization of vinyl chloride and acrylonitrile in the bulk of monomer. Due to the similarities between these monomers and acrylamide, we could develop them for our system. The first is the surface immobilization theory presented by Bengough and Norrish²¹, the second the radical occlusion theory by Banford et al.²² The surface immobilization theory is applicable for monomers, which readily undergo transfer reactions such as vinyl chloride. The mechanistic behaviors of monomers, like acrylonitrile, which do not transfer radical readily, are discussed by using the radical occlusion theory.

In order to study the mechanism and find out the optimum temperature of isothermal polymerization, we ran another reaction at 80°C with similar conditions. DSC thermogram of isothermal polymerization at 80°C is shown in Figure 6.

At first, acrylamide started melting and immediately a small exothermic transition was observed with-

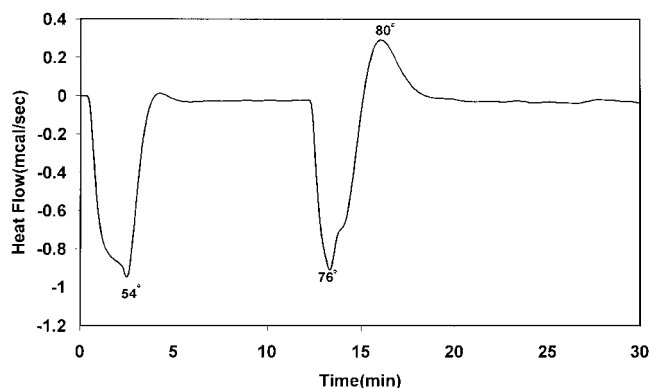


Figure 6 DSC thermogram related to the polymerization reaction of acrylamide at 80°C.

out significant rise in temperature. Differential scanning calorimetry of the obtained product shows an unusual exothermic behavior, just after the melting step was completed at 88°C (Fig. 7). This is related to the severe exothermic polymerization reaction performed and increases the reaction temperature up to 123°C. Then the temperature decreases to the isothermal condition temperature. Two postulates could be considered for this phenomenon. First, the isothermal polymerization must be performed in the completely melt state of acrylamide and, before that, the polymerization reaction does not proceed exceedingly. Therefore, after the temperature is increased to more than its melting point, the remaining monomers undergo the polymerization reaction.

Second, the presence of living radicals in the partially polymerized acrylamide-polyacrylamide mixture would be possible. This means that the polymerization reaction would be fully progressed after complete melting of acrylamide, that is, the immobilized radicals in the solid state were activated when exposed to the melt acrylamide.

According to the surface immobilization theory, acrylamide is a primary amide and would stabilize its

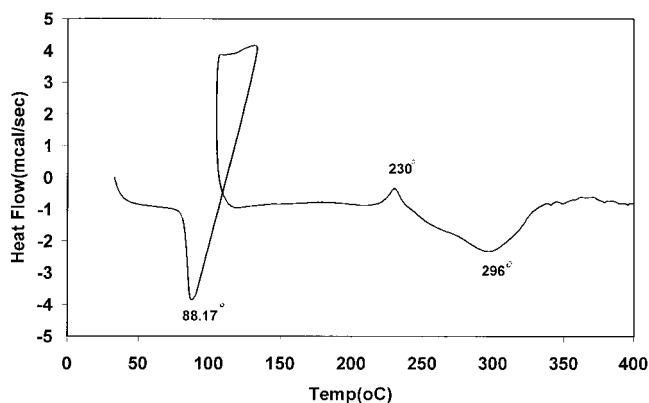


Figure 7 DSC thermogram of the obtained product of polymerization reaction of acrylamide at 80°C.

radicals due to the presence of the amide group.²³ So it could be assumed that the growing radicals undergo transfer reactions to dead polyacrylamide and subsequently immobilize free radicals with relatively long lifetime on the polymer particles' surfaces. The newly formed radicals are inactive in the solid state, and as the remaining monomer melts, radical activity is removed from the particle surfaces by transfer to monomer in the melt phase and eventually terminated by reaction with other radicals.

Radical occlusion theory could also account for the observations in this kind of polymerization. Chain growing radicals in the precipitating polymer will coalesce and consequently radical activity is trapped in the polymer medium. The occluded radicals remain inactive in the solid state of both acrylamide and its corresponding polymer. When the temperature increases, acrylamide melts and penetrates to the polymeric phase or makes it swell. Thus, living radicals would be able to progress the polymerization reaction up to 100% conversion.

Kinetic Studies

It should be noted that the isothermal method in differential scanning calorimetry, where it should be applied, offers the advantage of greater simplicity of interpretation of the data, leading to greater confidence in the values of derived kinetic parameters. An isothermal DSC trace is a plot of heat flow against time. It could be considered that the instantaneous heat flow (the DSC ordinate) at each time is proportional to the rate of reaction.

