

Experimental Investigation on High Conversion Free-Radical Polymerization of Behenyl Acrylate*

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SYNOPSIS

An experimental investigation on the kinetics of free-radical polymerization of behenyl (a mixture of 14.8% *n*-octadecyl, 15.1% *n*-eicosyl, and 70.1% *n*-docosyl) acrylate initiated with benzoyl peroxide was conducted at 70°C using a HAAKE rotational viscometer. Molecular weight measurements and differential scanning calorimetric studies of the samples are also described and the results are compared with those obtained by batch reactions conducted under a nitrogen atmosphere. A high monomer order of 1.61 ± 0.11 and a low initiator order of 0.35 ± 0.04 was obtained. The role played by the long methylene chain in behenyl acrylate is also discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A linear polymer with a pendent alkyl side chain of specific length is one of the general structural characteristics of flow improvers (FI)/pour-point depressants (PPD) for crude oils.^{1,2} The FIs/PPDs considerably reduce the natural pour point, viscosity, and yield value of the waxy crude, which enables the transportation of the crude well below the pour point. A number of patents describe the use of polymers of acrylates and methacrylates as PPDs/FIs. However, the kinetic data of the higher acrylate/methacrylate systems are scanty. Like many industrial polymers, polymerization to synthesize PPDs/FIs are conducted in high viscous media. Therefore, it is important to establish a quantitative relation between polymerization rate and solution viscosity.

The polymerization of alkyl acrylate in bulk or in solution shows a strong Trommsdorff effect or gel effect even though the polymerization is carried out above the glass transition temperatures (T_g). Due to the gel effect, considerable deviations from the normal kinetic parameters are observed in high-conversion polymerization. Onset of the gel effect

is reported to occur between 20 and 40% conversion, depending on the temperature and the amount of initiator used.³ During the radical polymerization, the conversion first increases according to first-order kinetics and then accelerates because of the gel effect, which is characterized by an increase in viscosity resulting from higher conversion and increase in chain length.⁴ When the gel effect predominates, the critical chain length above which the chain radicals are entangled also decreases due to higher viscosity. In the termination step of high-conversion kinetics, it is necessary to consider two types of polymer radicals: (i) those that are entangled and (ii) those that are not entangled. When the solution viscosity is very high, the chain-termination reaction and, eventually, the chain propagation reaction becomes diffusion-controlled.

The population of propagating radicals also decreases with the decrease of termination rate. At a very high degree of conversion, R_p slows down due to the consumption of monomers and the diffusion-controlled rate of propagation. Numerical studies⁴⁻⁹ on high-conversion polymerization confirmed that the gel effect is due to the diffusion-controlled termination. The mechanism of the diffusion-controlled termination process remains uncertain and is still a matter of active research. According to Lee and Turner,¹⁰ the onset of the gel effect decreases with increase in molecular weight. Therefore, in a

* Systematic IUPAC nomenclature: *n*-docosyl acrylate.

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high-conversion polymerization (where the gel effect predominates), k_t decreases with conversion and this decrease is greater when the molecular weight of polymer formed is high.¹¹ For higher alkyl acrylates and methacrylates, the deviation of initiator order from the normal kinetic scheme is due to the inverse dependence of diffusion-controlled termination rate on the alkyl chain length (polymer radical size) of the monomers.^{12,13}

The overall rate constant also decreases with increase in alkyl chain length. In the polymerization of alkyl acrylates and methacrylates, chain ends having a long or bulky side group are less approachable for the reaction that restricts the segmental diffusion of the radical chain. We have suggested¹⁴ that the deviation of kinetic parameters of butyl and *n*-octadecyl acrylates are due to the alkyl chain length and we have also suggested that the gel effect may also be responsible for the deviation from the normal kinetic scheme.

In a high-conversion polymerization system, one of the main cause of nonlinearity is due to the reduction of free volume with conversion. R_p is not accelerated by an increase in the rate of initiation (R_i), but by a decrease of k_t . The termination steps are more prone to diffusion control than are propagation reactions, because they involve reactions between macroradicals whose reactivity is drastically reduced by the diminishing free volume of the polymerizing mixture.¹⁵ It has been shown¹⁶ that the initiator efficiencies (f) decline drastically at high-conversion bulk polymerization and k_p changed slowly beyond the onset of the diffusion-controlled propagation step.

