Kinetic Study of Radical Polymerization. II. Solid-State Bulk Polymerization of Sodium Methacrylate by Differential Scanning Calorimetry

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ABSTRACT: The solid-state radical polymerization of sodium methacrylate was investigated. It was initiated by azobisisobutyronitrile, which was used as a radical initiator. Differential scanning calorimetry (DSC) was used to observe the endothermic and exothermic transitions during the polymerization reaction. Structural studies were performed with the DSC thermograms and Fourier transform infrared and ultraviolet–visible spectra, and all of the results confirmed the progress of the reaction. The obtained data revealed that the polymerization reaction proceeded completely with a 100% conversion. ΔH of this reaction was calculated with various amounts of the initiator, and the peak temperatures were determined at different heating rates. The activation energy (19.7 kcal mol^{-1}) was also obtained by the Kissinger method for this type of solid polymerization reaction. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1648–1654, 2003

Key words: radical polymerization; differential scanning calorimetry (DSC); solid-state polymerization; activation energy

INTRODUCTION

Research on polymerization in the solid state was begun in 1954 with a series of publications by Mersobian et al.[1] on the polymerization of crystalline acrylamide initiated by ionization radiation. They found the ideal method of initiation for the *in situ* production of radicals and eventually ions. After that, Bamford et al.[2] showed that this method of initiation is usually prevented by the optical inhomogeneity of the medium.

Benssason and Max[3] and Tabata and Sobue[4] revealed that polymerization in the solid state is not limited to solid monomers at the ambient temperature and higher; it can also be carried out at low temperatures.

Some organic monomers in the crystalline state can be polymerized into crystalline polymers under ultraviolet (UV) irradiation.[5–7] This method of polymerization is regarded as solid-state crystalline photopolymerization.

In most of the studies dealing with solid-state polymerization, the reaction has been initiated by either UV or high-energy radiation such as X-rays, γ-rays, or fast electrons. The solid-state polymerization of vinyl monomers such as acrylamide, acrylic acid, methacrylic acid, and the corresponding acrylates and methacrylates initiated by UV and γ irradiation have been extensively studied. Also, detailed kinetic studies of both in-source and post irradiation have been published.[8–13]

The heat of polymerization is a dominant component in determining the molar free energy of a compound. It is a driving force for the propagation reaction, which governs the rates and kinetics of polymerization. The accurate measurement of the thermochemical data for the heat of polymerization is important for (1) acquiring basic knowledge of the driving force for the propagation reaction and (2) better understanding the molecular structure of the monomers during polymerization.[14]

A number of studies have been carried out on the measurement of the heat of polymerization of vinyl monomers with various methods, such as calorimetry. Of the different types of calorimetry, differential scanning calorimetry (DSC) has been used with bulk monomers with either an isothermal or dynamic method.[15–19] However, a number of chemical reactions, such as polymerization, decomposition, and oxidation, can be observed with the controlled variation of the sample temperature (dynamic) and isothermal modes of operation.

Because of the development of polymerization engineering in theory and technology, the high-conversion kinetics of polymerization and the influence of the diffusion process on polymerization behavior have become the most important problems. However, most

