

# Synthesis, Characterization, and Thermal Properties of Copolymers of Behenyl Acrylate and Behenyl Fumarate

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**ABSTRACT:** Radical copolymerization of behenyl (systematic IUPAC nomenclature: *n*-docosyl) acrylate and behenyl fumarate has been carried out in toluene at 70°C using benzoyl peroxide as initiator. Gel permeation chromatography was used to determine molecular weights (MW) and molecular weight distribution (MWD) of behenyl acrylate-behenyl fumarate (BA-BF) copolymers. <sup>1</sup>H NMR and carbon analysis was used to determine the composition of BA-BF copolymers. Monomer reactivity ratios for high conversion polymerization were calculated by conversion-extended Kelen-Tudos plot. Differential scanning calorimetric (DSC)

measurements shows sharp melting peaks at about 64°C. Thermal stability studies were performed with thermogravimetric analyzer (TGA). By using these DSC and TGA data in several nonisothermal methods, the activation energies were calculated. X-ray diffraction studies show the linearity of the copolymers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2721–2726, 2003

**Key words:** copolymerization; activation energy; degradation; differential scanning calorimetry (DSC); thermogravimetric analysis (TGA)

## INTRODUCTION

A linear (co)polymer of alkyl (meth)acrylate having a pendent alkyl side chain of specific length is extensively used as flow improvers (FI)/pour point depressants (PPD) for crude oils, lubricating oils, and fuel oils.<sup>1–4</sup> The FIs/PPDs considerably reduce the natural pour point, viscosity, and yield value of waxy crude, which enables the transportation of crude well below the pour point. It is also well known that alkyl acrylate polymers with a long chain alkyl group have a good swelling property in the crude oil.<sup>3</sup> However, long chain alkyl acrylate polymers have a tendency to be in the crystalline state, and thereby its swelling property is reduced. Therefore, to improve its performance, long chain alkyl acrylates are copolymerized to derive amorphous products. Recent studies establish the structure–reactivity relationship<sup>5,6</sup> for the polymers of higher alkyl acrylates and methacrylates. The large demand for poly (*n*-alkyl acrylates) (co)polymers with narrow molecular weight distribution (MWD) prompted research towards improving processes for the polymerization of *n*-alkyl acrylates. Dialkyl fumarates particularly those bearing bulky ester alkyl groups, have been found to readily polymerize in the presence of a radical initiator to yield higher molecular weight polymers consisting of the carboalkoxymethylene repeated units.<sup>7</sup> Apparently, the steric factor

of the alkyl group plays an important role in facilitating the polymerization, whereas, propagation of dialkylfumarates has been predicted to encounter considerable steric hindrances.<sup>8</sup> This polysubstituted methylene have no methylene group (—CH<sub>2</sub>—) as a spacer in the main chain, and their backbones are surrounded easily with side chains. As a result, these polymers have a more rigid conformation due to bulkiness of the substituents, as distinguished from ordinary vinyl polymers. It is of interest to clarify the monomer structure–reactivity and the polymer structure–property relationship of these monomers and polymers.

The copolymerization behavior of behenyl acrylate (BA) and Behenyl Fumarate (BF) types of monomers have been largely unstudied so far, despite their academic/commercial importance. The objective of the present investigation is to study the copolymerization behavior of BA and BF initiated by benzoyl peroxide (BP) as a free radical initiator in toluene at 70°C. This article also reports the use of the conversion-extended Kelen-Tudos method for determination of reactivity ratio at high conversion. The degradation patterns of the copolymers have been investigated with several thermogravimetric analysis and differential scanning calorimetric models applicable to dynamic data. To determine the copolymer composition, <sup>1</sup>H NMR, and carbon analysis data have been used.

## EXPERIMENTAL

Behenyl acrylate (BA) and behenyl fumarate (BF) were prepared and purified as before.<sup>6</sup> The solvents and the initiator (BP) were purified by standard methods.

