

Copolymers of bulky fumarate: synthesis and their properties

Shashi D. Baruah · Diganta Sarmah ·
Narayan C. Laskar

Received: 16 November 2009 / Accepted: 11 February 2010 / Published online: 19 March 2010
© Springer Science+Business Media B.V. 2010

Abstract The free radical copolymerization of di-*n*-docosyl fumarate with vinyl acetate and *n*-alkyl (meth)acrylates was carried out in toluene at 70°C using benzoyl peroxide as an initiator. ¹H NMR and carbon analysis was used to determine the copolymer compositions. Monomer reactivity ratios for high conversion polymerization were calculated by Fineman-Ross, Kelen-Tüdös and conversion extension Kelen-Tüdös methods. Gel permeation chromatography was used to determine the molecular weights and polydispersity indexes. In order to determine the stability of polymers against thermal degradation, the kinetics and mechanism of the thermal degradation of copolymers were investigated by differential scanning calorimetry and thermogravimetric analysis techniques. The energy of activation of the degradation process was determined by several thermogravimetric analysis models.

Keywords Copolymerization · Dialkyl fumarate · Reactivity ratio · Differential scanning calorimetry (DSC) · Thermogravimetric analysis (TGA) · Degradation

Introduction

Dialkyl fumarates with long side chains may be considered as typical comb-like polymers. These 1,2-disubstituted ethylenic monomers have a more rigid conformation due to bulkiness of substituents [1, 2] and are generally recognized as unable monomers to homopolymerize due

to strong steric hindrance of the propagation step by the substituents in both 1- and 2- positions. The voluminous dialkyl fumarate group acts as the polymerization regulator being able to take over the radical function. The main characteristic of these monomers is their low polymerization rates which are attributed to the steric hindrance of the propagation reaction [3]. Due to steric hindrances of the group, free radical is not able to properly propagate the chain growth. The steric congestion at the poly(dialkyl fumarate) radical centre not only increases with the bulkiness of the alkyl substituents, but also with polymer chain length up to some critical chain length [4]. It has been revealed that the bulky ester groups promote propagation despite the steric repulsion [5]. This indicates that the polymerization of dialkyl fumarates shows unique characteristics different from ordinary vinyl polymerization [6]. The high density of substituents of the resulting carboalkoxymethylene repeated units, combined with the bulkiness of the substituents lead to stiff main chains [7–9]. The characteristic features of dialkyl fumarate homopolymerization are not observed in copolymerization with long chain alkyl (meth)acrylates, suggesting a low reactivity of the 1,2-disubstituted ethylene structure. In contrast with vinyl monomers, copolymers of dialkyl fumarate consisting of a substituted polymethylene side chain result in less chain flexibility. Fumarate readily undergoes copolymerization with electron rich monomers such as styrene and vinyl acetate. Poly(dialkyl fumarate) based materials have generated interest as pour point depressants/flow improvers (PPDs/FIs), viscosity index improvers and additives in petroleum based products. These comb-like polymers cocrystallize with hydrocarbon chains in crude and lubricating oils, resulting in a reduction of crystallite size in the mixture [10, 11]. Due to the cocrystallization of normal alkanes and long repeating units of polymers, polymeric

S. D. Baruah (✉) · D. Sarmah · N. C. Laskar
North East Institute of Science & Technology,
Council of Scientific & Industrial Research,
Jorhat 785 006, Assam, India
e-mail: baruah_shashi@yahoo.co.in

additives affect the habit of wax precipitation in crude oil and it results the lowering of pour point of crude oils. The copolymerization behavior of dialkyl fumarate has been investigated [12] in order to establish the effect of substitution group volume on the activity of the fumarates as well as to study the role of charge transfer complex in the copolymerization [13, 14]. The increase in polymerization reactivity of the fumarates by incorporating bulky groups is a consequence of the extremely slow bimolecular termination of the substituted polymethylene radicals with a rigid chain structure, which overcompensate the decrement of the propagation rate [15, 16]. Radical polymerization of dissymmetric fumarates with bulky alkoxyethyl group is recently documented. It was observed that monomer reactivities of dissymmetric fumarates were enhanced with the increase of alkoxyethyl chain length. The enhancement of reactivity was due to the suppression of the termination reaction, resulting from the increased hindrances induced by the alkoxyethyl chain length [17]. In free radical polymerization of dialkyl fumarate under microwave irradiation, a significant enhancement of the rate of polymerization was observed in comparison with thermal conditions [18].

In this paper, we describe the free radical copolymerization of di-*n*-docosyl fumarate (DDF) with vinyl acetate (VA), *n*-octadecyl acrylate (OA), *n*-docosyl acrylate (DA) and *n*-octadecyl methacrylate (OMA) in toluene in the presence of benzoyl peroxide as the initiator (Scheme 1). The objective of this study is to correlate, for the studied systems, the monomer structure with its reactivity, and the polymer structure with its properties. The reactivity ratios of monomers for high conversion polymerizations were calculated by Fineman-Ross, Kelen-Tüdös and conversion extended Kelen-Tüdös methods. The melting endotherms and thermal stabilities of each series of copolymers have been investigated by differential scanning calorimetry and thermogravimetric techniques. The thermal degradation kinetics and energy of activation of the degradation process were investigated by several thermogravimetric analysis models applicable to dynamic data.

