

Study on the Synthesis, Characterization, and Kinetic of Bulk Polymerization of Disproportionated Rosin (β -Acryloyl Ethyl) Ester

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ABSTRACT: Disproportionated rosin ((β -acryloyl ethyl) ester (DR-2-HEA) was synthesized by esterification of disproportionated rosin (DR) with 2-hydroxyethyl acrylate (2-HEA) and evaluated by FTIR spectroscopy, GC/MS, ¹³C-NMR spectroscopy. Kinetics parameters of bulk polymerization of DR-2-HEA in the presence of initiator AIBN was studied by using DSC. It has been assumed that the process of polymerization obey n th order empirical kinetic model to evaluate the kinetic parameters. The relative molecular weight and glass transition temperature of polymer of DR-2-HEA at different temperature was measured by GPC and DSC, respectively. The results showed that the

temperature had no significant effect on the enthalpy of polymerization and the velocity of polymerization increased by the increase of temperature. DSC experimental data fit the simulation well while the reacted fraction (α) in the interval of $0.4 < \alpha < 1$. The polymer of DR-2-HEA is oligomer. The molecular weight and T_g did not affect by polymerization temperature. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3757–3765, 2009

Key words: disproportionated rosin (β -acryloyl ethyl) ester; DSC; kinetics; polymerization

INTRODUCTION

Rosin is a solid resinous mass obtained naturally from the oleoresin of pine trees. It is principally composed of various resin acids, fatty acids, and a small amount of non-acidic components. The resin acids are the major portion of rosin with a basic molecular structure of one carboxyl and two double bonds on a hydrogenated phenanthrene ring. The predominant resin acid in natural rosin is abietic acid which has the empirical formula $C_{20}H_{30}O_2$. Carboxyl and two double bonds are the important functional groups of rosin and the center of chemical reactions.¹ Owing to their three-cyclic structure, resin acids present high chemical and thermal stabilities. Rosin and its derivatives are widely used in paints, varnishes, printing inks, chewing gums, and cosmetics.²

Polymerization can occur on the conjugated double bonds of abietic acid by radiation, heat, or catalyza-tion, and generally only dimmers and a few trimers were obtained.³ Owing to the retardation on radical polymerization by conjugated double bonds, rosin has to be chemically modified before it copolymerizes with vinyl monomers to obtain rosin-based polymers.⁴

Through catalyzed disproportionation, one molecule of hydrogen is lost from the abietic acid and the steady benzene ring structure can be obtained. It is the main character of disproportionated rosin (DR).^{2,5} To put DR in polymer synthesis, DR has to be transformed into unsaturated monomers containing vinylic^{5–10} or acrylic^{11–14} groups.

The purpose of this article was to present the synthesis, characterization, and kinetic of bulk polymerization of disproportionated rosin (β -acryloyl ethyl) ester (DR-2-HEA). DR-2-HEA was synthesized by esterification of DR with 2-hydroxyethyl acrylate (2-HEA). The acrylate groups on DR-2-HEA can be used for free-radical bulk polymerization for the application of heat activated adhesives and UV curing resin. However, the kinetics of bulk polymerization of disproportionated rosin (β -acryloyl ethyl) ester (DR-2-HEA) had not been reported so far.

Differential scanning calorimetry (DSC) is a basic approach for thermal analysis, so the kinetic data can be obtained by analyzing DSC curves for the exothermic nature of bulk polymerization of DR-2-HEA.^{15,16} In this article, the isothermal DSC was

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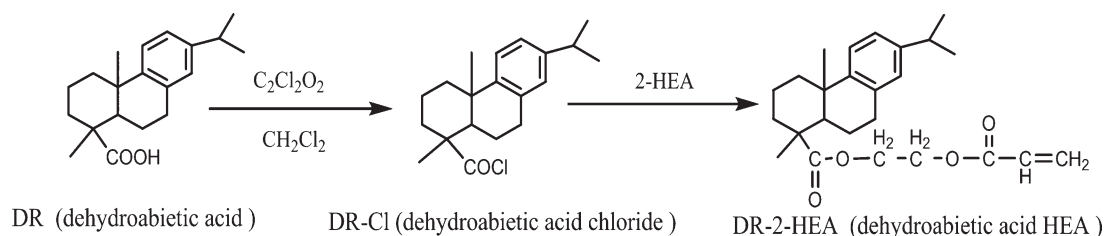


Figure 1 Schematic synthesis route of DR-2-HEA.

used to investigate the kinetics model and parameters for bulk polymerization of disproportionated rosin (β -acryloyl ethyl) ester (DR-2-HEA) in the presence of initiator AIBN. Isothermal methods of study offer the advantage of greater simplicity of interpretation of data.

EXPERIMENTAL

Materials

Disproportionated rosin (N grade) was obtained from Wuzhou Chemicals, China. 2-Hydroxyethyl acrylate (stabilized, 97%) was obtained from ARCOS. Oxalyl chloride ($C_2Cl_2O_2$) was obtained from Sino-pharm Chemical Reagent C, China. Azobisisobutyronitrile (AIBN, analytical grade) was obtained from Shanghai No.4 Reagent & H.V. Chemical Co, China. All the chemicals were of analytical grade and used as received.

Synthesis of disproportionated rosin (β -acryloyl ethyl) ester (DR-2-HEA)

Disproportionated rosin (10 g, 0.033 mol) was dissolved in 25 g dichloromethane in a four-neck glass reactor fitted with a condenser, a stirrer, and a temperature control arrangement. $C_2Cl_2O_2$ (5.66 g, 0.0363 mol) and a few drops of DMF (dimethyl formamide) were added. After the solution was refluxed for 3 h, excessive $C_2Cl_2O_2$ was excluded by azeotropic distillation with dichloromethane and disproportionated rosin chloride was obtained. Then pyridine (4.5 g, 0.057 mol) and 2-HEA (4.39 g, 0.037 mol) were added. The reaction mixture was heated at 50°C for 4 h and then 30 g petroleum ether was added. DR-2-HEA, a yellow high viscosity liquid was obtained after the solution was filtrated to remove the precipitation of pyridine hydrochloride and distilled under reduced pressure.

