

Polymerization of Hot Melt Adhesives from Dicarboxylic Fatty Acid for Introductory Organic Chemistry Laboratories

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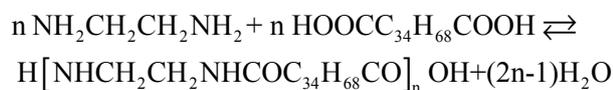
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Abstract Synthesis of hot melt adhesives from dicarboxylic fatty acid and ethylenediamine is presented for the undergraduate organic laboratory. The project fulfills the requirement of undergraduate chemistry and chemical engineering students. The experimental setup is utilized for the determination of polymerization reaction rate constants and reaction order. The apparatus also provides a safe method for observing polymer formation. In this experiment students prepare, react, and convert dicarboxylic fatty acid to hot melt adhesive. Students will find reaction order and specific reaction rate of stoichiometric proportions of ethylenediamine and dicarboxylic fatty acid to produce polyamide adhesives using batch reactor. The experiment will expose students to observe the steps of adhesive formation along with problems phasing polycondensation reactions due to foam formation.

Keywords Curriculum, Second-Year Undergraduate, Laboratory Instruction, Organic Chemistry, Polymerization, Kinetic, Synthesis

1. Introduction

The main objective of engineering education is to prepare students to practice engineering. The emphasis on laboratories has varied over the years. While much attention has been paid to curriculum and teaching methods, relatively little has been written about laboratory instruction [1, 2]. A one-term synthesis experimentation on the synthesis of nylon 6,6 was presented for the undergraduate organic laboratory by Dintzner et al. [3]. In the experiment students react, recycle and convert cyclohexanol to nylon 6,6. The task includes the principles of green chemistry. In the present work, dicarboxylic fatty acids is employed to synthesize and formulate hot melt adhesives. The polymerization reaction between dicarboxylic fatty acid ($\text{HOOC}_{34}\text{H}_{68}\text{COOH}$) and ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) is as follows [4-6]:



In the fatty polyamide industry, the water produced during the reaction is purged out to minimize the reverse reaction. Besides, the evaporation of ethylenediamine during the reaction is another important factor that needs to be

considered. If the evaporation becomes too great, the loss of ethylenediamine will cause an imbalance in the acid and amine values and this will affect the final products. The kinetics of the reaction between ethylenediamine and dicarboxylic fatty acids in the melt phase within the temperature range 210–250 °C has been experimentally investigated. The produced water vapor and vaporized ethylenediamine was purged by nitrogen bubbling, the analysis revealed that the reaction was second order with activation energy of 76.44 kJ/mole for conversions up to 90%. For higher conversions, the reaction was third order overall with activation energy of 68.88 kJ/mol [7-10]. Another work carried out on the kinetics of the reaction between C_{36} dicarboxylic fatty acids and diethylenetriamine and triethylenetetramine in the temperatures range 147–192 °C, disclosed that the reactions followed an overall second order kinetics and had activation energies of 60.8 and 51.7 kJ/mol, respectively [11]. These polyamides are known as reactive polyamides because they can be cross linked with other resins such as epoxy resins and they are not linear. Kinetic studies on the reaction between ethylenediamine and C_{36} dicarboxylic fatty acids using benzyl alcohol as a solvent was investigated. The reaction was performed in the temperature range 162–192 °C and the kinetics was determined from the change in acid values. The reaction was found to be third order overall and had activation energy of 128.9 kJ/mol [8]. The order of the reaction at conversions above 90% changed from 2nd to 3rd order. This phenomenon has been reported for many polycondensation

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polymerizations reactions such as with polyesters [12, 13]. The change in the order of reaction for fatty polyamides has been verified and its effect on the reverse reaction is evaluated. The reverse reaction at the end of the reaction is important in order to ascertain whether there is a need to apply a vacuum or nitrogen bubbling to complete the reaction. Nitrogen bubbling inside the reaction mass has been used and this causes the irreversibility of the reaction, where this differs from the work that the nitrogen was introduced from the top of the reactor and used to sweep the vapors (mainly water vapor and evaporated ethylenediamine) on the surface of the reaction mass. The kinetics of reaction up to 90% conversion was modeled [14]. In the present experiment, vacuum was used to sweep out water vapor and evaporated ethylenediamine.