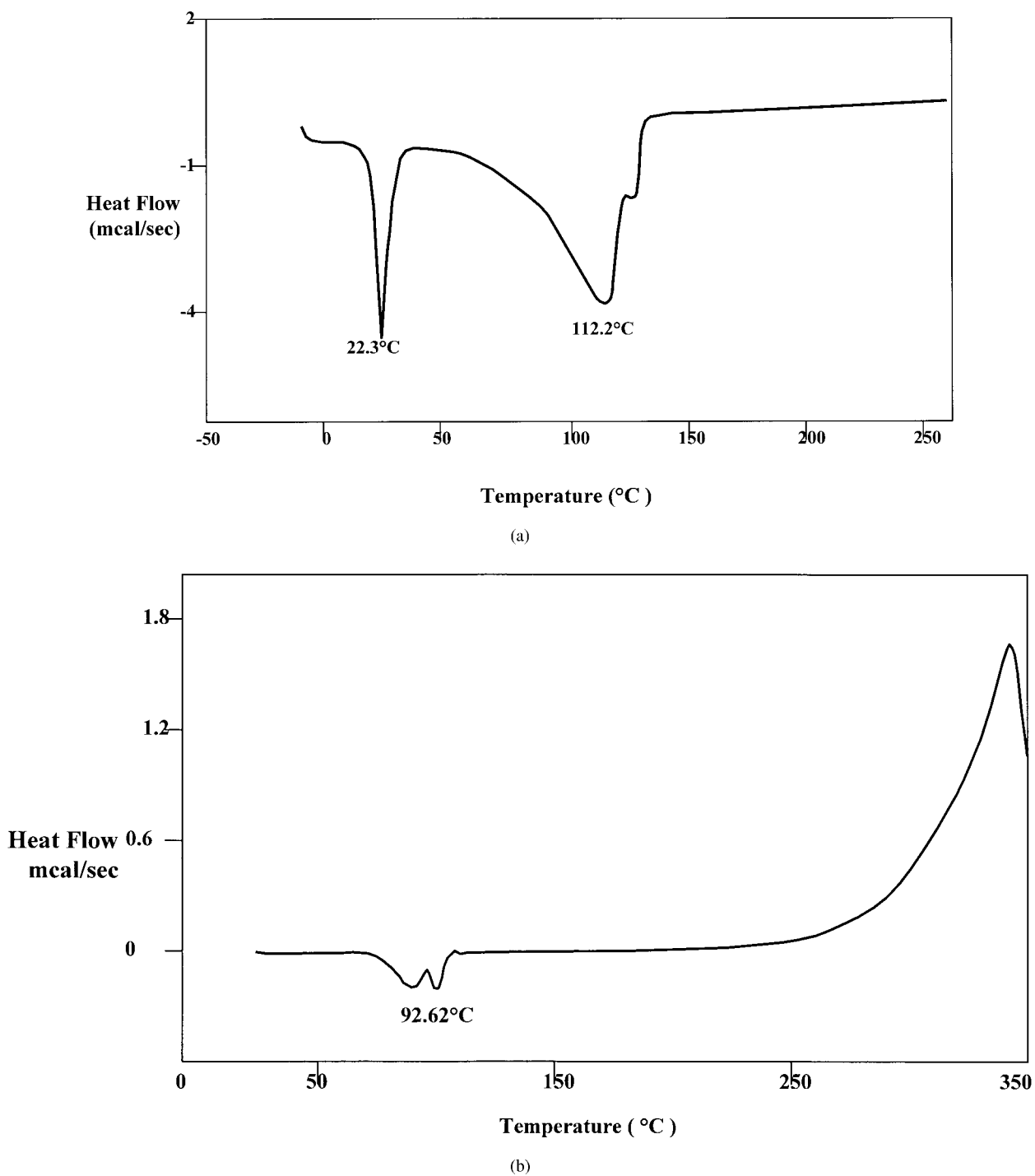*Correspondence to:* A.-R. Mahdavian (a.mahdavian@proxy.ipi.ac.ir).

Figure 1 Thermograms of (a) monomeric methacrylic acid and (b) monomeric sodium methacrylate.

studies are limited to the early stages of polymerization, during which the monomer conversion is small.

Previously, we applied this method to thermodynamic and kinetic studies of acrylamide in the melt state.[20] Here, we report a new technique in solid-state polymerization in which the sample preparation and initiation are different than those of the conventional methods. The polymerization reaction was initiated by azobisisobutyronitrile (AIBN), and variations in the

thermal and calorimetric behaviors were detected with DSC.