Measurements

Fourier transform infrared spectroscopy (FTIR) was used for DR-2-HEA characterization. Infrared spectra were recorded in KBr pellets using Nicolet 550 FTIR system.

Gas Chromatography-Mass Spectrometry (GC/MS) analysis was carried out on Agilent 6890N Network GC system and Agilent 5973 mass selective detector. GC was performed on Agilent HP-5 capillary column (30 m \times 0.25 mm \times 0.25 μ m) with an oven temperature of 200°C (2 min) \rightarrow 250°C (5°C/min, 10 min). Carrier gas was He at a flow-rate of 1.0 ml/min. The temperature of injection port was 250°C. A 0.2 μ l of sample was injected into the GC system. The mass spectrometer was operated in electron ionization mode. The temperature of ion source was 230°C. The ion of the investigated compounds was detected in the range from 10 to 800 amu. The compound was dissolved in tetrahydrofuran and the amount of the components respectively was determined by peak area normalization method.

The ^{13}C -NMR spectra of DR and DR-2-HEA were scanned on Bruker DRX500 with $CDCl_3$ as solvent.

Gel permeation chromatography (GPC) was performed at room temperature on a Waters 1515 equipped with a Waters 2487 absorbance detector and Waters 2414 refractive index detector. The columns were STYRAGEL HR1, HR2 (300 \times 7.8 mm) from Waters. HPLC grade THF was used as eluent at a flow rate of 1 ml/min. THF and samples were filtered over a filter with pore size of 0.45 μ m (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, USA). The columns were calibrated by using polystyrene standards with molecular weights in the range of 580 and 1.96×10^4 g/mol (with NMD for 1.02–1.11). The molecular weight and molecular weight distribution were determined by Waters 2487 absorbance detector and Waters 2414 refractive index detector. Waters Breeze GPC software (Version 5.3.1.4) was utilized for acquisition and analysis of data.

Study on bulk polymerization of disproportionated rosin (β -acryloyl ethyl) ester (DR-2-HEA) by DSC

A differential scanning calorimetry (Perkin Elmer Diamond DSC) equipped with an intracooler and supported by a computer for data acquisition and analysis was used for isothermal analysis of the bulk polymerization. For this purpose, 2–3 mg mixture of DR-2-HEA with AIBN was enclosed in aluminum pans. A dry nitrogen flow was used as protective gas. The temperature was quickly increased to the

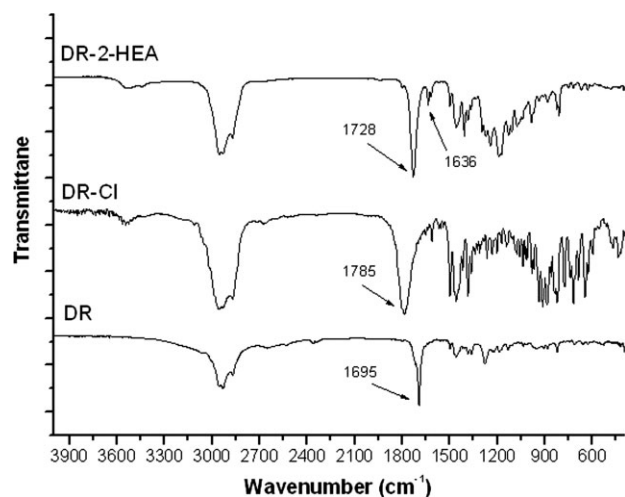


Figure 2 FTIR spectra from DR, DR-Cl, DR-2-HEA

designed point at rate of 100 K/min. By isothermal approach, the polymerization process was observed, and the effects on the enthalpy by the change of temperature or time were investigated. And the sec-

ond scan of the sample was carried out for measurement of the glass transition temperature of the polymer of DR-2-HEA from -50°C to 50°C at rate of 20 K/min.

RESULTS AND DISCUSSION

Synthesis and characterization of DR-2-HEA

DR is one of the important rosin derivatives. It was reported that the component mainly consisted of dehydroabietic acid and dihydropimaric acid.²

Synthesis route for DR-2-HEA was showed in Figure 1. DR was used as starting material, reacting with $\text{C}_2\text{Cl}_2\text{O}_2$ to obtain the DR-Cl. DR-Cl was easily reacting with hydroxyl of 2-HEA at room temperature. It could guarantee the 2-HEA and DR-2-HEA stable in preparation process.

FTIR spectroscopy was used to analyze the chemical changes during the synthesis of DR-2-HEA. Figure 2 showed a detail of FTIR spectra corresponding to DR, DR-Cl, and DR-2-HEA. Though a precise identification of all bands was difficult due to the nature of DR,