2. Construction



Figure 1. Experimental setup of the polyamidation reaction

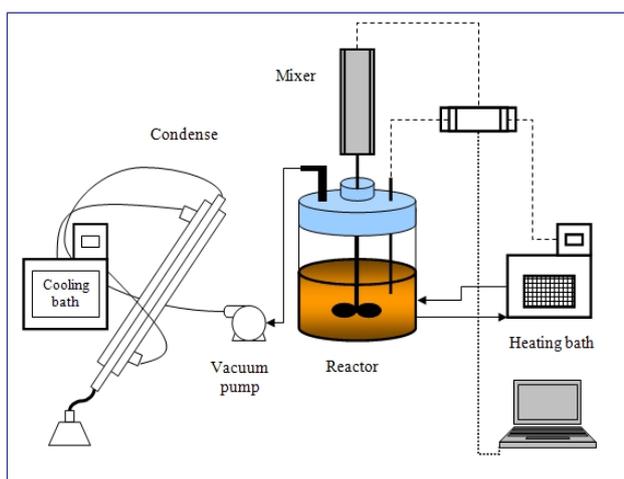


Figure 2. Schematic diagram of the experimental setup

The polyamidation reaction was carried out in one liter jacketed reactor (Janke & Kunkel IKA-labortechnik, Germany, Figure 1 and 2) equipped with anchor style mixer, sampling port, and thermometer for temperature measurement. Vacuum tube attached with vacuum pump for

removal of the generated water vapor. The temperature was maintained by oil bath. The reactor was charged with half mole of fatty acid and equivalent molar amount of ethylenediamine. The water generated by the polymerization reaction was sucked out of the system through the vacuum pump to a condenser attached to a water-cooling bath maintained at 4°C. Removal of water vapor from the system helped the reaction to go in the forward direction. The acid and amine values were determined as per ASTM D-1980-67 and ASTM D-2074-62T, respectively, with a neutral solution (1:1, v/v) of ethanol and toluene for dissolving the samples.

The polymer samples withdrawn from the reactor at certain time intervals via the sampling port were analyzed for acid and amine values, and hence, conversion measurements. The acid value was determined on the basis of ASTM D-1980-67 using a neutral solution (1: 1 v/v) of n-butanol and xylene for dissolving the samples. The amine value was determined using ASTM D-2074-62T with the same solvent as used for determining acid value. The water generated during the reaction and evaporated ethylenediamine were purged out of the reactor using vacuum. The acid value is defined as the number of mg of potassium hydroxide required to neutralize the acids in 1 g of fatty material. Weigh 5 gram of the sample to 0.1 mg in glass vial and dissolve in 75–100 ml of neutralized ethanol solution (if necessary by gentle heating; around 50°C). Agitation and further heating may be necessary to bring the fatty acid into complete solution. 0.5 ml of the phenolphthalein indicator solution was added to the solution. The solution was titrated immediately while shaking with 0.5 N KOH to the first pink color that persisted for 30 seconds. The acid value was calculated as follows:

$$\text{Acid value} = AV = \frac{V_b \times N_b \times 56.1}{S}$$

where V_b is the volume in ml of KOH solution required for the titration, N_b is the normality of the KOH solution, and S is the specimen weight in grams. The value 56.1 is the molecular weight of KOH. For the amine values, 5 g of the polyamide sample weighed to 0.1 mg was weighed and transferred into a 250-ml flask, 50 ml of xylene and isopropanol (1/1: v/v) was boiled for 1 min to drive off any free ammonia that may be present, and the boiled mixture was added to the 250 ml flask. The solution was cooled to room temperature and five drops of bromophenol blue indicator was added to the solution and titrated while swirling with 0.2 N HCl to the yellow ends. The total amine value was calculated as follows:

$$\text{Amine value} = AmV = \frac{V_a \times N_a \times 56.1}{S}$$

where V_a is the volume of HCl solution required for the titration in ml, N_a is the normality of the HCl solution, and S is the specimen's weight in grams. The number average molecular weight, M_n was calculated on the basis of the

following equation.

$$Mn = \frac{W}{(C_A V_A + C_B V_B)} \left(\frac{N_m}{1} + \frac{N_d}{2} + \frac{N_t}{3} \right)^{-1}$$

$$C_A = \frac{AV}{V_A \times M_{W,KOH} / W}$$

$$C_B = \frac{AmV}{V_B \times M_{W,KOH} / W}$$

where W is the weight of solid sample titrated; C_A , C_B , V_A , and V_B are the concentrations and actual volumes used from the standard solutions of the sodium hydroxide and the hydrochloric acid, respectively.