Experimental

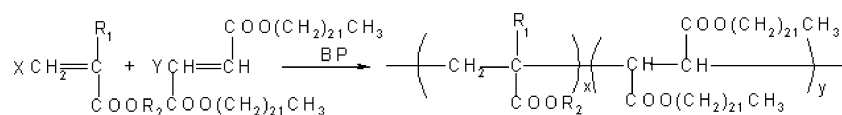
Materials and polymerization

n-alkyl (meth)acrylates and DDF were prepared and purified as indicated elsewhere [12]. Vinyl acetate, benzoyl

peroxide and the solvents were purified by standard methods. Polymerization was carried out in sealed glass ampoules placed in a bath thermostated at desired temperatures. The ampoule containing the reaction mixture is deaerated by three freeze-pump-thaw cycles and sealed with a rubber septum. After the polymerization, the ampoules were cracked open and the contents are poured into a beaker containing the precipitating solvent and traces of hydroquinone for isolation of the polymers. The polymers were then filtered, reprecipitated several times and dried in vacuum. The polymer yield was determined gravimetrically.

Instrumentation and analysis

Molecular weight (MW) and molecular weight distribution (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. The analysis was performed at room temperature with purified high-performance liquid chromatography grade tetrahydrofuran (THF) as eluent at 1.0 mL min⁻¹. Low polydispersed linear polystyrene standards supplied by Shodex Standards (M_n from 1290 to 498000) were used to construct the calibration curve based on universal GPC calibration [19]. Data acquisition and processing were performed using Waters Millennium³² software package. Differential scanning calorimetric (DSC) measurements were performed on a TA series DSC 2010 instrument in nitrogen atmosphere with 2–5 mg of polymer samples weighed in aluminum pans at a heating rate of 10°C min⁻¹. The instrument was calibrated with indium for correction of heat of transition. Thermal stability studies were performed using a TA series STD 2960. Such model was simultaneously equipped with DTA and TGA analyzer, which were operated in a nitrogen atmosphere at a heating rate of 10°C min⁻¹; in measurements were used between 10 and 15 mg of polymer sample. DSC and DTA-TGA runs were repeated thrice for each sample. The ¹H NMR spectra were recorded on a Bruker 300 MHz spectrometer in CDCl₃ with tetramethylsilane (TMS) as an internal standard. The X-ray diffractogram of polymer samples were recorded at room temperature on a model JDX-11P3A JEOL diffractometer with a solid sample using a Ni filter with Cu-Kα radiation at 35 kV and 10 mA in the wide angle range 2° < θ < 60°. The samples used for obtaining X-ray diffractograms were pre-



Scheme 1 Structure of di-*n*-docosyl fumarate copolymer

Table 1 Copolymerization of vinyl acetate, *n*-octadecyl acrylate, *n*-docosyl acrylate and *n*-octadecyl methacrylate (M_1) with di-*n*-docosyl fumarate (DDF) at 70°C in toluene. $[BP] = 2.0 \times 10^{-2} \text{ mol L}^{-1}$; reaction time=6 h

Copolymer	Feed composition in mol ratios		Copolymer composition in mol ratios		$10^5 \cdot R_p \text{ mol L}^{-1} \text{ s}^{-1}$	\overline{M}_n	$\overline{M}_w/\overline{M}_n$	mp (°C)	Heat capacity (J g^{-1})
	M_1	DDF	M_1	DDF					
VA-DDF1	0.50	1.00	38.2	61.8	4.07	7300	1.6	64.2	112.2
VA-DDF2	1.00	1.00	40.1	59.9	3.84	7700	1.6	64.0	113.7
VA-DDF3	1.50	1.00	42.1	57.9	3.56	10200	1.7	64.5	113.2
VA-DDF4	3.00	1.00	43.3	56.7	3.34	10700	1.7	63.2	120.7
VA-DDF5	5.00	1.00	45.5	54.5	2.97	12000	1.8	63.5	122.1
VA-DDF6	10.00	1.00	48.1	51.9	2.30	13200	1.9	62.9	125.4
OA-DDF1	0.50	1.00	35.1	64.9	12.89	35800	2.1	54.3	85.3
OA-DDF2	1.00	1.00	36.3	63.7	11.12	40600	2.5	56.6	88.8
OA-DDF3	2.00	1.00	37.8	62.2	10.45	42200	2.5	57.0	89.6
OA-DDF4	3.00	1.00	39.6	60.4	10.30	42400	2.4	57.2	89.8
OA-DDF5	5.00	1.00	41.1	58.9	9.99	42500	2.3	58.3	92.4
OA-DDF6	10.00	1.00	43.4	56.6	7.34	47100	2.1	60.3	93.1
DA-DDF1	0.50	1.00	40.3	59.7	11.23	21000	1.8	62.3	99.6
DA-DDF2	1.00	1.00	41.2	58.8	9.75	23100	2.7	63.7	108.9
DA-DDF3	2.00	1.00	42.2	57.8	9.12	23400	2.5	64.1	111.5
DA-DDF4	3.00	1.00	43.0	57.0	8.88	27200	2.7	63.9	117.1
DA-DDF5	5.00	1.00	44.5	55.5	6.61	31100	2.7	64.4	117.5
DA-DDF6	10.00	1.00	47.1	52.9	6.46	35400	2.5	63.5	118.4
OMA-DDF1	0.50	1.00	33.9	66.1	12.78	150200	2.6	69.8	130.1
OMA-DDF2	1.00	1.00	35.3	64.7	11.12	156000	2.2	68.6	128.8
OMA-DDF3	2.00	1.00	36.2	63.8	11.04	158000	2.4	68.4	128.2
OMA-DDF4	3.00	1.00	38.0	62.0	10.80	168000	2.2	68.2	127.8
OMA-DDF5	5.00	1.00	41.1	58.9	8.70	173100	2.1	68.0	125.7
OMA-DDF6	10.00	1.00	43.4	56.6	7.54	198700	2.2	67.5	124.8

sented in film form with a sample size of 7–10 mg. IR spectra were recorded on Perkin Elmer IR 833 spectrophotometer. Elemental analysis was done in a Perkin Elmer 2400 CHN/O analyzer.