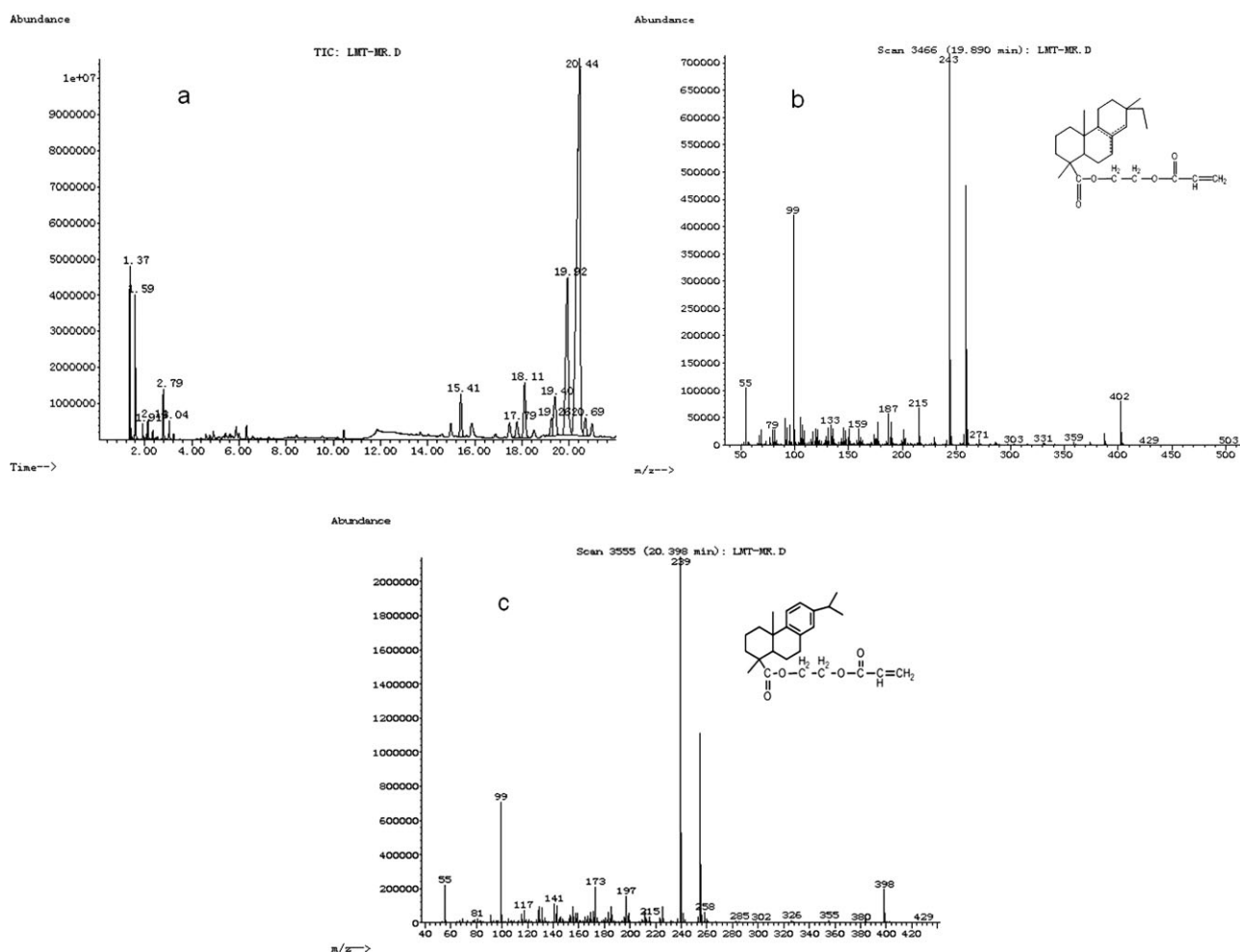


Figure 3 (a) GC spectrum of methyl DR-2-HEA. (b) Mass spectrum of component at 19.92 min. (c) Mass spectrum of component at 20.44 min..

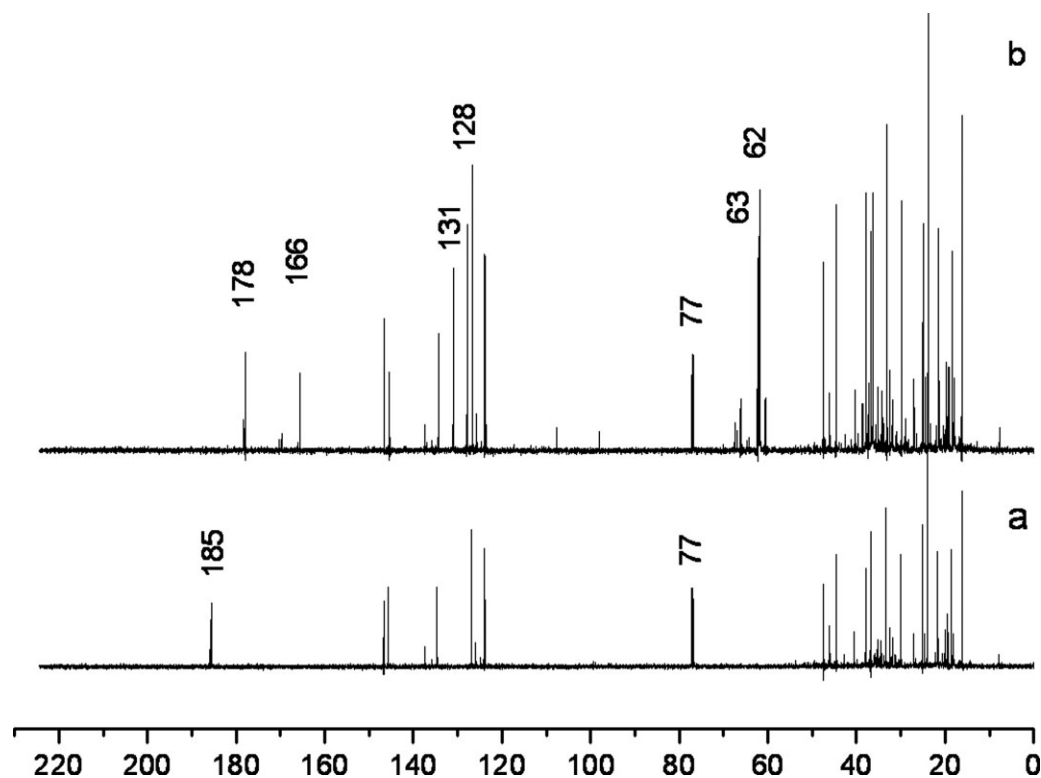


Figure 4 ^{13}C -NMR spectra of DR (a) and DR-2-HEA (b).

the disappearance of 1695 cm^{-1} band, which was related to $-\text{COOH}$ from DR (Fig. 2), can be clearly observed after complete reaction with $\text{C}_2\text{Cl}_2\text{O}_2$. At the same time, the appearance of 1785 cm^{-1} band indicates that DR-Cl was obtained. In the spectra of DR-2-HEA (Fig. 2), the characteristic absorption at 1728 cm^{-1} ($\text{C}=\text{O}$) suggested the formation of ester. Though the presence of ester group in the structure of 2-HEA, the disappearance of 1785 cm^{-1} from Fig. 2 (DR-2-HEA) indicated that the ester group was overlapped. Also, the appearance of 1636 cm^{-1} signal related to $\text{C}=\text{C}$ obtained from 2-HEA skeleton.