N_m , N_d and N_t are the percentage concentrations of the monomers with one, two, and three functional groups (acid and amide) in the products. Where AV is the acid value, and AmV is the amine value, $M_{W,KOH}$ is the molecular weight of potassium hydroxide ($MW = 56.1$ g/mol). Rearrange the previous equations yields:

$$Mn = 2 \times M_{W,KOH} / (AV + AmV)$$

Glass transition temperature, melting points, and heat of fusion were measured using differential scanning Calorimetry (DSC) with heating rate of $20^\circ\text{C}/\text{min}$ and under nitrogen atmosphere from room temperature to 200°C . Less than 1 gram of the produced polymer is melted on a glass slide as a film under vacuum for half an hour. The sample was kept at 120°C in an oven for the removal of water. The sample was then cooled. The melting point of the prepared sample was obtained using DSC.

3. Data Analysis

Methods to demine rate law parameters for homogenous reactions such as differential, integral and least squares method of data analysis is summarized elsewhere [15]. Advanced calculation methods can be performed using Easy-Fit software package [16]. Studies on the kinetics of polyamidation reaction of C_{36} dicarboxylic fatty acids and ethylenediamine for the synthesis of hot melt adhesives followed overall second-order with activation energy of 18.2 kcal/gmol up to 90% conversion, and overall third-order kinetics with activation energy of 16.583 kcal/mol. In the present experiment, the kinetics of polymerization at different reaction temperatures was investigated under vacuum. Acid concentration at four different reaction temperature (210 , 230 , 240 , 250°C) versus time is shown in Table 1. Figure 3 shows the effect of reaction temperature on the acid concentration with reaction time. Figure 3 reveals that, the acid value decreases with increase in reaction time due to consumption rate of the dicarboxylic fatty acid as

reaction proceeds. It can be seen that as reaction temperature increases the rate of the go down in the acid value increases due to the increase in consumption rate of dicarboxylic fatty acid. Assuming that the reaction is irreversible, because of the continuous removal of produced water using the strong vacuum, the following equations can be set to describe the batch reactor. Using the integral method and assuming the reaction is overall second order, the initial concentrations of amine and acid are equal, lead to the following first order differential equation [17].

$$-\frac{dC_A}{dt} = kC_A^2, \text{ integrating, } \frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

A plot of $1/C_A$ versus t (see Figure 4) will give values of specific reaction rate constant, k , at different reaction temperatures. Using the Excel software package, values of specific reaction rate constant at different reaction temperatures are shown in Table 2.

The data of reaction rate constant (k) vs. temperature were found to fit the Arrhenius equation, $k = Ae^{-E/RT}$,

$$\ln(k) = \ln(A) - \left(\frac{E}{R} \right) \frac{1}{T}$$

Table 1. Measured acid concentration with reaction time at different temperatures

Reaction time (min)	Acid concentration (mol/kg solution)			
	210 °C	230 °C	240 °C	250 °C
20	1.200	1.134	1.050	0.850
40	0.980	0.824	0.677	0.650
60	0.880	0.685	0.580	0.480
120	0.750	0.550	0.450	0.350
180	0.600	0.430	0.360	0.270
240	0.520	0.365	0.280	0.210
300	0.450	0.300	0.240	0.180

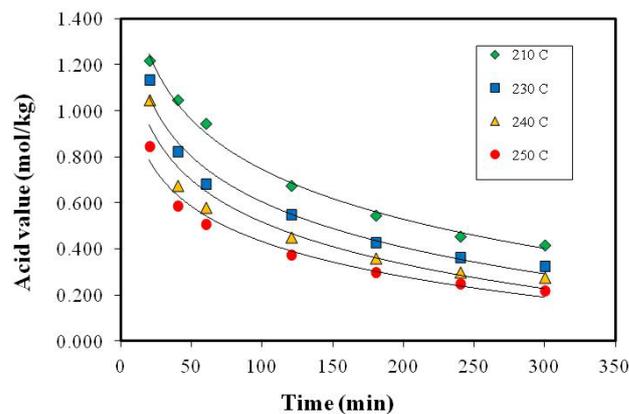


Figure 3. Acid concentrations various reaction times at different reaction temperatures