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TABLE I  
Copolymerization of Behenyl Acrylate (BA) and Behenyl Fumarate (BF)  
at 70°C in Toluene [BP] =  $2.00 \times 10^{-2}$  mol L<sup>-1</sup>

Sample	Feed composition in mol ratios		Copolymer composition in mol ratios		$10^5 \cdot R_p$ mol L <sup>-1</sup> s <sup>-1</sup>	$M_n$	$M_w/M_n$	m.p. (°C)	Heat capacity (J/g)
	BA	BF	BA	BF					
BA-BF1	19.72	1.00	49.0	51.0	6.15	36,500	2.7	63.68	109.2
BA-BF2	9.87	1.00	47.1	52.9	6.46	32,200	2.5	63.48	118.4
BA-BF3	4.90	1.00	44.5	55.5	6.61	29,600	2.8	64.35	117.5
BA-BF4	3.27	1.00	43.0	57.0	8.88	23,900	2.8	63.91	117.1

The copolymerization of BA and BF was carried out by the following general procedure: after the reaction components were charged into a dry glass ampoule, the ampoule was purged with nitrogen (99.99% pure). The solution was deaerated by three freeze-pump-thaw cycles and sealed with a rubber septum. After the desired polymerization time period, precipitating with acetone containing traces of hydroquinone isolated the polymers. The polymers were then filtered and dried under vacuum. It was reprecipitated for determination of chemical composition. The percent conversion was determined gravimetrically. Molecular weights (MW) and MWD of the polymers were determined using a Waters 515 gel permeation chromatograph equipped with three Styragel columns (HR1, HR3, and HR4) in series with a 2410 differential refractometer as the detector. Analysis was performed at room temperature using tetrahydrofuran (HPLC grade) as eluent at 1 mL min<sup>-1</sup>. Differential scanning calorimetry (DSC) was performed in a TA series DSC 2010 instrument in a nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup> with 2–5 mg of polymer weighed in aluminum pans. Thermal stability studies were performed using a TA series STD 2960 simultaneous DTA-TGA analyzer in a nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup>. The X-ray diffractogram of polymers were recorded on a model JDX-11P3A JEOL diffractometer with a solid sample using Ni filter with Cu-K $\alpha$  radiation at 35 kV and 10 mA in the wide-angle range  $2^\circ < 2\theta < 60^\circ$ . <sup>1</sup>H NMR spectrum was recorded on a Bruker 300 MHz spectrometer in CDCl<sub>3</sub> with tetramethylsilane (TMS) as the internal reference. Carbon analysis was done in a Perkin-Elmer 2400 CHN/O analyzer.

## RESULTS AND DISCUSSIONS

The physical properties of behenyl acrylate-behenyl fumarate (BA-BF) copolymers are listed in Table I. It was observed that the MW of polymers increases with the increase of mole fractions of BA in the feed. The GPC curves of BA-BF copolymers are shown in Figure 1 and the MWDs ( $M_w/M_n$ ) are uniform throughout the polymerization. The dibehenyl fumarate group acts as

the polymerization regulator being able to take over the radical function. Due to steric hindrances of the group, this radical is not able to propagate the chain growth. Also, no crosslinking was observed. The rates of polymerization, MW of the polymers and the flexibility of polymers of poly(dialkyl fumarates) depend intensively upon the structure (bulkiness) of the ester substituents, indicating that the polymerization of dialkyl fumarates shows unique characteristics different from ordinary vinyl polymerizations.<sup>9</sup> In radical copolymerization of BA with BF, monomer reactivity ratios of the monomers supported the occurrence of successive propagation of BF, which does not give a high polymer in radical homopolymerization.