Results and discussion

Synthesis of the di-*n*-docosyl fumarate copolymers

The results of radical copolymerization of DDF with VA, OA, DA and OMA are summarized in Table 1. Clearly, the average molar masses (\overline{M}_n and \overline{M}_w), polydispersities and R_p depend sensitively on the structure (bulkiness) of the ester substituents. For the copolymerization with DDF with *n*-alkyl (meth)acrylates, at any particular feed composition of *n*-alkyl (meth)acrylate the R_p of the copolymerization is in the order of OA ~ OMA > DA. This may be attributed to the higher stability of alkyl group substitution size. The

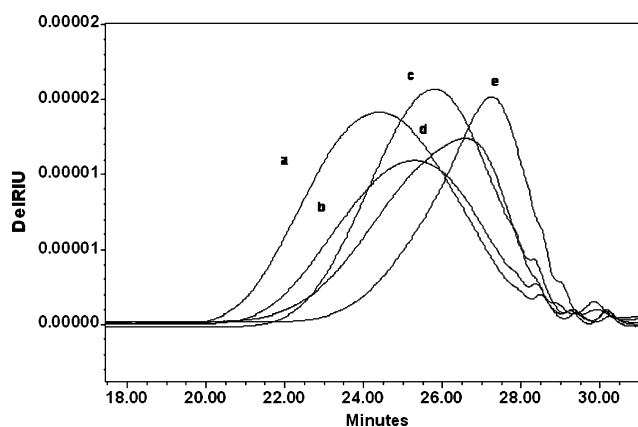


Fig. 1 GPC curves of VA-DDF copolymer prepared in toluene at 70°C with benzoyl peroxide (BP) as initiator. $[BP] = 2.0 \times 10^{-2} \text{ mol L}^{-1}$; reaction time: 6 h. Molar ratios of $[VA]:[DDF]$ for (a)=10.0:1.0, (b)=5.0:1.0, (c)=3.0:1.0, (d)=1.5:1.0 and (e)=.0:1.0

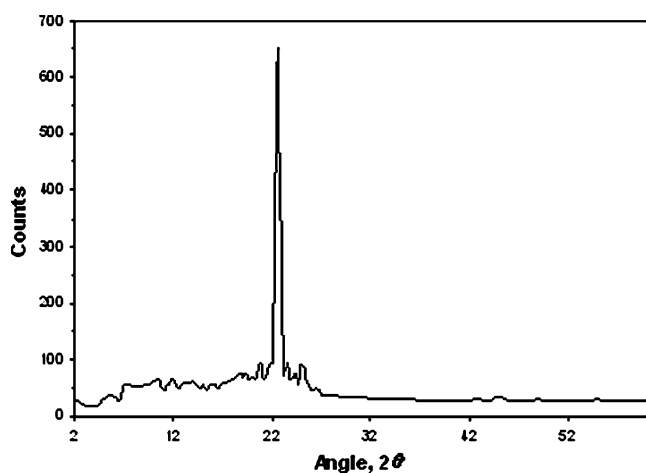


Fig. 2 Wide angle X-ray diffraction diffractogram of VA-DDF copolymer

steric factor and hindrance parameters increases with the increase of bulky ester substituents [20]. In ordinary vinyl polymerization, the direction of monomer addition and the opening mode of C=C double bond cannot be discriminated from each other. But in the case of polymerization of 1,2-disubstituted ethylenes, the direction of monomer addition determines the configuration of two carbon atoms. Also the stereochemical structures of dialkyl fumarate polymers are dependent on the structure of the ester alkyl groups. It was observed that the molecular weight (MW) of polymers increases with the increase of mole fraction of VA and n-alkyl (meth)acrylate fractions in the feed. The molecular weight results indicate the formation of copolymers with high polydispersity. Figure 1 presents the GPC chromatograms of VA-DDF copolymers and it is evident that molecular weight increases with the increase of VA fraction in the copolymer feed. Macromolecules with molecular weight less than 1290 which elutes after 28.7 min were ignored for computation of average molecular weight and MWD. In the copolymerization of DDF and VA, the rates of polymerization and molecular weights of the resulting polymer are low in comparison with those corresponding to the copolymerization of DDF with (meth)acrylates having

bulkier ester substituents. It is clear that MW increases with the increase in bulkiness of the alkyl substituents. DA which has more bulky substituent than OA showed low reactivities, primarily due to the bulkiness of the docosyl substituent was too large to exhibit high polymerization rates. However, the molecular weight increased significantly with methacrylate substituents.

In the IR spectra of the copolymers, the carbonyl peak of the ester bond which is located at about 1720 cm^{-1} for the monomer, is shifted to $\sim 1732\text{ cm}^{-1}$ upon polymerization. This is due to the increase of electron cloud intensity off the carbon carbon double bond of fumarate and consequently strong inductive effect of C=O to the carbon-carbon double bond of fumarate was weakened [21].

Wide angle X-ray diffraction (WAXD) of DDF copolymers shows a peak at about $2\theta=21.5^\circ$, which corresponds to 4.14 \AA (Fig. 2). This peak may be associated with the repeating alkyl segments of the rigid polymer backbone [22, 23], or the amorphous phase. The alkyl chains are packed together to form stereochemically acceptable sub-cell structure. 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. WAXD has revealed that copolymers with pendent alkyl side chains are paraffinic in nature in their ability to form hexagonal crystal lattice structure.