The model generally used to describe the kinetics of a chemical reaction by using the Arrhenius equation²⁴ is

$$\frac{d\alpha}{dt} = k_0 e^{-E_A/RT} (1 - \alpha)^n \quad (1)$$

where $d\alpha/dt$ is the rate of reaction (s^{-1}); k_0 the preexponential factor (s^{-1}); E_A the activation energy ($J mol^{-1}$ or $kcal mol^{-1}$); R the gas constant; T the temperature; α the reacted fraction ($0 < \alpha < 1$) where α_0 is 1; and n the reaction order.

Any changes in the enthalpy of system due to the polymerization reaction could be related mathematically to the fraction, which is polymerized²⁵:

$$\alpha = \frac{\Delta H_p}{\Delta H_t} \quad (2)$$

where ΔH_p is the measured enthalpy for each fraction ($mcal mg^{-1}$) and ΔH_t the total enthalpy of reaction ($mcal mg^{-1}$).

By assuming that

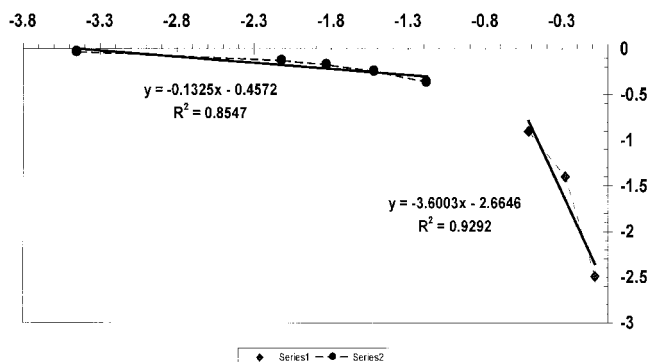


Figure 8 The curve related to eq. (5).

$$\Delta H_t = \Delta H_p + \Delta H_r \quad (3)$$

where ΔH_r is the remaining of the total enthalpy ($mcal mg^{-1}$), then

$$(1 - \alpha) = \frac{\Delta H_r}{\Delta H_t} \quad (4)$$

Substitution of the values of α and $(1 - \alpha)$ in eq. (1) and converting into logarithmic form respectively results in

$$\ln \frac{dH/dt}{\Delta H_t} = \ln k_0 + E_A \left(\frac{-1}{RT} \right) + n \ln \frac{\Delta H_r}{\Delta H_t} \quad (5)$$

Plot of the data obtained from the isothermal polymerization of acrylamide at $89^\circ C$ according to eq. (5) is shown in Figure 8. The nonlinearity of this plot reveals that the kinetic of our desired reaction does not obey the simple and general rate law and eq. (1) could not explain the kinetic behavior of the above system.

Hence, we were focused on the rate equations considered for autocatalyzed reactions. Waters and Paddy²⁶ have categorized and reported a series of rate equations, which were obtained according to isothermal analysis data. They assumed that the general rate equation for autocatalyzed reaction is

$$\frac{d\alpha}{dt} = k (1 - \alpha)^n (\alpha)^m \quad (6)$$

We tried to fit the obtained experimental data with equations derived from some specific cases ($n = m = 1/2$; $n = m = 1$; $n = m = 3/2$; and $n = m = 2$). The curve fitting data reveals that there is no conformation between experimental data and the proposed equations. So the following possibilities could be considered.

First, n and m values in the equation rate of this isothermal polymerization system are different from those specific cases designated by Waters and Paddy.²⁶ So the above equation should be considered with

different amounts of n and m that fit well with our experimental data.

Second, it would be possible that the kinetic behavior of this polymerization system does not obey the general rate of eq. (6) for autocatalyzed reactions and has a specific and more complex rate equation.

Third, according to the mechanistic studies of acrylamide polymerization presented here, it is probable that the polymer particles' concentration, including living radicals, would participate in the corresponding rate equation as a new parameter in the melt state and complicate it.

As the above system is a specific one and does not fit with common and reported rate equations, deriving the exact rate equation of the above polymerization reaction system is under investigation and we hope to report it in the future.

CONCLUSIONS

Due to the wide application of polyacrylamide in different industries, basic studies on polymerization of acrylamide are of great importance. In this work, acrylamide was bulk-polymerized in the presence of potassium persulfate as a radical initiator in the melt state and isothermal condition. Kinetic studies were performed by differential scanning calorimetry and their experimental results were compared with the reported ones. The experimental data obtained from thermograms are in conformance with the proposed mechanisms for precipitation polymerization. It is notable that the polymerization reaction proceeds with 100% conversion and without any weight loss. Also, the main advantage of this method is fast polymerization reaction with high conversion and yield but little amount of energy consumption in comparison with previous methods.

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