Copolymer compositions have been found by carbon analysis and <sup>1</sup>H NMR spectroscopy using the percentage of hydrogen and ratios of the intensities of downfield protons at 4.00 ppm (—CH<sub>2</sub>—) to that of the total protons.<sup>10–12</sup> Peaks at 4.20 ppm (—CH—), 4.00 ppm (—CH<sub>2</sub>—), 1.60 ppm (—OCH<sub>2</sub>—), 1.26 ppm (—CH<sub>2</sub>—)<sub>n</sub> and 0.89 ppm (—CH<sub>3</sub>) have been taken for total peak ratio calculation. The values thus obtained were used to calculate the mole fractions of BA and BF in the copolymers. The <sup>1</sup>H NMR spectra of a typical BA-BF copolymer is shown in Figure 2.

To determine the copolymerization behavior at high conversion polymerization, the reactivity ratios for the

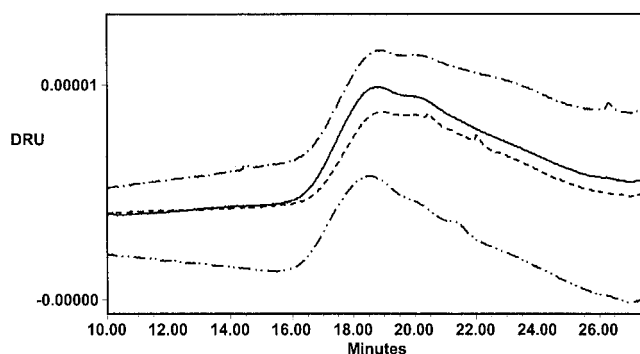


Figure 1 Gel permeation chromatography traces (refractive-index detector) of BA-BF copolymers prepared with BP as an initiator in toluene at 70°C. [BP] =  $2.00 \times 10^{-2}$  M. Molar ratios of [BA] : [BF] for: (— · · ·) = 19.72 : 1.00; (—) = 9.87 : 1.00; (—) = 4.90 : 1.00; (· · ·) = 3.27 : 1.00.