Monomer reactivity ratios

The copolymerization behaviour of comonomers can be better understood by the determination of reactivity ratios of monomer pair. Monomer feed compositions were planned according to the approximate design scheme proposed by McFarlane et al [24]. The ^1H NMR spectra of DDF containing copolymers show the loss of the signals at 6.9 ppm characteristic for the protons of the double bond in DDF. Copolymer compositions have been found by total organic carbon analysis and ^1H NMR spectroscopy using the percentage of hydrogen and ratio of the intensities of downfield protons at 4.00 ppm ($-\text{CH}_2-$) to that of the total

Table 2 ^1H NMR and total organic carbon data of VA-DDF copolymer for calculation of copolymer composition. Copolymer prepared in nitrogen atmosphere at 70°C in toluene with BP as initiator. $[\text{BP}] = 2.0 \times 10^{-2}\text{ mol L}^{-1}$; reaction time=6 h

Peak	Peak intensities for copolymers					
	VA-DDF1	VA-DDF2	VA-DDF3	VA-DDF4	VA-DDF5	VA-DDF6
$-\text{OCH}_2-$	0.06	0.10	0.10	0.12	0.20	0.20
$-\text{CH}_2-$	0.05	0.08	0.08	0.10	0.12	0.14
$-\text{CH}-$	0.40	0.45	0.58	0.60	0.60	0.50
$-(\text{CH}_2)_n-$	5.00	5.50	5.50	6.00	5.80	5.40
$-\text{CH}_3$	0.50	0.50	0.56	0.60	0.60	0.50
Total	6.01	6.63	6.82	7.42	7.32	6.74
%C	75.0	81.9	80.5	82.5	84.9	87.4

Table 3 Monomer reactivity ratios for copolymers containing vinyl acetate, *n*-octadecyl acrylate, *n*-docosyl acrylate and *n*-octadecyl methacrylate (r_1) with di-*n*-docosyl fumarate (r_{DDF}) obtained by Fineman-Ross (FR), Kelen-Tüdös (KT) and conversion based Kelen-Tüdös (NLLS-KT) methods

Copolymer	Methods	r_1	r_{DDF}
VA-DDF	FR	0.833	0.675
	KT	0.523	0.214
	NLLS-KT	0.498±0.050	0.755±0.089
OA-DDF	FR	0.523	0.420
	KT	1.247	0.821
	NLLS-KT	0.499±0.050	0.758±0.090
DA-DDF	FR	0.933	0.994
	KT	0.523	0.321
	NLLS-KT	0.519±0.051	0.776±0.091
OMA-DDF	FR	0.485	0.308
	KT	0.811	0.322
	NLLS-KT	0.520±0.051	0.778±0.092

protons. The values thus obtained were used to calculate the mole fraction of monomers in the copolymers [25, 26]. For VA-DDF copolymer system, peaks at 4.20 ppm (-CH-), 4.00 ppm (-CH₂-), 1.60 ppm (-OCH₂-), 1.26 ppm (-CH₂-)_n and 0.89 ppm (-CH₃) have been taken for total peak ratio calculation (Table 2).

To determine the copolymerization behavior at high conversion polymerization, the monomer reactivity ratios r_1 and r_2 were determined by the least square method according to Fineman and Ross (FR) equation:

$$G = Fr_1 - r_2$$

Where the transformed variables are

$$G = x(y - 1)/y \text{ and } F = x^2/y$$

x and y are defined as

$$x = M_1/M_2 \text{ and } y = dM_1/dM_2$$

Where M_1 and M_2 are the concentration of monomers and dM_1/dM_2 corresponds to the concentration ratio of copolymer components. The reactivity ratios r_1 and r_2 can be obtained from the plot of G versus F . The ordinate intercept is $-r_2$ and the slope of the line is r_1 . Values of r_1 and r_2 obtained from the FR procedure are summarized in Table 3.

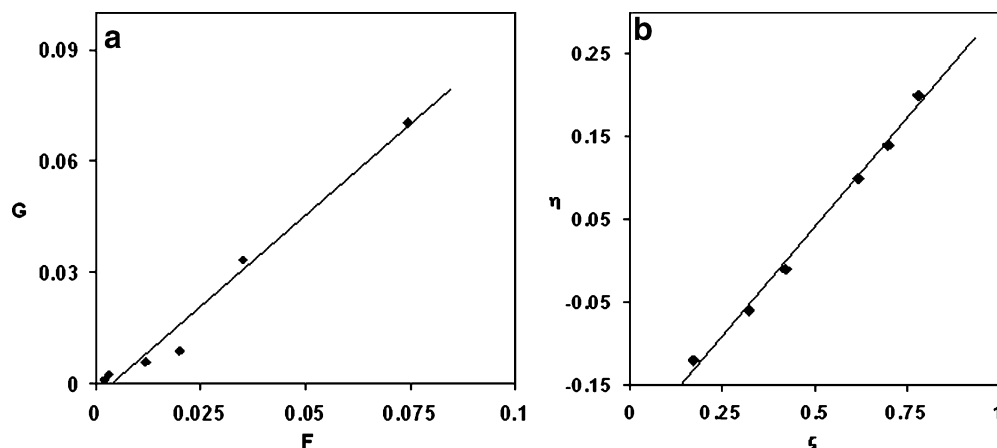
The FR method is no longer considered proper except for a quick determination of reactivity ratios of monomer pairs, therefore, the slope of the best fit FR plot is used to obtain the correct values of reactivity ratios [27]. The reactivity ratios were also determined by the conversion based modified Kelen and Tüdös [28, 29] (KT) treatment, according to the equation:

$$\eta = \xi(r_1 + [r_2/\alpha]) - r_2/\alpha$$

where η and ξ are mathematical functions of the mole ratios of monomers in the feed and in the copolymer, defined as $\eta = G/(\alpha + F)$ and $\xi = F/(\alpha + F)$ and α is a symmetrical parameter ($\alpha > 0$), which according to the authors [28] has a best value of $\alpha = (F_{\min} * F_{\max})^{0.5}$, where F_{\min} and F_{\max} are the lowest and highest values of F calculated from a series of experiments. From the linear plot of η as a function of ξ , the values of r_1 and r_2/α were obtained from the intercept at $\xi=1$ and $\xi=0$, respectively. The experimental data were evaluated by the method of least square. Parts a and b of Fig. 3 represent the FR and KT plots for VA-DDF copolymers as an example of this type of polymerization system.