Starting material DR was first identified by GC/MS analysis. Before analyses, Methyl DR was prepared by using TMAH (tetramethyl ammonium hydroxide) as reactant in the solution of methanol. Due to the presence of a carboxylic acid group, DR could not be gasified without changing its chemical structure.¹⁷ The composition of DR can be deduced from the results of GC-MS of methyl DR. Referring to NIST (National Institute of Standards and Technology) mass spectrometry database search, the components of methyl DR were identified as methyl dihydropimic acid methyl dehydroabietate, respectively. Therefore, it was concluded that the main chemical composition of DR are dihydroopimic acid (20.91 wt %) and dehydroabietic acids (60.51 wt %), and the rest of components (18.58 wt %) are other types organic acid and related neutral materials.^{3,18}

The GC/MS spectra of DR-2-HEA were showed in Figure 3. Components with retention time at 19.92 min and 20.44 min in Figure 3(a) were confirmed by MS to be (β -acryloyl ethyl) esters of dihydropimic acid and (β -acryloyl ethyl) esters of dehydroabietic acids by molecular ion peak, respectively. They were the main components of DR-2-HEA. Figure 3(b) showed the MS spectrum of the component with retention time at 19.92 min. It can be seen that molecular ion peak m/z 402 is assigned to the (β -acryloyl ethyl) esters of dihydropimic acid. The peaks of 177^+ , 187^+ , 243^+ , and 258^+ are the fragments of dihydropimic acid groups. The peak at 258^+ is due to removed of $\text{HCOOCH}_2\text{CH}_2\text{OOCCH}=\text{CH}_2$ anion from the base peak of 402. The peak of 99^+ is the fragment of $\text{HCOOCH}_2\text{CH}_2\text{OOCCH}=\text{CH}_2$.

Figure 3c is the MS spectrum of the component with retention time at 20.44 min. The ion peak is similar to Figure 3(b). The peaks at 173^+ , 185^+ , 239^+ , and 254^+ are also the characteristic of the fragments of dehydroabietic acid groups. The 254^+ peak is due to removing of $\text{HCOOCH}_2\text{CH}_2\text{OOCCH}=\text{CH}_2$ anion from the base peak of 398. The peak of 99^+ is the fragment of $\text{HCOOCH}_2\text{CH}_2\text{OOCCH}=\text{CH}_2$.^{19,20}

The obtained DR-2-HEA was also analyzed by ^{13}C -NMR spectroscopy. Figure 4 showed the ^{13}C -NMR spectra of DR and DR-2-HEA.

As seen in Figure 4, the peak at 185 ppm in the spectra a represents the carbon of carboxylic groups,

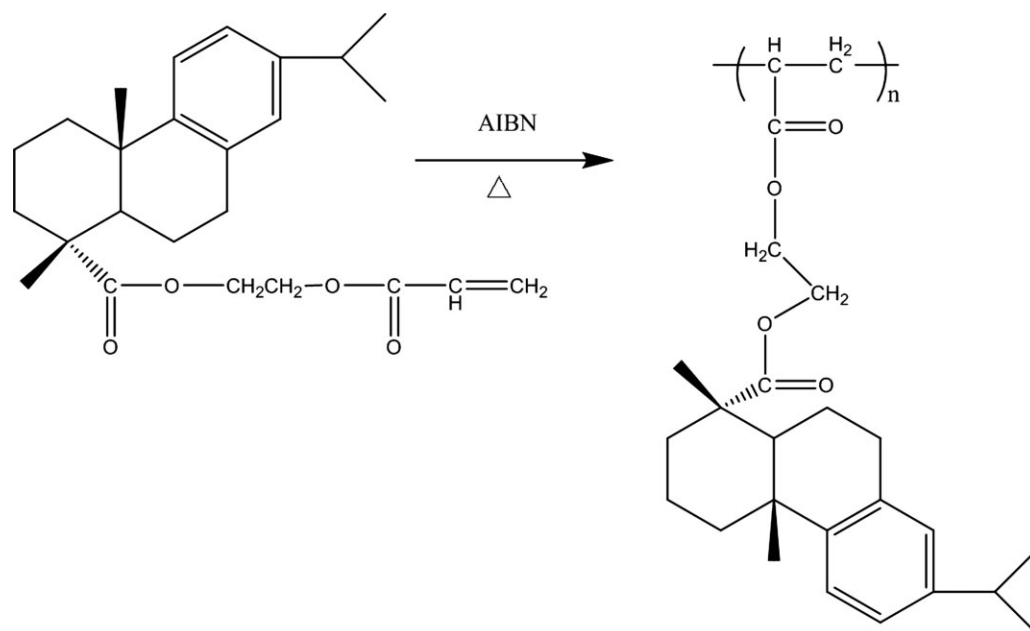


Figure 5 Bulk polymerization of DR-2-HEA.

which disappeared in the spectra **b** and as a result of the appearance of the peak at 178 ppm, indicated that the esterification of DR occurred in the structure of DR-2-HEA. This signal was well correlated to the observed FTIR spectra (Fig. 2) at 1695 cm^{-1} and 1728 cm^{-1} . Comparing the spectrum **b** with spectrum **a**, the appearance of peak 166 ppm, 131 ppm, 128 ppm, 63 ppm, and 62 ppm were characters of HEA fractions of DR-2-HEA.