The kinetics of solution polymerization of acrylates/methacrylates, which show a strong solvent effect, have been investigated extensively.^{17,18} Dilution of monomers with an inert solvent decreases the average degree of polymerization, whereby k_t increases and this may be due to the change in thermodynamic properties of the polymer/solvent system. Studies¹⁹ have shown that k_t is inversely proportional to the solution viscosity at low conversion. However, the reports on the viscosity effect of long side-chain acrylates/methacrylates on k_t are inconclusive.

In the present study, solution polymerization of behenyl acrylate (BA) was carried out in a rotational viscometer to understand the effect of shear rate and solution viscosity on the course of the high-conversion polymerization of long-chain alkyl acrylates. Separate experiments were carried out under nitrogen to elucidate the rate dependency on monomer and initiator concentrations.

EXPERIMENTAL

Materials

Though BA (Sidobre-Sinnova) used in the present work is a mixture of *n*-octadecyl (C_{18} , 14.8%), *n*-eicosyl (C_{20} , 15.1%), and *n*-docosyl (C_{22} , 70.1%) acrylates, kinetic studies were undertaken as these mixed alkyl acrylates were reported for preparation of FIs/PPDs for waxy crudes. The purification of behenyl acrylate was reported in an earlier communication.²⁰ Different solvents and benzoyl peroxide were purified by standard methods.

Procedure

The polymerization was conducted in a HAAKE rotational viscometer (Rotovisco RV20) with CV 20 measuring system. The sensor system used was ME 46. The coaxial cylinder system consists of a beaker and a cylinder and the inner cylinder slides into the measuring shaft of CV 20. The gap between the inner and outer cylinders was 0.8 mm and the sample volume was 5 mL. Before putting the reactants in the rotational viscometer, oxygen-free nitrogen was passed through the reactants at room temperature for about 1 h to expel dissolved oxygen. An appropriate quantity of the reactants was transferred to the viscometer with a syringe and the shear rate was applied initially at room temperature for 1 h. Reaction was conducted at constant and variable shear rates as a function of time to monitor the viscosity/time dependence. A PC-AT was used to control the shear rate through a Rheocontroller RC 20 that is connected to a Rotovisco RV 20. With the HAAKE software Rotovisco RV 20, the flow curve was obtained and the viscoelastic behavior of the polymerization system was measured. By circulating thermostated water from a Julabo circulator F 30 HC, the reaction temperature around the suspension cell was controlled at $70 \pm 0.01^\circ\text{C}$. After the polymerization was carried out for different time periods, the product was precipitated into a large amount of acetone containing hydroquinone and then dried under reduced pressure. The purification of the polymer was performed by repeated reprecipitation. R_p was evaluated from the weight of polymer obtained. Polymerization was also done under a nitrogen atmosphere in a three-necked reaction flask under similar reaction conditions. After the reaction period, poly(BA) was precipitated by acetone containing hydroquinone. The amount of polymer formed was determined gravimetrically and R_p was calculated.

Gel permeation chromatography (GPC) was performed using a Waters Model 510 solvent delivery system at a flow rate of 1.0 mL/min through a set of four Ultrastaygel columns (Waters) of exclusion sizes 10^6 , 10^5 , 10^4 , and 500 Å. The analysis was performed at room temperature using purified high-performance liquid chromatography (HPLC)-grade THF as the eluent. A differential refractometer Model R401 from Waters was used as the detector. The sample concentration was 0.2% w/v, and the volume of the polymer injected was 50 μ L. The GPC curves were analyzed with the calibration curve obtained by nine narrow-molecular weight distributed polystyrene samples.

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer PC Series DSC 7 with 2–5 mg of polymer samples weighed in aluminum pans with a heating rate of 10°C/min. All experiments were carried out under a nitrogen atmosphere and the measurement was started as soon as the heat flow in the DSC cell was stabilized.