The above method is applicable only for low conversion and azeotropic copolymerization. Kelen and Tüdös modified their equation of low conversion polymerization for high conversion data by redefining F and G as:

$$F = (m_1/m_2)/(\log z_1/\log z_2)$$

Fig. 3 (a) Fineman-Ross and (b) Kelen-Tüdös plots of the copolymerization parameters for VA-DDF copolymer system

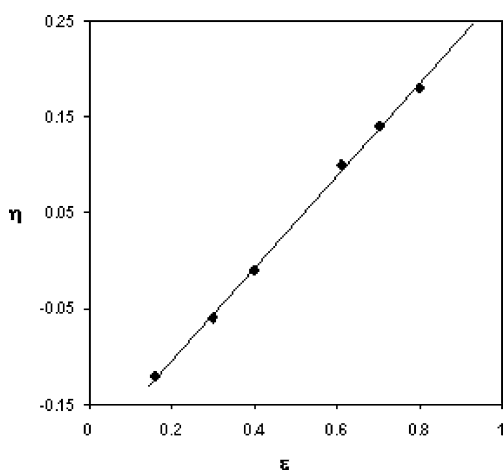


Fig. 4 Extended Kelen-Tüdös plot based on conversion data for VA-DDF copolymer system

and

$$G = (m_1/m_2 - 1) \times (\log z_1 / \log z_2)$$

where

$$z_1 = M_{1F}/M_{10}$$

and

$$z_2 = M_{2F}/M_{20}$$

M_{10} , M_{1F} , M_{20} , and M_{2F} represent the initial and final concentrations of monomer 1 and monomer 2, respectively. m_1 and m_2 are the mol fractions of monomer pair in the copolymer.

Figure 4 shows the conversion-extended KT plot for VA-DDF copolymerization system. The modified KT method can be used with relatively high conversion data. This modified methods does not suffer from reindexing errors,

and can be used with relatively high conversions [27]. The reactivity ratios of all four copolymer systems determined by the above methods are summarized in Table 3. This indicates that the structure of ester substituents has no affects the reactivity of monomers in the investigated copolymerization systems.

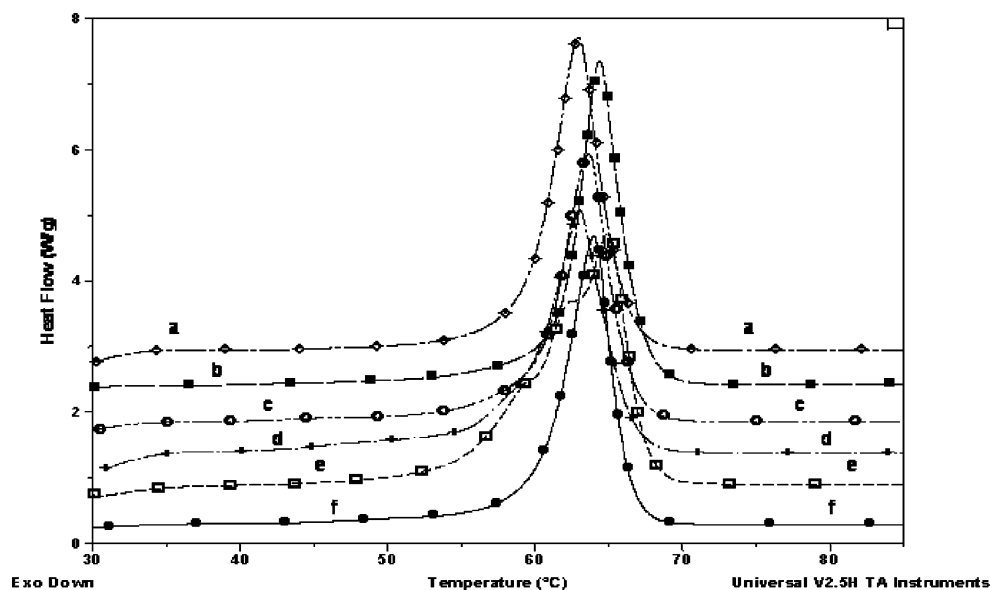
Differences in the values of the reactivity ratios obtained by both methods are expected according to the data generally reported [28–30] and inaccuracies have been well established in the use of linear estimation methods [31, 32]. Reactivity ratios are usually estimated by using procedures based on statistically valid error-in-variables model (EVM). The 95% confidence limits for the above estimates were calculated according to the standard procedures given by Kelen-Tüdös. Considering the joint confidence limits, it is recommended [27] that an non linear least square (NLLS) method or Kelen-Tüdös modified method may be used to determine reliable reactivity ratio values.

For a system with the simple binary copolymerization method, Kelen-Tüdös introduced a quantitative measure of the confidence, δ , which is defined by the relative value of confidence intervals:

$$\delta = (\Delta r_1 \Delta r_2 / r_1 r_2)$$

In a high conversion system, Kelen-Tüdös defined a class I system as that is strictly linear and has a δ value < 1 . For the present copolymerization systems, the δ values determined by the Kelen-Tüdös procedure are in the range of 0.15–0.40. The correlation coefficients of the systems are also in the range of 0.94–0.98 indicating that the copolymerization deviates slightly from ideal copolymerization. This also categorized the copolymerization systems as class I copolymer as defined by Kelen and Tüdös [29].