Kinetic parameters for the study on bulk polymerization by DSC

The determination of kinetic parameters characterizing the process of bulk polymerization of DR-2-HEA was obtained by DSC measurements. The scheme of polymerization was formulated in Figure 5. To describe the kinetics of free-radical bulk polymerization, the Arrhenius equation combines with Borchardt-Daniels approach was used as the model.^{16,21}

$$\frac{d\alpha}{dt} = A \exp(-E_a/RT)(1 - \alpha)^n \quad (1)$$

$$k(T) = A \exp(-E_a/RT) \quad (2)$$

where $d\alpha/dt$ is rate of reaction; A , preexponential factor; E_a , the activation energy; R , the universal gas constant; T , the absolute temperature; α , the reacted fraction ($0 < \alpha < 1$) and n , the reaction order.

The polymerization reaction can change the enthalpy of the system, the relationship between α and enthalpy is defined as

$$\alpha(t) = \Delta H_t / \Delta H \quad (3)$$

where ΔH_t is the amount of heat released by the reaction up to time t , ΔH is the total amount of heat released, calculated by interpolation of DSC isothermal signal

Substitution of values of $\ln A - \frac{E_a}{RT}$ and eq. (1) is converted into logarithmic form respectively results in

$$\ln(d\alpha/dt) = \ln k(T) + n \ln(1 - \alpha) \quad (4)$$

Plot of the data is obtained from the isothermal bulk polymerization of DR-2-HEA according to eq. (3). However, only the linearity of this plot of eq. (4) could reveal the kinetic parameters.

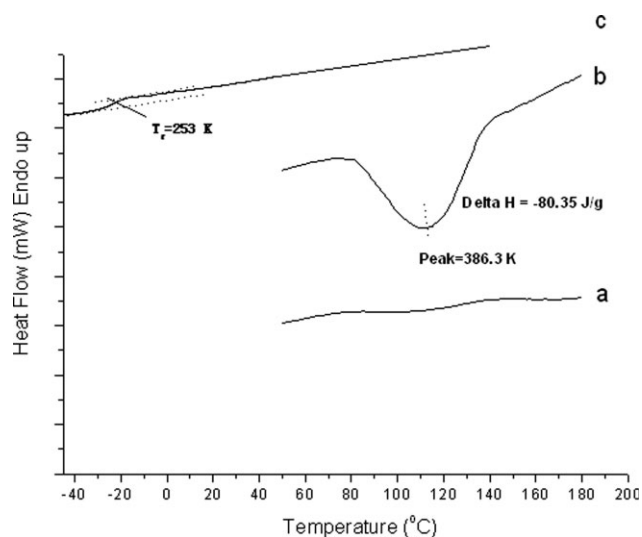


Figure 6 DSC curves of DR-2-HEA with or without AIBN.

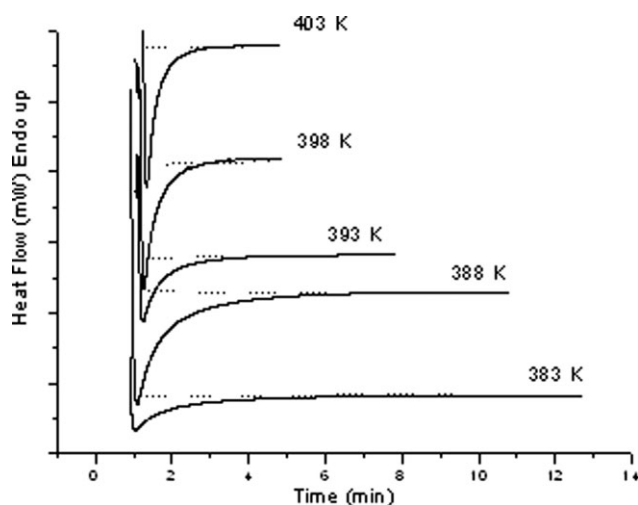


Figure 7 DSC curves of isothermal bulk polymerization.

The rate equations for isothermal bulk polymerization could be divided in two categories: n th and autocatalytic types. To simplify the process of determination of kinetic parameters and based on the high viscosity of DR-2-HEA, the research presented here assumed the n th type.²¹⁻²⁴ The general rate equation for n th type is

$$\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n \quad (5)$$

It is according with the eq. (4), so the order of the reaction and $k(t)$ can be calculated from the $\ln d\alpha/dt$ vs $\ln(1-\alpha)$ plot. Based on eq. (2), a plot of $\ln k(T)$ against $1/T$ should yield a linear relationship. Values for E_A and A is obtained.²⁵⁻²⁷

To select the proper temperature for the required isothermal experiments, DR-2-HEA with AIBN (2% wt %) was heat in DSC at 10 K/min between 30 and 180°C was carried out to see whether or not the polymerization could take place. A second scan was performed to determinate the glass-transition temperature (T_g) and confirmed the completion of polymerization.

Figure 6 showed that the peak exothermal temperature T_p was 386.3 K and the time for complete polymerization was 6 min in curve b with ΔH -80.35 J/g. However, there were no any heat flow in curve(a), which indicated that DR-2-HEA is stable without

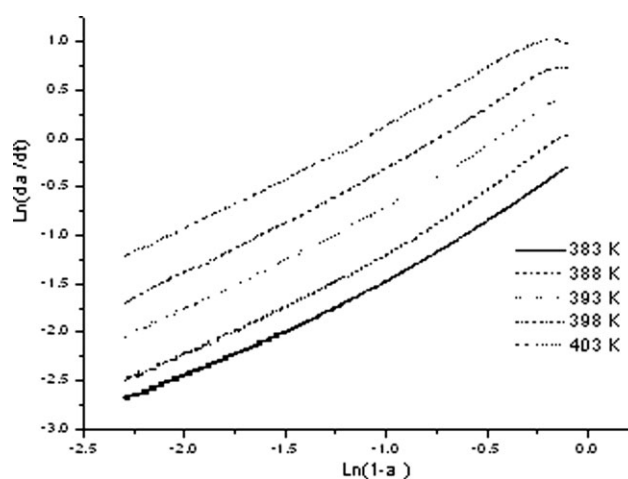


Figure 8 Relationship between $\ln(d\alpha/dt)$ and $\ln(1-\alpha)$.

initiator in raising temperature. By the second scan, there was an obvious T_g at 253 K in curve (c), which confirmed the complete polymerization.