EXPERIMENTAL

Sodium methacrylate salt was prepared by the titration of methacrylic acid (Merck Chemical Co., Darmstadt, Germany) with an aqueous sodium hydroxide solution. The obtained white crystals were used in a
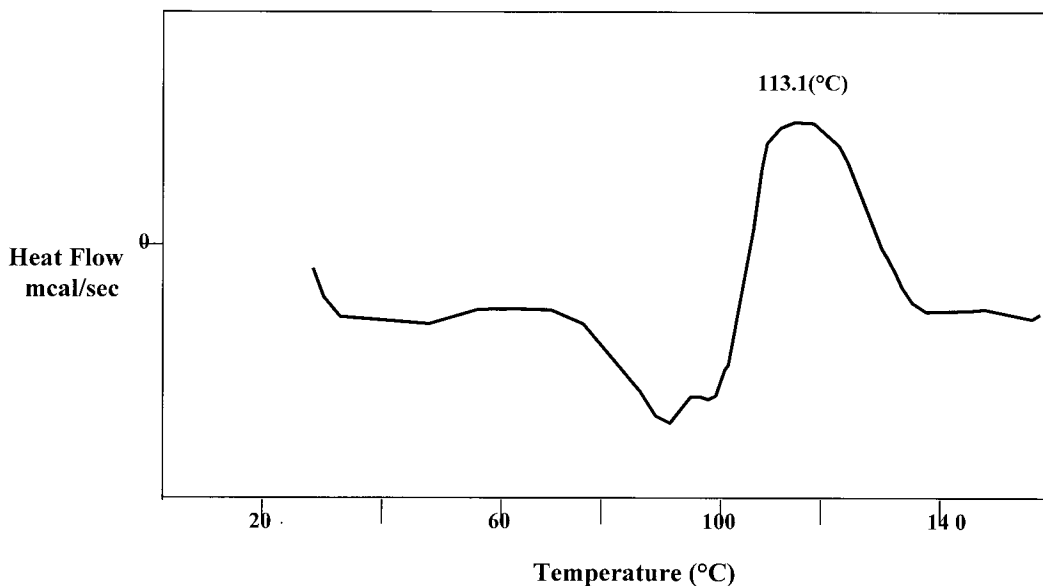
Figure 2 Thermogram of the sodium methacrylate polymerization reaction in a closed cell.

polymerization reaction with AIBN (Merck Chemical) through simple mixing in a mortar. DSC thermograms were recorded on a DSC-PL instrument (Surrey, England). The essential operations were carried out according to the manufacturer's instructions. The samples, containing different amounts of the initiator, were weighed on a Shimadzu Librore AEU-120 analytical electrobalance (Kyoto, Japan) 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 was repeated two or three times to confirm the obtained data. Also, all the reactions were performed under a nitrogen atmosphere to prevent side and retarding reactions. Fourier transform infrared (FTIR) spectra were recorded on a Bruker (Ettlingen, Germany) IFS 48 FTIR spectrophotometer with KBr pellets. UV spectra of the dilute aqueous solutions of the samples were also recorded on a Philips UV spectrometer (Cambridge, UK).

RESULTS AND DISCUSSION

The sodium salt of methacrylic acid was prepared by the titration of neat methacrylic acid with an aqueous solution of sodium hydroxide to the equivalent point. So that the monomer would not polymerize because of
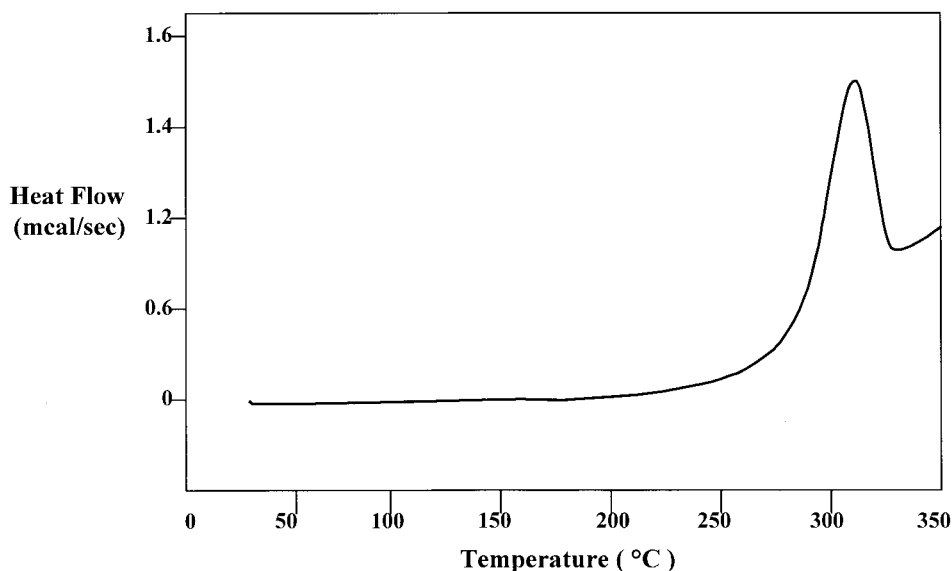