RESULTS AND DISCUSSION

The effect of shear rate on the course of polymerization of BA was studied from the plot of viscosity (in cP) vs. reaction time (in min) at different shear rates and is presented in Figure 1. It is apparent that the rate of solution viscosity increase increases with increasing shear rate. It is surprising to note that polymerization commenced after an initial induction period. As solution viscosity increases with percent conversion, it is evident that for a given reaction time after the induction period percent conversion increased with increasing shear rate. It was found that the variation of induction periods were indistinguishable for higher shear rates (Table I and Fig. 1). But the induction period at a shear rate of 50 s^{-1} was almost double that of the three higher ones. The same phenomenon was observed in the repeated experimentation under identical reaction conditions. We are not aware of any reports on the induction period in the free-radical polymerization

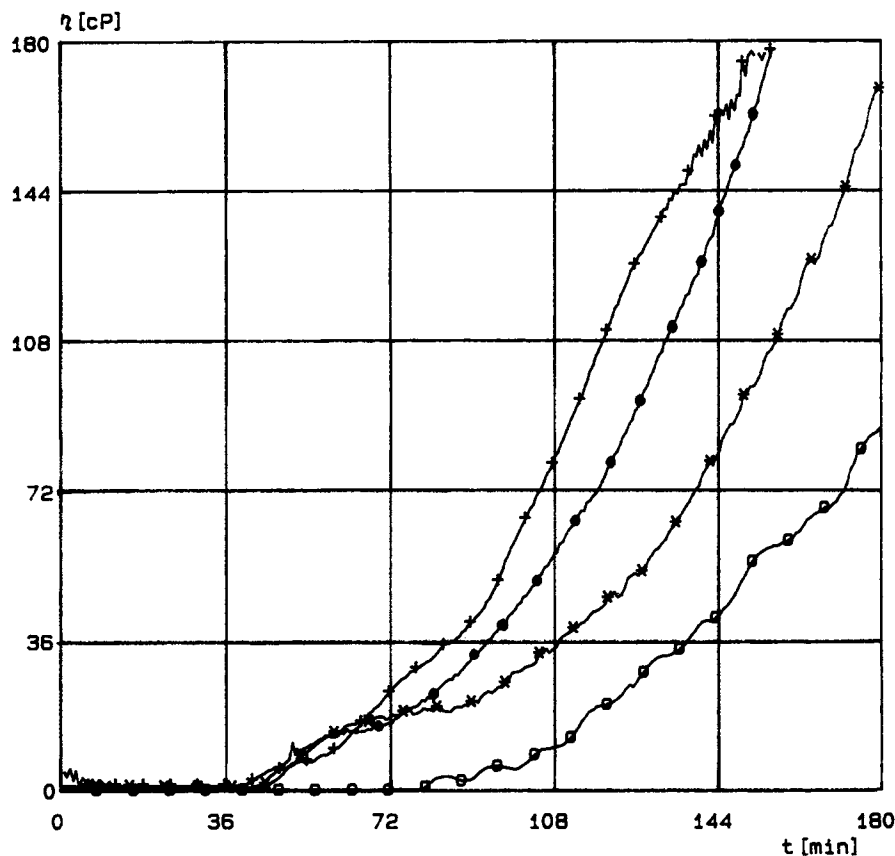


Figure 1 Plot of viscosity (in cP) vs. time (in min) for BA polymerization at 70°C initiated by BPO in benzene at different shear rates. [BA] = 0.847 mol L⁻¹; [BPO] = 7.74 × 10⁻³ mol L⁻¹; [benzene] = 7.00 mol L⁻¹. Shear rates in s⁻¹ for (+) 300, (●) 200, (*) 100, and (O) 50.