According to the T_p of the dynamic mode of operation, 383K, 388K, 393K, 398K, and 403K were assigned for the isothermal bulk polymerization of DR-2-HEA in the presence of initiator AIBN for the determination of the kinetic parameters. It is assumed that the polymerization do not begin until it reached the assigned temperature at heating rate of 100 K/min. As shown in Figure 7, the area under the isothermal curve up to any time t represents the heat of the reaction at time t . The enthalpy was calculated by the software utility on Perkin Elmer Diamond DSC. The ΔH at different temperatures are given in Table I, it could be seen that there was little difference among the resulted values from the Figure 7. It suggests the complete polymerization for each temperature.

Figure 8 shows that there is linear fitting for the data of $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ for reactions at various temperatures in the interval of $0.1 < \alpha < 0.9$. It confirms the assumption that n th type can be used for the isothermal bulk polymerization of DR-2-HEA in present of AIBN.

A line ($0.1 < \alpha < 0.9$) is obtained by plotting in $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ having an intercept $k(T)$ and slope n . The value of n and $k(T)$ was listed in Table I, it is not remarkable difference for the value of n .

TABLE I
Kinetic Parameters of Isothermal Polymerization at Different Temperature

Temperature/(K)	Enthalpy ΔH /(J/g)	n	$\ln k(T)$	R^2
383	-80.17	1.07	-0.3353	0.9920
388	-81.22	1.14	0.0109	0.9916
393	-79.28	1.13	0.4709	0.9958
398	-78.91	1.14	0.8665	0.9972
403	-80.31	1.08	1.2316	0.9978

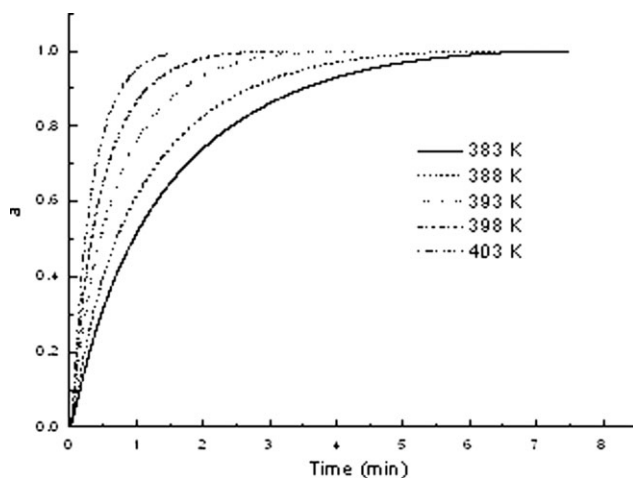


Figure 9 Relationship between polymerization degree and time.

Plotting $\text{Ln}k(t)$ and $1/T$ according of the logarithm of eq. (2), The linear equation could be described as: $y = -12308x + 31.779$, $R^2 = 0.9977$. Activation energy E_A and preexponential factor A were obtained. The value of E_A and A was 102.3 kJ/mol and $6.33 \times 10^{13} \text{ s}^{-1}$, respectively. So the eq. (1) can express as

$$\frac{d\alpha}{dt} = 6.33 \times 10^{13} \times \exp\left(-\frac{102.3 \times 10^3}{RT}\right) (1 - \alpha)^n \quad (6)$$

Effect of temperature on reaction rates of bulk polymerization

Based on eq. (3), the relationship between the reaction degree α and polymerization time for DR-2-HEA was showed in Figure 9. The results clearly show that at a given temperature, the reaction degree increased with increasing reaction temperature at isothermal approach, and the polymerization time shorten from 15 min to 4 min when the reaction temperature increased from 383 to 402 K.

The relationship of $d\alpha/dt$ versus time is shown in Figure 10 and the reaction rate increased quickly in initial stages of the polymerization. After the maximum reaction rate, it decreased slowly.²⁸ The curve of rate equation is similar to autocatalytic types for the curing of epoxy resin or unsaturated resin. However, it is quite different. For the free radical bulk polymerization, showed in Figure 11, there was an induction period in the interval of $0 < \alpha < 0.1$, the rate of free radical bulk polymerization increased with the increasing α . When the reacted fraction reached the interval of $0.1 < \alpha < 0.9$, the rate of polymerization decreased. It is a characteristic of the n th-order reaction. This was attributed to the high viscosity of DR-2-HEA during the polymerization, the decreased in the ability for diffusive movement of DR-2-HEA result in the decreased in the rate of

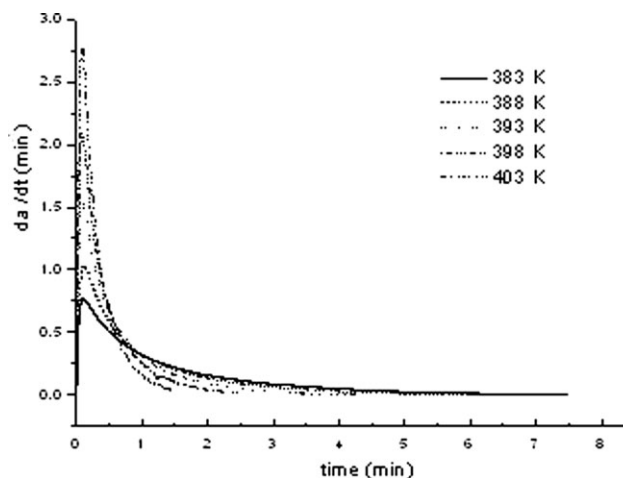


Figure 10 Relationship between polymerization rate and time.

polymerization with increase of α . It was in stage of diffusion control and also confirmed the polymerization obeyed the n th-order reaction rule.