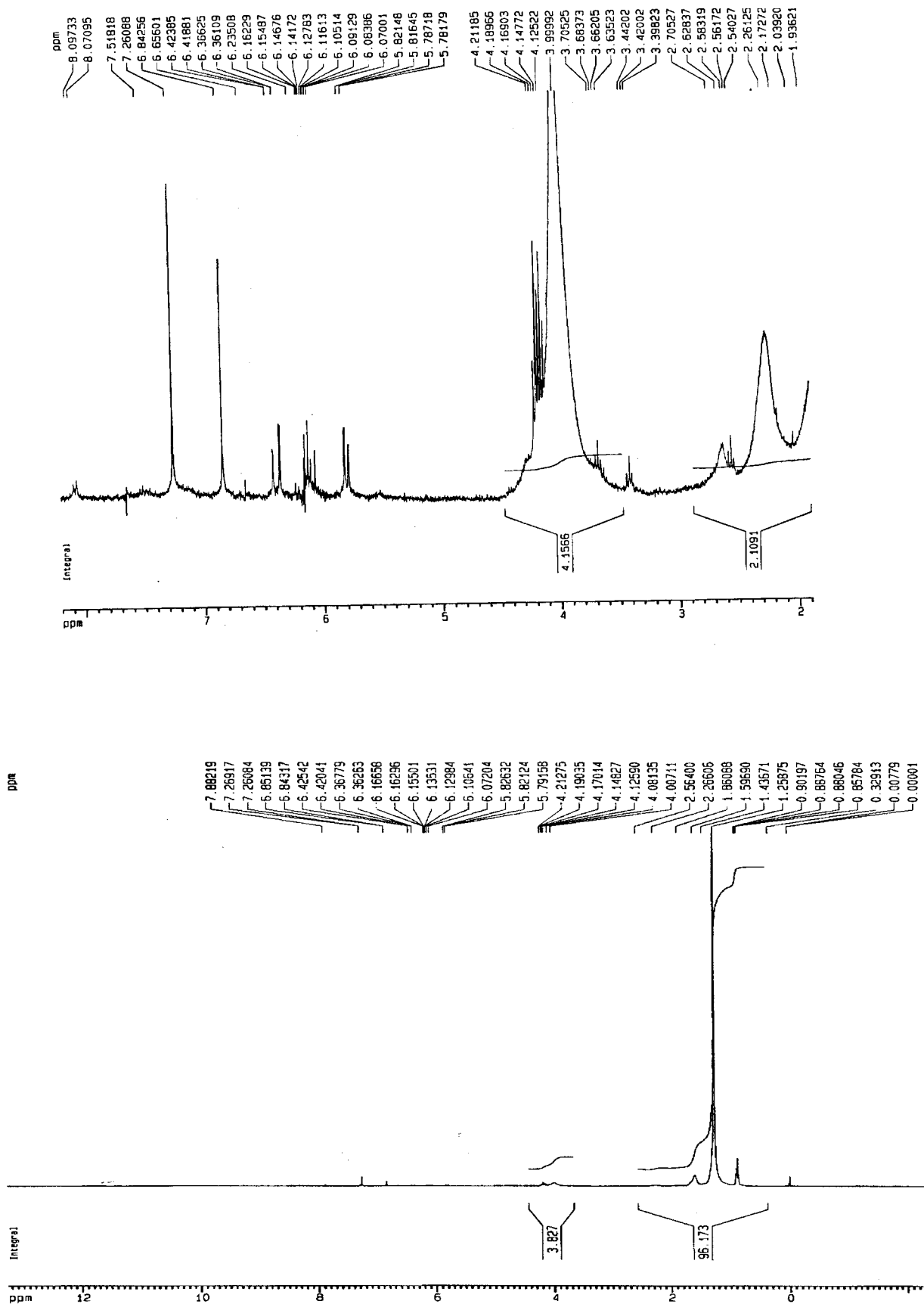


Figure 2 <sup>1</sup>H NMR spectrum of the BA-BF copolymer prepared with BP as an initiator in toluene at 70°C. [BP] = 2.00 × 10<sup>-2</sup> M. Molar ratio of [BA] : [BF] = 19.72 : 1.00.

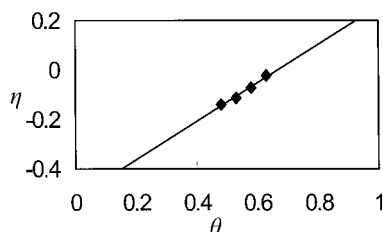


Figure 3 Conversion-extended Kelen-Tudos plot.

BA-BF system were calculated by using the modified method of Kelen and Tudos.<sup>13,14</sup> This modified method does not suffer from reindexing errors, and can be used with relatively high conversions.<sup>15</sup> Figure 3 shows the conversion-extended Kelen-Tudos plot for the BA/BF system and it gives  $r_{BA} = 0.519 \pm 0.051$  and  $r_{BF} = 0.776 \pm 0.091$ .

The BA-BF copolymers will find use as PPDs/FIs for the transportation of waxy crude oils. When use as PPDs/FIs, the copolymers will encounter temperatures far in excess lower critical solution temperature behavior (LCST) in the course of their lifetime. Therefore, the thermal properties of the copolymers, especially the thermal decomposition, were investigated.

DSC measurements of the copolymer samples were carried out at a heating rate of  $10^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. Melting endothermic peaks were observed at  $50\text{--}72^\circ\text{C}$  for the copolymer samples (Fig. 4). The melting point and the heat capacity of copolymers were determined from the endothermic peaks and the values are shown in Table I. All the polymers exhibit a single peak indicating the formation of random co-

polymers. The melting point and heat capacity values were almost constant, regardless of the feed composition of monomer pair, conversion percentage and also of the MW and MWD of resulting copolymers.