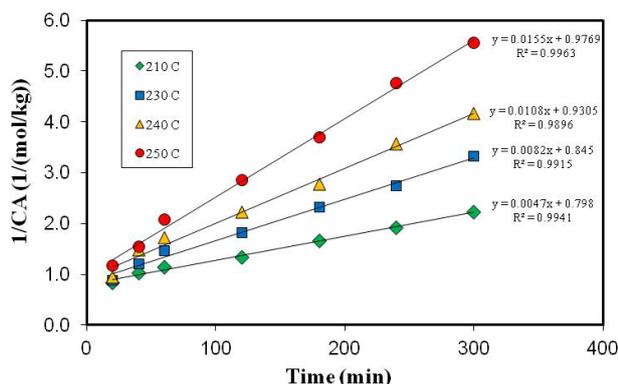


Figure 4. Reaction rate constant at different reaction temperatures

Table 2. Reaction rate constant

Temperature (°C)	K
210	0.0047
230	0.0082
240	0.0108
250	0.0155

A plot of $\ln(k)$ versus $1/T$ as shown in Figure 5 gives the slope of 7399.2 K:

$$\frac{E}{R} = \text{Slope},$$

$$R = 0.008314 \text{ kJ/mol K},$$

$$E = 61.52 \text{ kJ/mol}$$

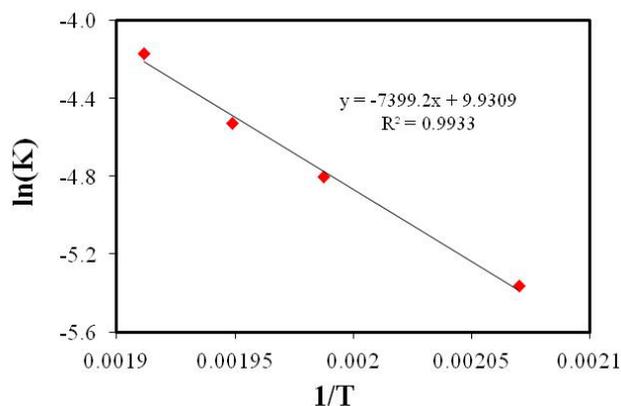


Figure 5. Forward specific reaction rate constant versus inverse of reaction temperatures

As the estimation of the parameters and the statistical analysis of the results, depend strongly on the given or estimated standard deviations of the measurement errors, attention should be paid to the formulation of the variance model and the values of the respective variance model parameters. Students are encouraged to specify the variance model and the values of the according parameters as precisely as possible. Note that, if the available data are insufficient for the estimation, the statistical analysis may show large confidence intervals for the associated

parameters, even though the fit may be very good. Using Arrhenius equation, the plot of $\ln(k)$ vs. $1/T$ gives the values of activation energy and pre-exponential factor. In the current experiment, the activation energy was found to be 61.52 kJ/mol which is in the range of the other values obtained using nitrogen bubbling or nitrogen sweeping the surface of the reactor. Students are encouraged to discuss the accuracy of three methods (i.e. using nitrogen bubbling, surface sweeping, or vacuum). The efficiency of any of the three methods is based on how effective these approaches to remove the water vapor produced to forbid the reversible reactions from taking place, otherwise the reversible reaction should be considered in the data analysis as the case of nitrogen sweeping of the surface of the reactor.

4. Conclusions

The introduction of polyamidation reaction between C_{36} dicarboxylic fatty acid and ethylenediamine for the undergraduate organic laboratories provides students with background concerning the principles of synthesis of adhesives. Students are also gaining hands-on experience with polymerization reaction rate and how to accelerate reaction by adding catalyst such as Ortho-phosphoric acid and avoiding reversible reactions through removing one of the products such as water in this case. The students will be aware on the effects of certain operating conditions such as; effect of vacuum, flashing with nitrogen, and nitrogen bubbling on the polymerization reaction.

5. Safety Precautions

Lab coat, mask and safety glasses should be worn throughout the experiments. The apparatus should be placed in vacuum hood to get rid from vapors and smell. The apparatus should be cleaned while the polymer is hot otherwise it will stick with reactor walls.

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