Figure 3 Thermogram of poly(sodium methacrylate).
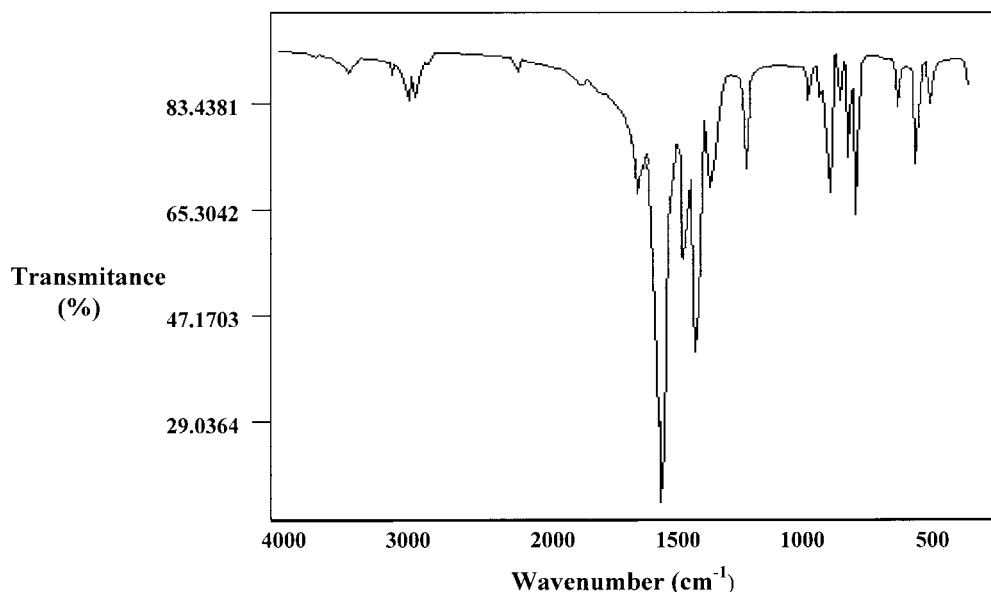
Figure 4   FTIR spectrum of poly(sodium methacrylate).

the higher exothermic neutralization reaction, the container was cooled with an ice bath during the process. After that, water was evaporated, and white, flaky crystals of sodium methacrylate salt were formed. DSC, one of the most reliable techniques, was used to record any exothermic and endothermic transitions during the reaction progress.

For the study of the thermal behavior of sodium methacrylate itself, a sample was heated to 350°C at a heating rate of 5°C/min in an open cell and under a nitrogen atmosphere.

The DSC thermogram of methacrylic acid showed two endothermic transitions. The first at 22.3°C was related

to the melting transition (mp = 18–20°C), and the second was due to monomer evaporation [Fig. 1(a)]. However, in the thermogram of sodium methacrylate, there was no sign of these transitions, and this salt was completely resistant toward heating up to about 280°C [Fig. 1(b)]. We could see only an endothermic transition at 90–95°C according to the presence of hydrated aqua. Therefore, sodium methacrylate has no specific calorimetric transition from 100 to 250°C.

AIBN was used as a radical initiator for this polymerization reaction. A sample of a fully ground mixture containing 10% (w/w) initiator/monomer salt was prepared. This sample was heated in an open cell at a heating rate of 5°C/min. There was no significant change in the obtained thermogram in comparison with the corresponding monomer salt.

In another experiment, we used a closed cell instead of an open cell for the polymerization reaction. An exothermic transition appeared at 113.1°C (Fig. 2). This was related to the polymerization process, which was an exothermic transition, and it was not observed in the sodium methacrylate thermogram [Fig. 1(b)]. To be sure about the absence of adsorbed humidity in the salt, we heated the sample to 60°C and held it at this temperature for 20 min. Heating up to 200°C was continued in the closed cell. This procedure also proved that the transition at 90–95°C was due to the presence of hydrated aqua.