Table I Effect of Shear Rate and Benzoyl Peroxide Concentration [BPO] on the Molecular Weight (\bar{M}_n), Polydispersity Index, and Thermal Behavior of Poly(BA) Prepared in a Rotational Viscometer at 70°C in Benzene^a

$10^3 \cdot [\text{BPO}]$ (mol L ⁻¹)	Shear Rate (s ⁻¹)	Induction Periods (min)	$10^5 \cdot R_p$ (mol L ⁻¹ s ⁻¹)	$10^{-4} \cdot \bar{M}_n$	Polydispersity Index	mp (°C)	ΔH_m (kJ mol ⁻¹)	ΔS_m (J K ⁻¹ mol ⁻¹)
26.50	300	18	9.2	10.4	7.4	64.0	33.0	98.8
13.60	300	32	8.6	12.7	5.7	67.9	32.8	96.1
7.74	300	38	7.4	13.0	6.7	65.2	35.6	105.3
4.38	300	61	6.8	17.5	6.8	65.7	37.2	109.9
7.74	200	42	5.2	13.1	7.7	64.0	37.6	111.5
7.74	100	43	3.9	12.1	6.8	67.6	36.8	108.2
7.74	50	78	3.8	11.2	8.1	65.7	36.7	108.2

^a [Behenyl acrylate] = 0.847 mol L⁻¹; [benzene] = 7.00 mol L⁻¹.

of alkyl acrylates/methacrylates. Unfortunately, direct experimental or theoretical evidence for or against such a phenomenon currently appears to be lacking.

The relationship between viscosity (in cP) and initiator concentration [I] (benzoyl peroxide) for the polymerization of BA at a constant shear rate is shown in Figure 2. As expected, for a given re-

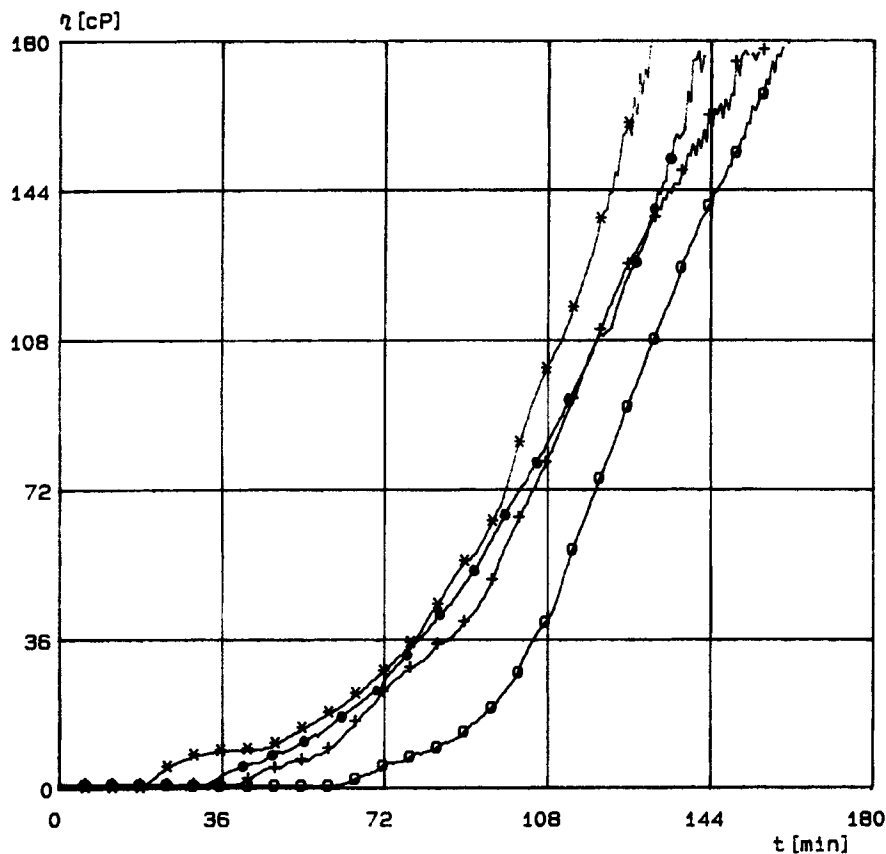


Figure 2 Plot of viscosity (in cP) vs. time (in min) for BA polymerization at 70°C with varying benzoyl peroxide concentration [BPO] in benzene at a constant shear rate of 300 s⁻¹. [BA] = 0.847 mol L⁻¹; [benzene] = 7.00 mol L⁻¹. [BPO] in (*) 2.65×10^{-2} mol L⁻¹, (●) 1.36×10^{-2} mol L⁻¹; (+) 7.74×10^{-3} mol L⁻¹, and (○) 4.38×10^{-3} mol L⁻¹.

action time after the induction period, the increase of viscosity was observed with the increase of [I]. It was also found that the induction period increased with decreasing [I] (Table I and Fig. 2), but it did not followed any pattern. Therefore, no definite relationship could be established between the induction period and [I].