Effect of temperature on T_g and molecular weight

The T_g and molecular weight of polymer of DR-2-HEA at the different temperature are presented in Table II. The polymer of DR-2-HEA is oligomer, and its molecular weight is less than 5000, which due to the steric hindrance of DR-2-HEA and there are still few amount of double bound in DR-2-HEA, this generally result in the low molecular weight of the polymer of DR-2-HEA. So DR-2-HEA is suitable for copolymerization with vinyl or acrylate monomer. T_g of polymer of DR-2-HEA at different temperature is not remarkable different and it is in agreement with the result of molecular weight. (β -acryloyl ethyl) esters of dehydroabietic acids, the main component of DR-2-HEA was extracted in the previous work, the glass transition temperature of polymer of

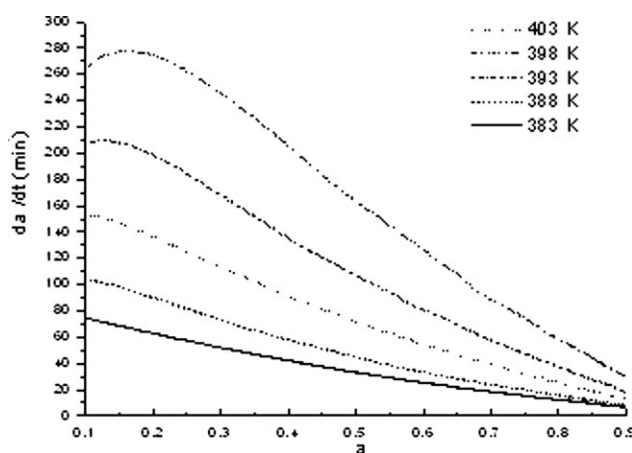


Figure 11 Relationship between polymerization rate and polymerization degree.

TABLE II
Properties of the Bulk Polymerization of Dr-2-HEA

Temperature(K)	T_g (°C)	Delta Cp (J/g°C)	M_w (g/mol)* 10^{-4}	M_n (g/mol)* 10^{-4}	M_w / M_n
383	-25.04	0.298	0.4763	0.4720	1.12
388	-21.75	0.260	0.4762	0.4220	1.11
393	-25.96	0.265	0.5034	0.4377	1.13
398	-27.19	0.266	0.4763	0.4135	1.14
403	-20.49	0.249	0.4589	0.3968	1.14

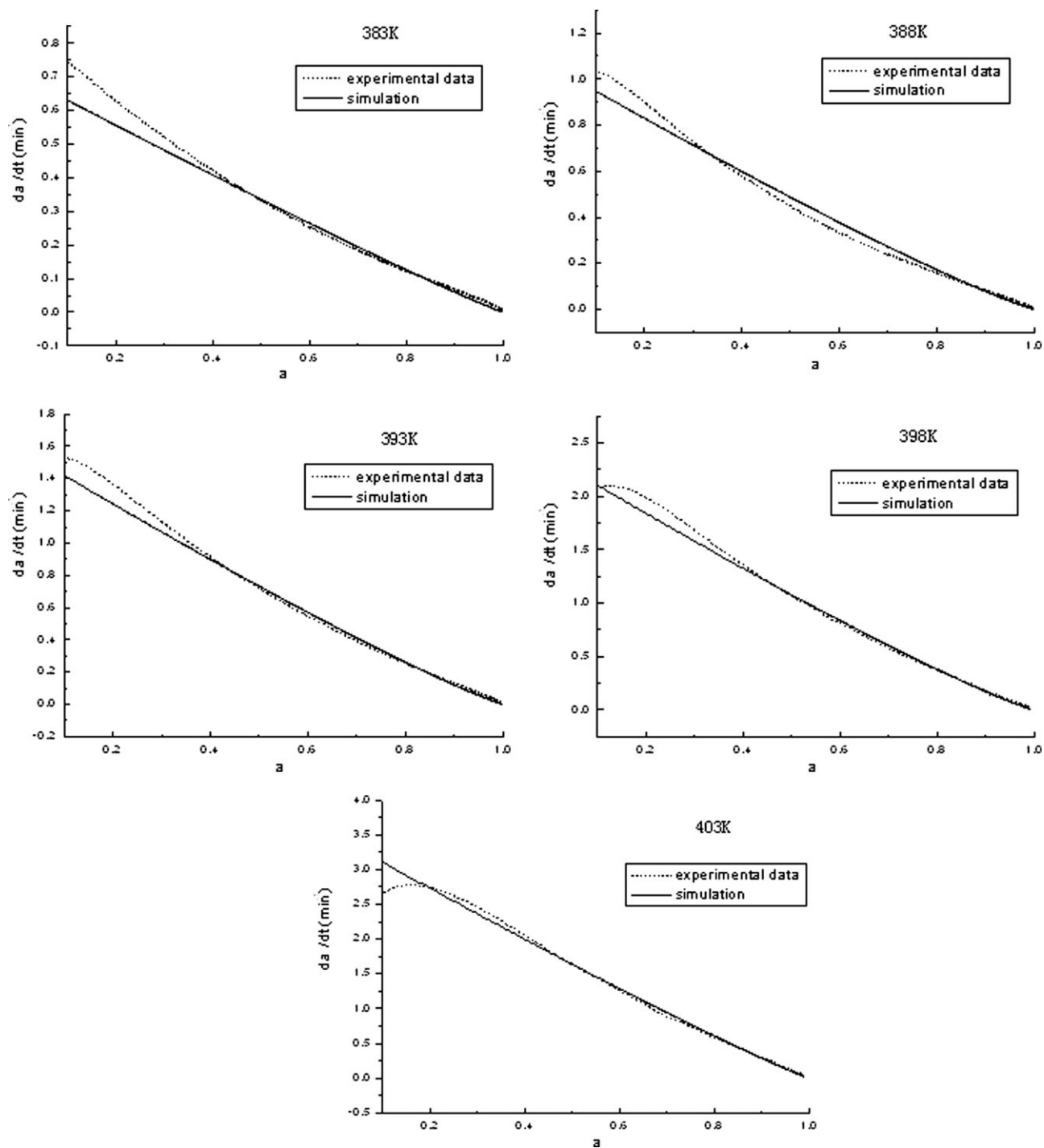


Figure 12 Comparison between experimental data and simulation.