The thermal behavior of the obtained polymer was investigated in a closed cell (Fig. 3). According to this thermogram, there was no transition up to 250°C, and above that, thermal degradation of the polymer occurred. The thermal behavior of the obtained poly(sodium methacrylate) (Fig. 3) also confirmed a 100% conversion of the monomer during the progress of the
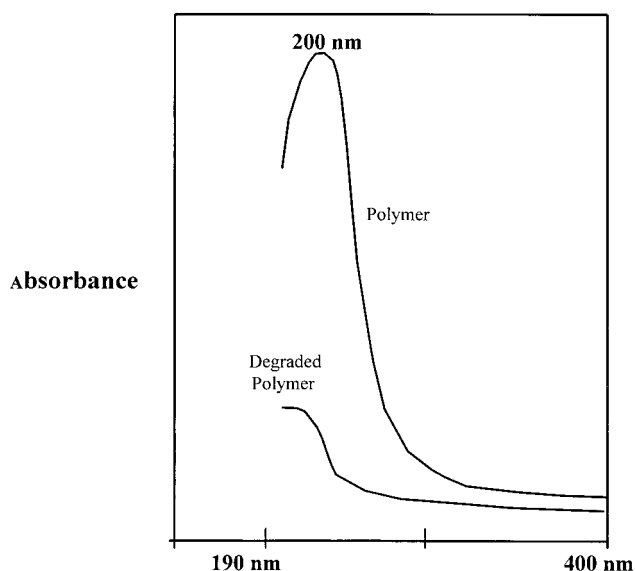

Figure 5   UV spectra of poly(sodium methacrylate) and degraded poly(sodium methacrylate).
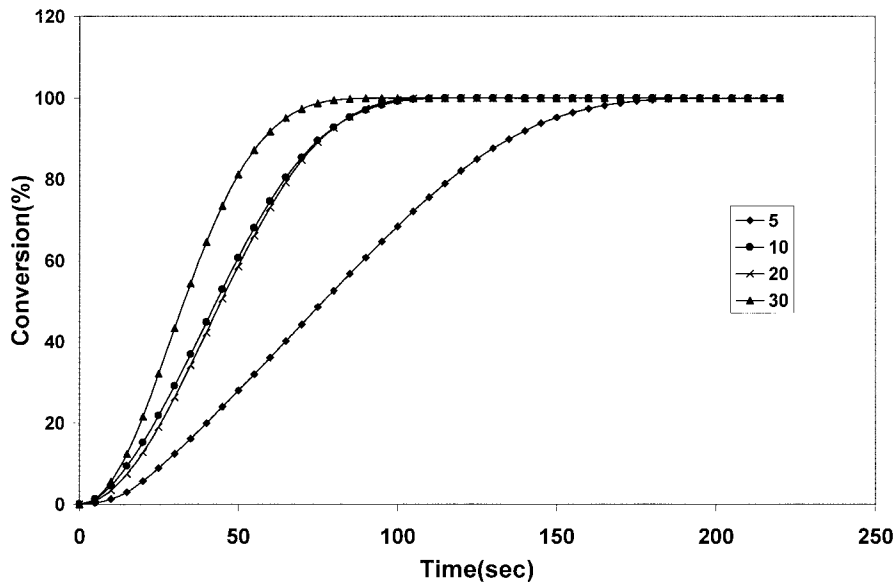
Figure 6 Variation of the conversion versus the polymerization reaction time at different heating rates.

polymerization reaction. This could be concluded from the absence of any transition related to the unreacted monomer. The FTIR spectrum of the obtained polymer also conformed to that reported for poly(sodium methacrylate)[21] (Fig. 4).

For greater assurance, to the obtained cool product of the thermal polymerization (up to 200°C; Fig. 2), another 10% (w/w) AIBN was added, and the resulting mixture was heated to 200°C from room temperature again. The thermal behavior of this new mixture was similar to that of poly(sodium methacrylate) (Fig. 3). This result also confirmed the aforementioned high conversion of the monomer (100%) and the absence of unreacted monomer.