Fig. 5 DSC curves under nitrogen at the heating rate of 10°C/min of VA-DDF copolymer system. Mole ratio of [VA]: [DDF], (\diamond)=10.0:1.0; (\bullet)=5.0:1.0; (+)=3.0:1.0; (\blacksquare)=1.5:1.0; (\square)=1.0:1.0; (\circ)=0.5:1.0



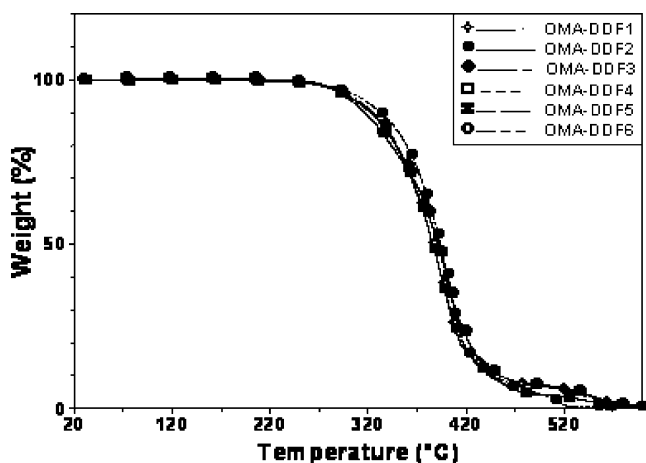


Fig. 6 TGA curves under nitrogen at the heating rate of 10°C/min of VA-DDF copolymer system. Molar ratios of [OMA]:[DDF] for: (●)=10.0:1.0; (⊗)=5.0:1.0; (□)=3.0:1.0; (◆)=2:1; (★)=1.0:1.0; (◇)=0.5:1.0

Thermal properties

When the polymers are used as PPDs/FIs for the transportation of crude oils, the polymers encounter temperature far excess lower critical solution temperature in the course of their lifetime. Therefore, thermal properties of the polymers against thermal stress are of great importance. Hence the goal of this study was to determine thermal degradation behavior of copolymers of dialkyl fumarate and the thermal stability of polymers was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC studies showed that poly(fumarates) typically do not show a glass transition temperature (T_g) below their degradation temperature [7, 32]. This observation is also valid for the copolymers prepared in this study. From DSC measurements, melting endothermic peaks were observed for the copolymer systems. Typical DSC endotherms for the second heating scan of the VA-DDF copolymer system are shown in Fig. 5. The melting point (mp) and the heat capacity of copolymers were determined from the endothermic peaks and the values are shown in Table 1. The melting behaviour of copolymers can be

ascribed to the crystallization of alkyl chains. All polymers exhibit a single peak indicating the formation of random copolymers. The melting point and heat capacity values were almost constant, regardless of the feed composition of monomer pair, MW and MWD of resulting copolymers.

TGA which measures the weight loss kinetics at elevated temperatures has been used to predict the stability of polymeric materials because it is very simple and accurate [33]. The effect of alkyl groups on the thermal degradation kinetics of long chain poly(alkyl acrylates) and its copolymers has been extensively studied. The thermal degradation occurs by hemolytic scission followed by inter- and intramolecular transfer reactions [34]. The TGA study of fumarate based copolymer systems under nitrogen atmosphere supports apparent single-step decomposition and the decomposition starts above 220°C. Above 350°C, where the main mass loss occurs, random main chain scission can also occur. The decomposition curves of OMA-DDF system are shown in Fig. 6. From the TGA curves, it can be seen that the degradation mechanism of copolymers is probably similar to that of the polymers of *n*-alkyl (meth) acrylates. Thermal decomposition of poly(alkyl acrylates) generates radicals that would abstract tertiary hydrogen atoms from the main chain, resulting in the formation of resonance stabilized radical and that all major decomposition reactions in poly(alkyl acrylates) would be initiated by this radical [35]. At temperatures above 350°C, there is sufficient energy in the system for the random main chain scission of the C–C bonds to occur [36]. Furthermore, the copolymer systems leave nearly no residue at and above 550°C. There are also no relevant changes in the shape and size of the TGA curves with different heating rates. To make an accurate quantitative prediction of thermal degradation of copolymers, the information of the underlying chemical mechanisms is insufficient [37]. Therefore, the development of a molecular-level understanding of the thermal degradation of polymers is an increasingly important area of research. The overall thermal degradation activation energies (E_a) of the copolymer samples were calculated from non-isothermal TG curves using non-

Table 4 Activation energies and correlation Coefficients of copolymers of di-*n*-docosyl fumarate with vinyl acetate, *n*-octadecyl acrylate, *n*-docosyl acrylate and *n*-octadecyl methacrylate by various methods

Copolymer systems	Temperature range (°C)	Activation energies, E (kJ mol ⁻¹) and correlation coefficients, r					
		Freeman and Carroll		Flynn and Wall		Coats and Redfern	
		E	r	E	r	E	r
VA-DDF	220.00–400.00	87.6	0.96	79.5	0.94	75.8	0.94
OA-DDF	220.00–400.00	81.9	0.95	74.2	0.96	68.4	0.94
DA-DDF	220.00–400.00	90.1	0.94	80.3	0.93	74.9	0.92
OMA-DDF	220.00–400.00	98.9	0.95	88.2	0.94	81.8	0.94

mechanistic equations of Freeman and Carroll [38] Flynn and Wall [39] and Coats and Redfern [40] at heating rates of 2.5, 5.0, 10.0 and 20.0°C min⁻¹. In this study a first order reaction was assumed to be applicable for the studied copolymerization systems, and all methods were evaluated assuming first order kinetics. The results are found to be in good agreement with each other.