The effect of variation of shear rate and [I] on R_p and molecular weight (\bar{M}_n) of polymers is shown in Table I. It was found that R_p increased with the increase in [I] and also with shear rate. At a high shear rate, the polymer radical chain is expected to be more elongated. Molecular weight (\bar{M}_n) decreased with increasing [I] (Table I). Though at lower shear rates the increase of \bar{M}_n with shear rates were prominent, the variation of \bar{M}_n at higher ones (200 and 300 s⁻¹) was indistinguishable. Scott and Senogles suggested that initial viscosity of the polymerization mixture controls the polymerization rate.^{12,13} They also suggested that R_p is proportional to (viscosity)^{0.2}.

To determine the rate dependency on [BA] and [I], polymerization was conducted in batch reactions with a positive pressure of oxygen-free pure nitrogen. The effect of [BA] and [I] on the polymerization rate at 70°C in benzene is presented in Figures 3 and 4, respectively. Experimentally, R_p was found

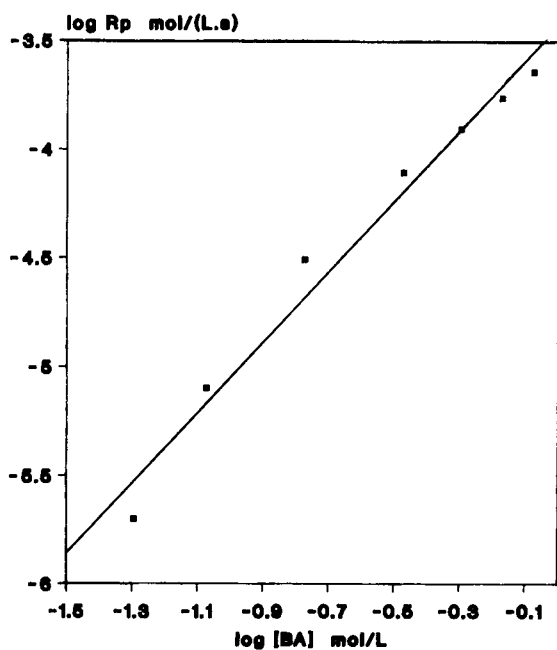


Figure 3 Dependence of the overall rate of polymerization R_p on behenyl acrylate concentration [BA] at 70°C in benzene. Benzoyl peroxide concentration [BPO] = 7.74×10^{-3} mol L⁻¹.

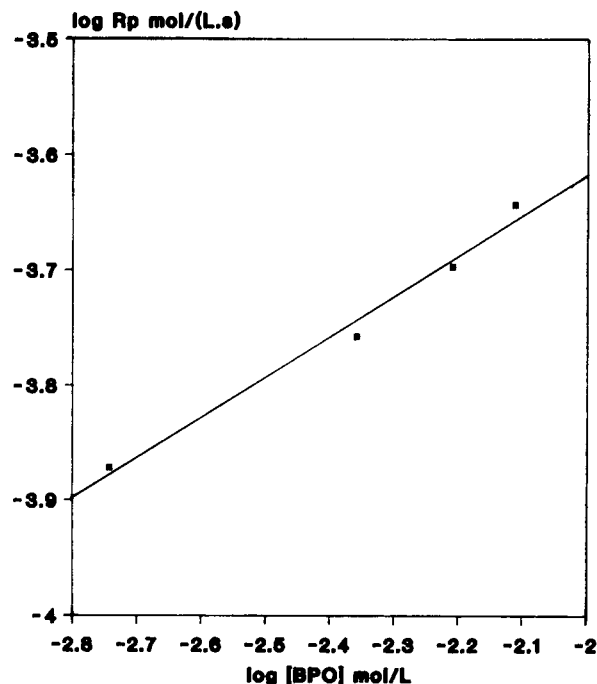


Figure 4 Dependence of the overall rate of polymerization R_p on benzoyl peroxide concentration [BPO] at 70°C in benzene. Behenyl acrylate concentration [BA] = 0.847 mol L⁻¹.