Sodium methacrylate has two functional groups, and each of them has two identical transitions in the UV range. The double bond has a $\pi \rightarrow \pi^*$ transition (maximum > 200 nm) and a carbonyl group maximum wavelength absorption band at 210–220 nm related to the $n \rightarrow \pi^*$ transition.[22] In poly(sodium methacrylate), the $\pi \rightarrow \pi^*$ transition is not observed, but the $n \rightarrow \pi^*$ one already exists. However, because of the vicinity of these two absorption bands and their overlapping, their discrimination is somewhat difficult. UV spectra of the degraded polymer (at 350°C) showed neither of these bands (Fig. 5). This means that the ester group of poly(sodium methacrylate) is decomposed and degraded at early stages of thermal degradation.
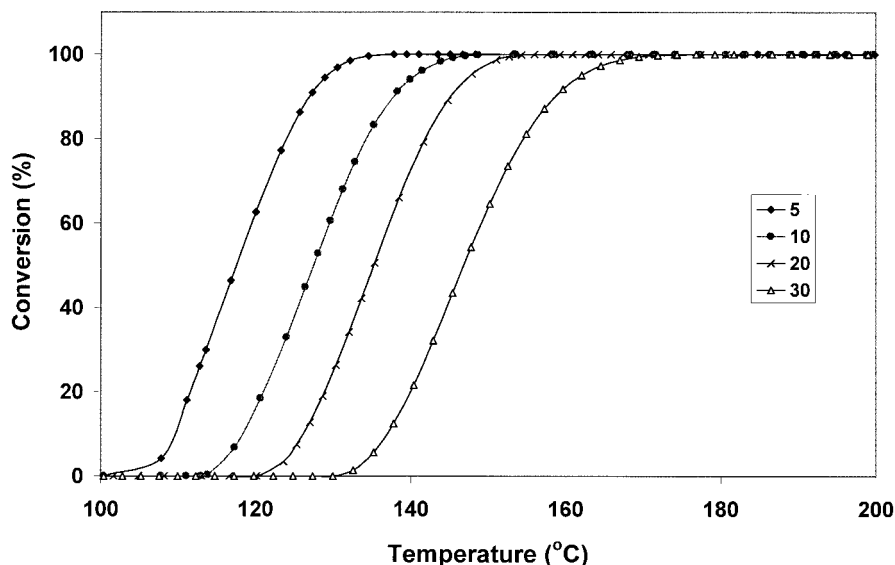

Figure 7 Variation of the conversion versus the recorded temperature (by DSC) at different heating rates.

TABLE I
Peak Temperatures at Different Heating Rates

Heating rate (°C min^{-1})	Peak temperature (°C)
5	116.4
10	127.2
20	135.3
30	145.4

TABLE II
Amounts of Released Heat with Different Weight Percentages of the Initiator

Initiator (wt%)	ΔH (kcal mol^{-1})
5	0.5
10	8.3
20	27.3
30	28.6

Kinetic data and determination of the activation energy (E_a)

The thermal behavior of the polymerization reaction under different conditions and the obtained numerical data could lead us to interpret some kinetic behaviors of the system during the polymerization reaction such as the variation of the conversion with time or temperature. As such, DSC thermograms contain very useful data for evaluating the conversion at any time and temperature during the polymerization reaction, and this has been discussed exclusively in our previous article.[20]

As shown in Figure 6, the conversion rate is dependent on the heating rate. Of course, no remarkable difference was observed for heating rates of 10 and 20°C/min, but the heating rate does have a significant effect on the rate of conversion overall.

The variation of the conversion with temperature changes at different heating rates in the polymerization process has been plotted in Figure 7, and the conversions vary with similar slopes. However, when the heating rate is lowered, greater conversions are obtained at lower temperatures. This means that less heat is transferred during the polymerization reaction at lower heating rates, and this is an important result

for designing this polymerization process in the solid state.

For the determination of E_a, the samples containing sodium methacrylate and AIBN (10% w/w) were heated to 350°C in closed cells at different heating rates. The peak temperatures at each heating rate were measured, and these are listed in Table I (Fig. 8).

E_a of this polymerization reaction was determined by the Kissinger method,[23] with the correlation between the peak temperatures and heating rates. Therefore, the calculated E_a value of the polymerization reaction of sodium methacrylate was 19.7 kcal mol^{-1} according to the aforementioned method.