Differential method of Freeman and Carroll [38]

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

$$\log[Q(dw/dT)/W_r] = -E/2.303RT + \log A$$

where, $W_r = W_o - W_t$, W_o is the total mass loss in the decomposition process, W_t is the total weight loss at any time t , Q is the constant heating rate which is 10°C min⁻¹ (4.66°K min⁻¹), A is the Arrhenius pre-exponential factor, R is the universal gas constant, and E is the activation energy. E and A can be calculated from the slope and intercept, respectively.

Differential Flynn and Wall equation [39]

The simplified differential rate expression and weight loss-time equation of the Flynn and Wall can be represented in the form of

$$\log[(dw/dT)/(W_o - W_t)^n] = -E/2.303RT + \log A$$

where the terms have the same meaning as that of the Freeman and Carroll equation. 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 the 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.

Integral method of Coats and Redfern [40]

For a first-order reaction process, Coats and Redfern derived the following relation by using a series of approximations. The final results may be expressed as:

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

Where β is the fractional decomposition and other terms have the same meaning as that of the Freeman and Carroll equation. Since $(1 - 2RT/E) \approx 1$, a plot of the left hand side of the equation versus $1/T$ should result a straight line with a slope of $-E/2.303RT$.

Table 4 summarizes the activation energy obtained by three different methods examined in this work. These

values are compared favourably with the literature values reported for copolymers containing *n*-alkyl acrylate with pendent alkyl side chains [12]. The thermal degradation profiles indicated that the thermal stability of the copolymer systems follow the order OMA-DDF > DA-OMA > OA-DDF > VA-DDF. Table 4 also provides that the degradation mechanism can be approximated by first order kinetics, since the results obtained from Flynn-Wall method closely match those of other two methods. In Flynn-Wall method no assumption about the order of the reaction is made for calculations of activation energies. If the degradation pattern deviates from the first order, then the other methods would give quite different values for activation energies. The different analysis models are in agreement for determination of activation energies associated with the degradation.

Conclusion

Well defined copolymers containing dialkyl fumarate were prepared using radical initiator. The resultant copolymers were analyzed by composition and molecular weight. In radical copolymerization of di-*n*-docosyl fumarate with vinyl acetate and *n*-alkyl (meth)acrylates, monomer reactivity ratios of the comonomers supported the occurrence of successive propagation of DDF, which does not give high polymer in radical homopolymerization. It showed that introduction of higher alkyl pendent side chains on the copolymer backbone adopt more compact packing mode and thus have higher regularities, which results higher attraction energy. The molecular weight of polymers produced increased as the bulkiness of the ester substituents decreased. The polymers obtained are colorless powders and undergoes one step degradation at nearly 350°C. Exhibiting a single step degradation mechanism, the data were analyzed using three different techniques that have been reported in the literature for analysis of dynamic TGA data. WAXD has revealed that polymers having long flexible *n*-alkyl side chains crystallize into layered structures in which the rigid backbones form backbone layers and the side chains form a separated crystal region.

Acknowledgment The authors wish to thank Dr P. G. Rao, Director, NEIST - Jorhat for permission to publish the results.

References

1. Matsumoto A, Sano Y, Yoshioka M, Otsu T (1996) Radical polymerization of dicyclohexyl fumarate and its derivatives as studied by electron spin resonance spectroscopy. *Eur Polym J* 32:1079–1085