to vary as $[BA]^{1.61 \pm 0.11}$ and $[I]^{0.35 \pm 0.04}$. This is in conformity with our previous report¹⁴ where we suggested that increase in monomer order and decrease in initiator order is dependent on the alkyl chain length. Various theories^{13,21} have been proposed to explain high monomer orders and the involvement of modification of the initiation, termination, and propagation steps of the reaction. Deviation from low-conversion kinetics has been suggested to be due to the primary radical termination,²² degradative chain transfer,²² monomer/solvent radical complex,²³ cage effect,²² and hot radical concept.²¹ Mahabadi and O'Driscoll showed that for the polymerization of *n*-lauryl methacrylate (LMA) the kinetic results deviate from the classical behavior and the deviation could be explained by the chain-length dependency of less flexible poly(LMA) coil on k_t than poly(methyl methacrylate).²⁴

The effect of variation of [BA] and [I] on \bar{M}_n and the polydispersity index of poly(BA) is presented in Table II. It was found that with increasing [BA] both R_p and \bar{M}_n increased. The increase in polydispersity with increasing [BA] may be attributed to branching reactions and or to gel effect. Similarly, the decrease in \bar{M}_n and increase in the polydispersity index with increase of [I] (from 1.81×10^{-3} to 7.74×10^{-3} mol L⁻¹) also suggest the

Table II Effect of Behenyl Acrylate Concentration [BA] and Benzoyl Peroxide Concentration [BPO] on the Molecular Weight, Polydispersity Index, and Thermal Behavior of Poly(BA) Prepared in a Nitrogen Atmosphere at 70°C in Benzene^a

[BA] (mol L ⁻¹)	10 ³ · [BPO] (mol L ⁻¹)	10 ⁵ · R _p (mol L ⁻¹ s ⁻¹)	10 ⁻⁴ · \bar{M}_n	Polydispersity Index	mp (°C)	ΔH_m (kJ mol ⁻¹)	ΔS_m (J K ⁻¹ mol ⁻¹)
0.847	7.74	22.7	20.3	5.6	66.0	32.6	96.1
0.678	7.74	17.2	10.3	4.8	59.5	36.8	110.7
0.508	7.74	12.4	6.3	3.3	62.2	35.6	106.1
0.339	7.74	7.8	4.8	3.3	63.8	33.5	99.6
0.169	7.74	3.2	2.6	2.2	65.6	36.1	106.5
0.085	7.74	0.8	1.8	1.8	63.8	36.2	107.5
0.051	7.74	0.2	1.6	1.6	63.2	36.0	107.1
0.847	13.70			Gel formation			
0.847	11.60			Gel formation			
0.847	6.20	20.1	21.5	4.8	64.3	34.5	102.3
0.847	4.39	17.5	23.4	4.0	62.7	36.5	108.8
0.847	1.81	13.1	26.8	3.0	61.0	33.1	99.0

^a [Benzene] = 7.00 mol L⁻¹; time = 1 h.

influence of chain branching and the gel effect on the molecular weight of poly(BA). Under the experimental conditions used, gel formation was observed from 1.16×10^{-2} mol L⁻¹ of [I]. This may be due to the very high degree of branching reactions. The branching may be due to the extraction of a large number of hydrogen atoms from the long alkyl groups of the alkyl chain.²⁵

In this work, it was observed that with a similar reactant composition the \bar{M}_n of the polymer formed in the rotational viscometer was less than that formed in batch reactions. It is probable that when the polymerization is carried out in a rotational vis-

cometer the increasing shear rate diminishes the entanglement density²⁶ of chain radicals and results in a polymer of lower molecular weight with higher polydispersity.