Effect of the amount of the initiator on the heat of polymerization

We also investigated the effect of the amount of the initiator on the enthalpy or exothermic transition of the polymerization reaction. The AIBN initiator (5, 10, 20, and 30 wt % with respect to sodium methacrylate) was tested, and the amount of the released heat was measured (Table II). With 5% initiator, no measurable heat was sensed. That is, with this amount of the initiator, no polymerization reaction occurred, or in
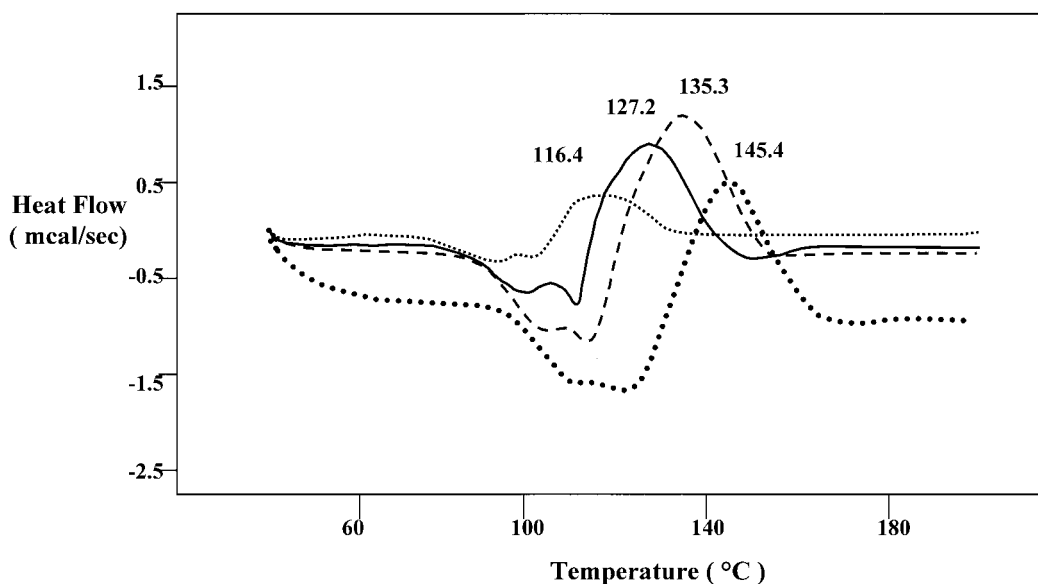

Figure 8 Thermograms of the sodium methacrylate polymerization reaction at different heating rates: (· · ·) 5, (—) 10, (– – –) 20, and (●●●) 30°C/min.
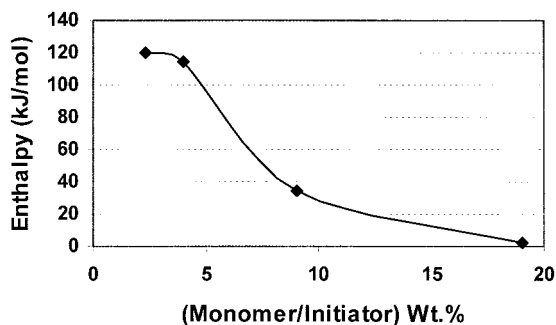
Figure 9 Variation of the heat of polymerization versus the amount of the initiator.

any case, its propagation was negligible. When the amount was raised to 10%, the polymerization reaction progressed according to the released heat. With the increase from 10 to 20%, the observed enthalpy increased suddenly.

The increased addition of the initiator from 20 to 30% remarkably did not affect ΔH of the polymerization reaction. The variation of ΔH versus the amount of the initiator has been plotted in Figure 9. It can be concluded that because of the limited mobility in solid-state polymerization, the amount of the initiator plays an important role in propagation and side reactions such as grafting and network formation.

CONCLUSIONS

We investigated the solid-state radical polymerization of sodium methacrylate initiated by AIBN used as a radical initiator.

DSC, a reliable technique, was used to detect endothermic and exothermic transitions during the polymerization reaction. The obtained products were analyzed with DSC thermograms and FTIR and ultraviolet–visible spectra, and all the results confirmed the formation of the polymer during the progress of the reaction. The results showed that the polymerization reaction proceeded completely with 100% conversion. ΔH of this reaction was calculated for various amounts of the initiator, and the peak temperatures were determined at different heating rates. E_a (19.7 kcal mol^{-1}) was also obtained by the Kissinger method for this type of solid polymerization reaction.

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