(β -acryloxyethyl) esters of dehydroabiatic acids is 54.18°C ,¹⁴ it is different from the polymer of DR-2-HEA, it can be explained that the related neutral materials and few unreactive DR-2-HEA may play the role of plasticizer, so the T_g decreased.

Simulation of free radical bulk polymerization

Based on eq. (6), the simulation for a plot of $(d\alpha/dt)$ versus α at different temperature is showed on Figure 12. Compared with the experimental data obtain from the DSC, the experimental data does not fit with the simulation until the value of α reach 0.4 and the deviation of two lines decrease with the increase temperature of polymerization. The possible explanations of the deviation of experimental curve in Figure 12 is that the polymerization would enter into state of diffusion control rapidly at the high temperature due to the fast rate of polymerization which leading to the high viscosity of reaction medium. Therefore, the eq. (6) is more suitable to predict the bulk polymerization profiles of DR-2-HEA in the interval of $0.4 < \alpha < 1$.

CONCLUSIONS

Disproportionated rosin ((β -acryloxyethyl) ester (DR-2-HEA) was synthesized and characterized. The syntheses were carried out by esterification of disproportionated rosin (DR) with 2-hydroxyethyl acrylate (2-HEA) and the chemical changes occurring during the synthesis of DR-2-HEA has been evaluated by FTIR spectroscopy, GC/MS, ^{13}C -NMR spectroscopy. The main chemical composition of DR-2-HEA are (β -acryloxyethyl) esters of the dihydroopimaric acid and dehydroabiatic acids. Few of related neutral materials was also found.

DR-2-HEA were found polymerizable by DSC. Using this technique, DR-2-HEA was bulk polymerized in the presence of AIBN as a radical initiator in isothermal condition to evaluate the kinetic parameters. The reaction order n , activation energy E_A and preexponential factor A were obtained by n th-order reaction model. The enthalpy of bulk polymerization of DR-2-HEA in presence of initiator AIBN at different temperatures was basically the same. The rate of polymerization decreased with increase of α in the interval of $0.1 < \alpha < 0.9$. the polymer of DR-2-HEA

is oligomer and the molecular weight a did not affect by polymerization temperature. However, the T_g of the polymer of DR-2-HEA is lower than the polymer of its main components.

Based on the kinetic results and simulation of free radical bulk polymerization of DR-2-HEA, eq. (6) is more suitable to predict the bulk polymerization profiles of DR-2-HEA in the interval of $0.4 < \alpha < 1$.

References

1. Song, Z. Q. *J Chem Ind Forest Prod* 2004, 4, 29.
2. Ren, T. R.; Li, Y. H. *Rosin Chemistry and Application*; Chemical Industry Press: Beijing, 2006.
3. Maiti, S.; Ray, S. S.; Kundu, A. K. *Prog Polym Sci* 1989, 14, 297.
4. Biccu, I.; Mustata, F. *J Appl Polym Sci* 2004, 92, 2240.
5. Hays, J. T.; Drake, A. E.; Pratt, Y. T. *Ind Eng Chem* 1947, 39, 1129.
6. Lewis, J. B.; Hedrick, G. W. *J Polym Sci, Part A-1* 1966, 4, 2026.
7. Fukuda, W.; Marvel, C. S. *J Polym Sci, Part A-1* 1968, 6, 1281.
8. Fukuda, W.; Marvel, C. S. *J Polym Sci, Part A-1* 1968, 6, 1050.
9. Lewis, J. B.; Lloyd, W. D.; Hedrick, G. W. *J Org Chem* 1960, 25, 1206.
10. Sowa, J. R.; Marvel, C. S. *J Polym Sci, Part B: Polym Lett* 1966, 4, 431.
11. Lee, J. S.; Hong, S. *Eur Polym J* 2002, 38, 387.
12. Duan, W. G.; Chen, C. H.; Jiang, L. B.; Li, G. H. *Carbohydr Polym* 2008, 73, 582.
13. Atta, A. M.; El-Saeed, S. M.; Farag, R. K. *React Funct Polym* 2006, 66, 1596.
14. Wang, J. F.; Lin, M. T.; Chu, F. X.; Wang, C. P. *Fine Chemicals* 2008, 25, 1135.
15. Schawe, J. E. K. *Thermochim Acta* 2002, 388, 299.
16. Thakur, A.; Banthia, A. K.; Maiti, B. R. *Appl Polym Sci* 1995, 58, 959.
17. ASTM D5974-00 (2005).
18. Sadhra, S.; Gray, C. N.; Foulds, I. S. *J Chromatogr B* 1997, 700, 101.
19. Shao, L. P.; Gäfvert, E.; Nilsson, U.; Karlberg, A. T. *Phytochemistry* 1995, 38, 853.
20. Fonseca, T.; Gigante, B.; Matilde Marques, M.; Gilchrist, T. L.; Clercq, E. D. *Bioorg Med Chem* 2004, 12, 103.
21. Mahdavian, A.; Zandi, M. *Appl Polym Sci* 2003, 87, 2335.
22. Mahdavian, A.; Zandi, M. *Appl Polym Sci* 2003, 90, 1648.
23. Luo, Z. H.; Wei, L. H.; Li, W. W.; Liu, F.; Zhao, T. *Appl Polym Sci* 2008, 109, 525.
24. Pan, Z. R. *Polymer Chemistry (enhanced edition)*; Chemical Industry Press: Beijing, 2007;
25. Worzakowska, M. *Polymer* 2007, 48, 1148.
26. Chen, W. M.; Li, P.; Yu, Y. H.; Yang, X. P. *Appl Polym Sci* 2008, 107, 1493.
27. Ghaemy, M.; Khandani, M. H. *Eur Polym J* 1998, 34, 477.
28. Gao, J. H.; Zhao, M. I.; Li, G. *Appl Polym Sci* 2006, 101, 3023.