During the use of the copolymers, the stability of these copolymers against thermal stress is of great importance. Hence, thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$ . The decomposition curves of some of the selected polymers are shown in Figure 5. The TGA study on the copolymers under nitrogen supports apparent single-step decomposition and the decomposition starts above  $350^\circ\text{C}$ . This corresponds to the random scission within the copolymer chain. As the decomposition temperature is high enough, it can tolerate the applied thermal stress during the usage. Furthermore, when the BA-BF copolymer degrades, it leaves nearly no residue at and above  $550^\circ\text{C}$ . To make an accurate quantitative prediction on thermal degradation of polymers, the information of the underlying chemical mechanisms is insufficient.<sup>16</sup> Therefore, the development of a molecular-level understanding of the thermal degradation of polymers is an increasingly important area of research.

#### Kinetic analysis of TG thermograms

A reaction rate is defined as the derivative of conversion with respect to time. In a TGA, conversion is defined<sup>17</sup> as the rate of final mass loss to total mass loss corresponding at a particular stage of degradation process, i.e.,

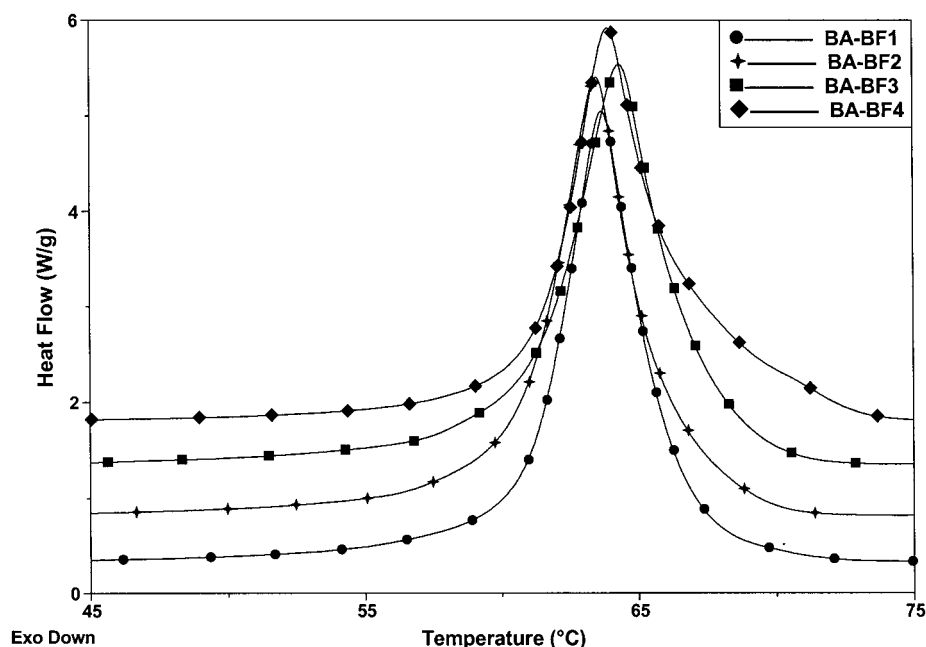
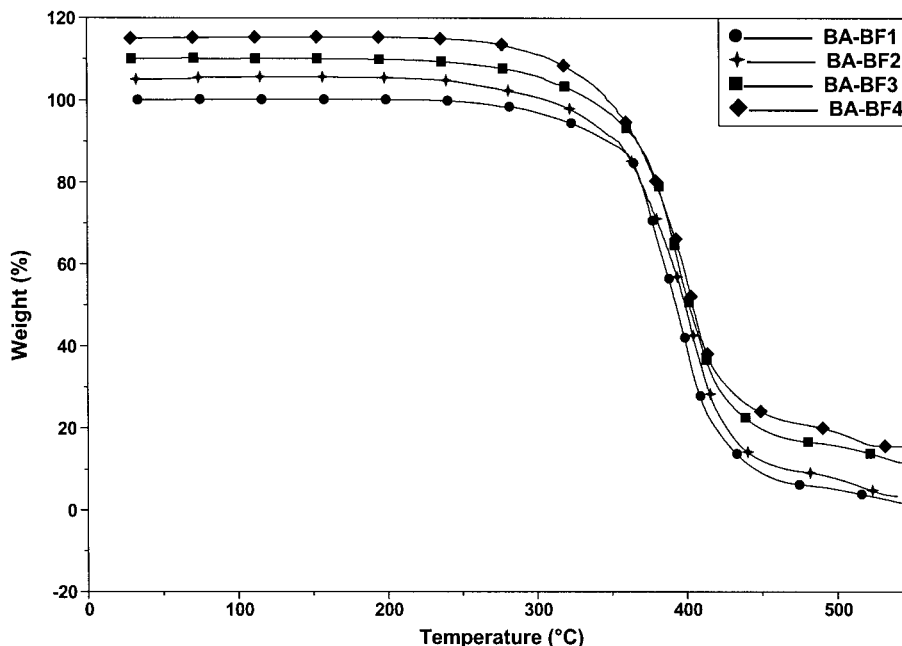