The solvent effect on the polymerization of BA was investigated at 70°C. The results are presented in Table III. The solvents were found to affect the polymerization significantly. At high conversion, the values of R_p and \bar{M}_n were lower in toluene and xylene. In benzene, the increase of \bar{M}_n was observed with increasing R_p. This is in conformity with the observation of Sato et al.^{27,28} on the polymerization of alkyl itaconates in different solvents. In the case

Table III Effect of Solvents on Molecular Weight, Polydispersity Index, and Thermal Behavior of Poly(BA) Prepared in a Nitrogen Atmosphere with BPO as Initiator at 70°C^a

Solvent	[Solvent] (mol L ⁻¹)	10 ⁴ · R _p (mol L ⁻¹ s ⁻¹)	10 ⁻⁴ · \bar{M}_n	Polydispersity Index	mp (°C)	ΔH_m (kJ mol ⁻¹)	ΔS_m (J K ⁻¹ mol ⁻¹)
Benzene	7.00	2.3	20.3	5.6	66.0	32.6	96.1
Benzene	10.50	1.7	11.8	4.1	64.1	33.6	99.8
Benzene	14.00	1.1	5.7	3.0	66.1	34.2	100.9
Benzene	21.00	0.5	5.2	2.0	64.2	39.2	116.1
Toluene	7.00	0.9	9.7	3.3	64.4	36.0	106.8
Xylene	7.00	0.8	5.7	2.1	64.4	36.7	108.5
Heptane	7.00	2.1	19.4	5.4	62.1	37.7	112.4
CCl ₄	7.00	2.4	10.6	3.9	61.4	33.5	100.3

^a [BA] = 0.847 mol L⁻¹; [BPO] = 7.74×10^{-3} mol L⁻¹; time = 1 h.

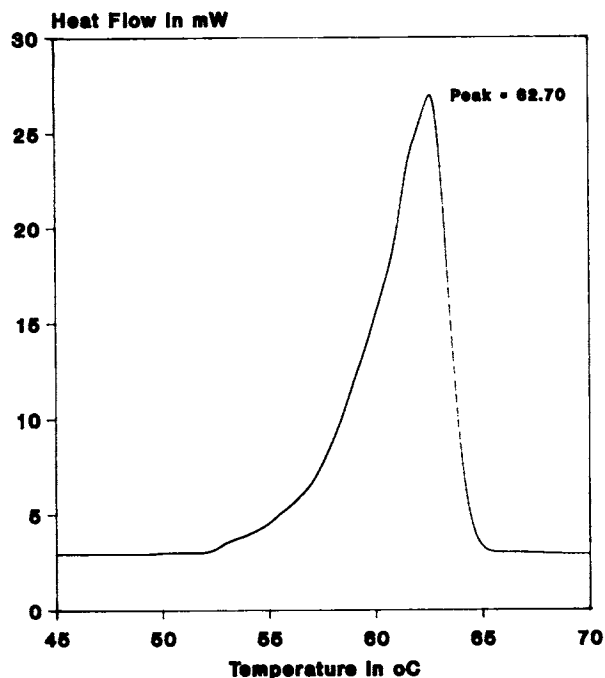


Figure 5 Typical DSC thermogram (scanning rate = 10°C/min) of poly(BA) prepared by using BPO as initiator at 70°C in benzene.

of polymerization in CCl_4 , the higher R_p could be partly due to the higher initial viscosity of the medium.

DSC measurements of poly(BA) were carried out at a heating rate of 10°C/min in nitrogen medium. Figure 5 shows a typical DSC curve of poly(BA). Melting endothermic peaks were observed at 50–72°C for the polymer samples. The melting point (mp) and heat of fusion (ΔH_m) were determined from the endothermic peaks. These values are shown in Tables I–III. The apparent heat of fusion (ΔH_m) can be obtained from the area of the endothermic peak. The melting point and ΔH_m values were almost constant regardless of percent conversion and molecular weight of the polymer. The entropy of fusion (ΔS_m) calculated from the mp and ΔH_m values is also shown in Tables I–III. Like ΔH_m values, the values of ΔS_m are also constant, which results in the fact that the mp changes are not very predominant.

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