- Matsumoto A, Nakagawa E (1999) Evaluation of chain rigidity of poly(diisopropyl fumarate) from light scattering and viscosity in tetrahydrofuran. *Eur Polym J* 35:2107–2113
- Yamada B, Yoshikawa E, Shiraishi K, Miura H, Otsu T (1991) Determination of absolute rate constants for radical polymerization of diisopropyl fumarate based on a quantitative scavenging of propagating radical. *Polymer* 32:1892–1896
- Yamada B, Yoshikawa E, Otsu T (1992) Observation of steric effect in radical polymerization of dialkyl fumarates by spin trapping with 2, 4, 6-tri-tert-butyl nitrosobenzene. *Polymer* 33:3245–3251
- Matsumoto A, Sano Y, Yoshioka M, Otsu T (1996) Kinetic study of radical polymerization of dialkyl fumarates using electron spin resonance spectroscopy. *J Polym Sci Part A: Polym Chem* 34:291–299
- Yoshioka M, Matsumoto A, Otsu T (1991) *Meso* and *racemo* additions in propagation for radical polymerization of dialkyl fumarates I. Stereoregularity of poly(dialkyl fumarate)s. *Polymer J* 23:1191–1196
- Cochin D, Laschewsky A, Pantoustier N (2000) New substituted polymethylenes by free radical polymerization of bulky fumarates and their properties. *Polymer* 41:3895–3903
- Matsumoto A, Tarui T, Otsu T (1990) Dilute solution properties of semiflexible poly(substituted methylenes): Intrinsic viscosity of poly(diisopropyl fumarate) in benzene. *Macromolecules* 23:5102–5105
- Yoshioka M, Matsumoto A, Otsu T (1992) Opening mode in the propagation of dialkyl fumarates and maleates as 1, 2-disubstituted ethylenes in radical polymerization. *Macromolecules* 25:2837–2841
- Inomata K, Sakamani Y, Nose T, Sasaki S (1996) Solid-state structure of comb-like polymers having n-octadecyl side chains I. CocrySTALLIZATION of side chain with n-octadecanoic acid. *Polymer J* 28:986–991
- Inomata K, Sakamani Y, Nose T, Sasaki S (1996) Solid-state structure of comb-like polymers having n-octadecyl side chains II. Crystalline-amorphous layered structure. *Polymer J* 28:992–999
- Sarmah D, Baruah SD (2003) Synthesis, characterization, and thermal properties of copolymers of behenyl acrylate and behenyl fumarate. *J Appl Polym Sci* 90:2721–2726
- Al-Arbash AH, ElSagheer FA, Ali AAM, ElSabee MZ (1999) Glass-transition temperature of polydialkyl fumarate copolymers. *J Polym Sci Part A: Polym Chem* 37:1839–1845
- Sato T, Shimooka M, Seno M (1998) Radical polymerization of ortho-(1, 3-dioxolan-2-yl)phenyl ethyl fumarate involving intramolecular hydrogen abstraction and ring opening of cyclic acetal. *J Polym Sci Part A: Polym Chem* 36:563–572
- Yoshioka M, Otsu T (1992) Kinetic studies on the radical polymerization of isopropyl tert-butyl fumarate initiated with 2, 2'-azobis(isobutyronitrile) and dimethyl 2, 2'-azobis(isobutyrate): rates of addition and termination of the primary radicals. *Macromolecules* 25:559–562
- Hirano E, Zetterlund PB, Takaoka T, Yamada B, Buckley R, Jenkins ID, Busfield WK (2003) Initiation in the free radical (co) polymerization of dialkyl fumarates and dicyclohexyl fumarate/tert-butyl vinyl ether investigated by a nitroxide trapping technique. *Polym Int* 52:1683–1688
- Ohnishi M, Uno T, Kubo M, Itoh T (2009) Synthesis and radical polymerization of diisymmetric fumarates with alkoxyethyl and bulky siloxy groups. *J Polym Sci Part A: Polym Chem* 47:420–433
- Cortizo MS, Laurella S, Alessandrini JL (2007) Microwave-assisted radical polymerization of dialkyl fumarates. *Rad Phys Chem* 76:1140–1146
- Grubisic Z, Rempp P, Benoit H (1967) A universal calibration for gel permeation chromatography. *Polym Lett* 5:753–759
- Odian G (2002) Principles of polymerization, 3rd edn. Wiley, Singapore, chapter 6
- Peng HY, Yang YS, Qi GR (2002) n-Dioctadecyl fumarate-vinyl acetate copolymer: Synthesis, characterization and application as flow improver for oils. *Petrol Sci Tech* 20:65–75
- Laschewsky A, Cochon D (1994) Synthesis of homopolymers and copolymers of bulky fumarates, and their spreading behaviour in insoluble monolayers. *Eur Polym J* 30:891–899
- Zhengzhe S, Jiping X (1993) Structures and properties of dialkyl fumarates polymers. *Eur Polym J* 29:919–921
- McFarlane RC, Reilly PM, O'Driscoll KF (1980) Comparison of the precision of estimation of copolymerization reactivity ratios by current methods. *J Polym Sci Polym Chem Ed* 18:251–257
- Pitchumani S, RamiReddy C, Rajadurai S (1982) Reactivity ratios of ethyl acrylate, n-butyl methacrylate copolymer system by ¹H-NMR. *J Polym Sci Polym Chem Ed* 20:277–282
- Brar AS, Singh G, Sankar R (2004) Analysis of quaternary carbon resonances of vinylidene chloride/methyl acrylate copolymers. *Eur Polym J* 40:2679–2688
- Kress AO, Mathias LJ, Cei G (1989) Copolymers of styrene and methyl α -(hydroxymethyl)acrylate: Reactivity ratios, physical behavior, and spectral properties. *Macromolecules* 22:537–546
- Braun D, Czerwinski WK, Disselhoff G, Tüdös F, Kelen T, Turcsanyi B (1984) Analysis of the liner methods for determining copolymerization reactivity ratios, VII. *Angew Makromol Chem* 125:161–205
- Braun D, Czerwinski WK, Tüdös F, Kelen T, Turcsanyi B (1990) Analysis of the liner methods for determining copolymerization reactivity ratios, VIII. *Angew Makromol Chem* 178:209–219
- Bauduin G, Boutevin B, Belbachir M, Maghabar R (1995) Determination of reactivity ratios in radical copolymerization: A comparison of methods for a methacrylate/N-vinylpyrrolidone system. *Macromolecules* 28:1750–1753
- Dube M, Sanayei RA, Penlidis A, O'Driscoll KF, Reilly PM (1991) Microcomputer program for estimation of copolymerization reactivity ratios. *J Polym Sci Polym Chem* 29:703–708
- Otsu T, Yasuhara T, Matsumoto A (1988) Synthesis, characterization, and application of poly[substituted methylene]s. *J Macromol Sci Chem A* 25:537–554
- Kodera Y, McCoy BJ (2002) Distribution kinetics of polymer thermogravimetric analysis: a model for chain-end and random scission. *Energy Fuels* 16:119–126
- Konaganti VK, Madras G (2009) Photooxidative and pyrolytic degradation of methyl methacrylate-alkyl acrylate copolymers. *Polym Degrad Stab* 94:1325–1335
- Cameron GG (1964) The thermal degradation of poly(methyl Methacrylate). *J Polym Sci B* 2:693–697
- Milovanović M, Bošković R, Tošić T, Katsikas L, Popović IG (2006) The thermal degradation of poly(diethyl fumarate). *Polym Degrad Stab* 91:3221–3229
- Stoliarov SI, Westmoreland PR, Nydem MR, Forney GP (2003) A reactive molecular dynamics model of thermal decomposition in polymers: I. Poly(methyl methacrylate). *Polymer* 44:883–894
- Freeman ES, Carroll B (1958) The application of thermoanalytical techniques to reaction kinetics. The thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate. *J Phys Chem* 62:394–397
- Flynn JH (1991) A general differential technique for the determination of parameters for $d(\alpha)/dt=f(\alpha) A \exp(-E/RT)$ energy of activation, preexponential factor and order of reaction (when applicable). *J Thermal Anal* 37:293–305
- Coats AW, Redfern JP (1964) Kinetic parameters from thermogravimetric data. *Nature* 201:68–69