Figure 4 DSC thermograms for BA-BF copolymers prepared with BP as an initiator in toluene at  $70^\circ\text{C}$ .  $[\text{BP}] = 2.00 \times 10^{-2}$  M. Molar ratios of  $[\text{BA}] : [\text{BF}]$  for: (●) = 19.72 : 1.00; (+) = 9.87 : 1.00; (■) = 4.90 : 1.00; (◆) 3.27 : 1.00.



**Figure 5** Thermogravimetric curves for BA-BF copolymers prepared with BP as an initiator in toluene at 70°C. [BP] = 2.00 × 10<sup>-2</sup> M. Molar ratios of [BA] : [BF] for: (●) = 19.72 : 1.00; (+) = 9.87 : 1.00; (■) = 4.90 : 1.00; (◆) 3.27 : 1.00.

$$\beta = W/W_r \tag{1}$$

where,  $W_r = W_\infty - W$ ,  $W_\infty$  is the mass loss at the end of the particular stage of a reaction, and  $W$  is the mass loss up to time  $t$ .

The rate of conversion in a dynamic TGA experiment at a constant heating rate can be expressed as:

$$d\beta/dt = Q(d\beta/dt) = k(T)f(\beta) \tag{2}$$

where  $Q$  is the heating rate,  $k(T)$  is the rate constant and  $f(\beta)$  is the conversion functional relationship.

Arrhenius expression, which describes the temperature dependence of the rate constant, may be expressed as:

$$k(T) = A \exp(-E/RT) \tag{3}$$

where  $A$  is the preexponential factor,  $E$  is the activation energy, and  $R$  is the universal gas constant.

The integral form of the rate equation in a dynamic heating expression experiment may be expressed as.<sup>17</sup>

$$g(\beta) = (AE/QR)p(x) \tag{4}$$

where  $p(x) = \int_a^x \exp(-x)/x^2 dx$ , and  $x = E/RT$ .  $g(\beta)$  is the integral form of conversion dependence function.

Several methods using different approaches have been developed for solving the integral  $p(x)$  equation. In the present investigations three different nonisothermal methods are used for the computation of the kinetic parameters. The equations employed are the

Freeman and Carroll,<sup>18</sup> Flynn and Wall,<sup>19</sup> and Coats and Redfern.<sup>20</sup> The activation energies calculated from these models for all the four synthesized copolymers are presented in Table II.

**Freeman and Carroll equation**

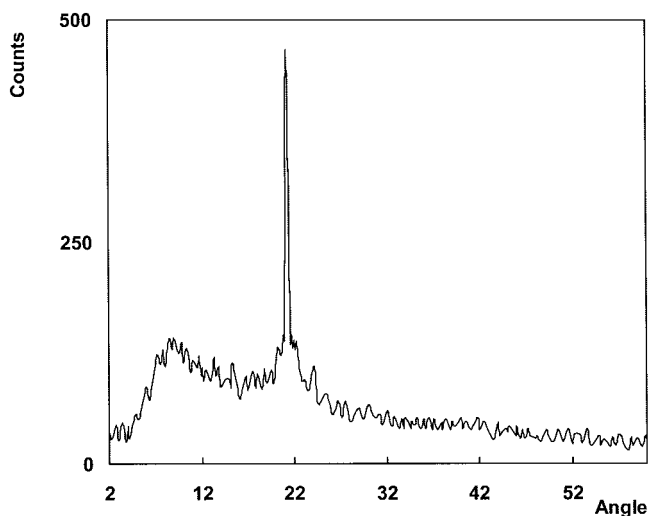
This is a differential method. The final equation derived from the modified treatment of the Freeman and Carroll method can be represented in the form of:

$$\log[Q(dW/dT)/W_r] = (-E/2.303RT) + \log A \tag{5}$$

The terms have their usual meaning.  $E$  and  $A$  can be calculated from the slope and intercept, respectively.

**TABLE II**  
Activation Energies and Correlation Coefficients of Copolymers of Behenyl Acrylate (BA) and Behenyl Fumarate (BF) by Various Methods

Sample	Activation energies, $E$ (kJ mol <sup>-1</sup> ) and correlation coefficients, $r$					
	Freeman and Carroll		Flynn and Wall		Coats and Redfern	
	$E$	$R$	$E$	$r$	$E$	$r$
BA-BF1	105.13	0.99	92.96	0.99	87.48	0.99
BA-BF2	96.20	0.99	88.78	0.99	84.60	0.99
BA-BF3	94.11	0.99	82.74	0.99	78.80	0.99
BA-BF4	90.45	0.99	80.43	0.99	74.85	0.99



**Figure 6** Typical X-ray diffraction pattern of BA-BF copolymer prepared with BP as an initiator in toluene at 70°C.

### Flynn and Wall equation

This is also a differential rate expression and weight loss-time equation. The simplified equation of this treatment can be represented in the form of:

$$\log[(dW_t/dt)/(W_o - W_t)^n] = (-E/2.303RT) + \log(A/B) \quad (6)$$

where the terms have their usual meaning. Curves can be drawn for different values of  $n$  in the range of 0–2, and  $E$  was fixed from the value of  $n$ , which gave best fit line. Slope of the plot of left-hand side of the equation vs.  $1/T$  is  $-E/2.303R$ , from where  $E$  can be calculated.

### Coats and Redfern equation

For a first-order reaction process, Coats and Redfern provided an approximation. This is an integral form of the rate equation. The simplified form of the equation:

$$\log[-(\log(1 - \beta)/T^2)] = [\log(AR/QE)(1 - 2RT/E)] - E/2.303RT \quad (7)$$

Because  $(1 - 2RT/E) \approx 1$ , a plot of the left-hand side of eq. (7) vs.  $1/T$  should result a straight line with a slope of  $-E/2.303R$  and  $E$  can be calculated from the slope.

Table II shows the activation energy  $E$  and the value of the correlation coefficient  $r$  obtained by three different methods employed in this work.

The X-ray diffraction pattern of BA-BF copolymers shows a peak at about  $2\theta = 21.5^\circ$ , which corresponds to 4.14 Å spacing (Fig. 6). This value corresponds to the value of several long chain acrylates and methacrylates comb like polymers,<sup>21</sup> attributed to the van der Waals contract of nonbonded atoms.<sup>22</sup> The spacing at 4.14 Å correspond to the typical hexagonally packed cylinders of  $n$ -alkane crystals close to their melting points. These results are the same with those observed for the conventional widely spaced comb-like polymers and indicate the hexagonal packed long alkyl side chains. A shoulder appeared at  $23.5^\circ$  ( $d = 3.75$  Å). This peak may be assigned to the orthorhombic packing.<sup>23</sup> On the basis of a detailed study of the conventional comb-like polymers, Yokota et al.<sup>24</sup> proposed peculiar layered structure made up of several parallel alkyl side chains arranged in both sides of the main chain.

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