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Kinetics of the Polymerization of 4-Acetoxybenzoic Acid and 6-Acetoxy-2-naphthoic Acid

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ABSTRACT: Kinetics of the initial stages of the bulk polymerization of 4-acetoxybenzoic acid (ABA) and 6-acetoxy-2-naphthoic acid (ANA) were investigated. A method to analyze the kinetics by measuring the amount of evolved acetic acid trapped in a sodium hydroxide solution by titrimetry was developed. All polymerizations followed second-order reaction kinetics up to 70% conversion. Two kinetic regions were observed in the homopolymerization of ABA and copolymerization of ABA and ANA in the melt, visible by a break in the time−conversion curve. The average degree of polymerization at the change of mechanism point from a homogeneous to a heterogeneous system was 3.5. The time of the change in mechanism and the reaction rate were dependent on the temperature and the initial concentration ratio of ABA and ANA used in the polymerization. The higher the temperature and the concentration of ABA, the earlier the break takes place and the faster the reaction proceeds. The corresponding reaction rate constants and activation energies were obtained.

Introduction

Thermotropic liquid-crystal polymers prepared with fully aromatic monomers are well-known for their high mechanical strength and modulus, stability to chemicals, and heat resistance. These properties are due to their high crystallinity and are obtained from the extension and orientation of the polymer chain during processing. These polymers have many applications in electronic devices, fiber-optic coupling devices, automotive components, components for chemical pumps, and distillation towers. Poly(1,4-oxybenzoyl), obtained by self-reaction of 4-hydroxybenzoic acid (HBA), was one of the first commercial thermotropic liquid-crystal polymers but has found limited utility because of difficult processing. As a result, the corresponding copolymer of HBA and 6-hydroxy-2-naphthoic acid (HNA) has been developed. Today, most of the commercially available thermotropic liquid crystal polymers are (HBA/HNA) copolymers.

The synthesis, structure, and properties of these (HBA/HNA) copolymer products have been extensively studied.[1−8] The commercial (HBA/HNA) copolymers are prepared in the melt state by the exchange reaction between acetoxyaryl groups and carboxylic acid groups with the elimination of acetic acid at a temperature above the crystalline melting point of the polymer. The corresponding processes are divided into two steps. In the first step, HBA and HNA are converted into 4-acetoxybenzoic acid (ABA) and 6-acetoxy-2-naphthoic acid (ANA) by acetylation. The polymer is obtained by the bulk copolymerization of ABA and ANA in the second step. Although this process has been known since the 1980s, the kinetics for the bulk copolymerization of ABA and ANA has not been examined. It is essential to study the kinetics of this copolymerization because the knowledge of the correct rate equations and of the relative kinetic parameters is of primary importance for the precise control of the copolymer properties and process reproducibility. A few studies concerning the kinetics and mechanism of the acidolysis process have been reported in other polymerization systems. The monomers studied were Bisphenol A diacetate with isophthalic acid, [9,10] *p*-*tert*-butylphenyl acetate with benzoic acid,[11] ABA,[12−15] and ANA.[14]

The most obvious way to follow the kinetics of the copolymerization of ABA and ANA is by monitoring the acetic acid evolution. In their studies of the ABA polymerization, Vulic[12] and Mathew[13] followed the acetic acid formation by measuring the weight and volume, respectively, while for the polymerization of Bisphenol A diacetate with isophthalic acid, Zhou et al.[10] trapped acetic acid in water and titrated this solution. In this work, a more precise method based on the measurement of evolved acetic acid trapped in a sodium hydroxide solution by titrimetry was developed to study the kinetics of the initial stages of the bulk copolymerization of ABA and ANA. The effect of temperature and initial concentration ratios of ABA and ANA on the phase transition from homogeneous to heterogeneous and on the reaction rate was investigated in this copolymerization. The corresponding kinetic equation, reaction rate constants, and activation energies were obtained. The bulk homopolymerizations of ABA and ANA were also investigated briefly.

Experimental Section

Materials. 4-Hydroxybenzoic acid (99.8% by DSC) and 6-hydroxy-2-naphthoic acid (99.5% by DSC) were provided by Hoechst Celanese Co., Summit, NJ. 4-Acetoxybenzoic acid and 6-acetoxy-2-naphthoic acid were prepared by the sodium hydroxide-catalyzed reaction of HBA and HNA, respectively, with acetic anhydride and were recrystallized with methanol.

Polymerization. All kinetic studies of bulk co- and homopolymerizations of ABA and ANA were carried out in 50 mL round bottom flasks with a long neck sealed by a rubber septum. A long needle was used to introduce a dry nitrogen stream. A narrow bore Teflon tube passed through the rubber septum was used for the out-flow of nitrogen and for the removal of acetic acid. The other end of the Teflon tube was immersed into the trapping solution which had a known concentration of 0.95 M sodium hydroxide in a graduated cylinder. The flask containing starting materials was heated in a thermostated silicone oil bath at the respective polymerization temperatures 250, 275, and 300 °C. All polymerization kinetics studies were conducted with 10 g of monomer (comonomer) under atmospheric pressure. Two initial concentration

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ratios of ABA and ANA, namely, 73:27 and 30:70 mol % of ABA:ANA, were investigated.

Measurement of Trapping Efficiency of the Medium. The measurement of the concentration of evolved acetic acid is a key factor in the study of copolymerization kinetics. Several methods including physical and chemical methods have been used by previous researchers to measure the evolution of acetic acid produced during the polymerization. Physical methods such as the measurement of weight and volume of evolved acetic acid have been developed by Vulic[12] and Mathew.[13] The reported chemical measurement of evolved acetic acid was the titration of acetic acid trapped in the water.[10] The measurement of evolved acetic acid by titrimetry was used in this work. Therefore, in order to search for a suitable medium for the titration, the trapping efficiency of various media was measured. The trapping efficiency of the medium is tested by placing 2.5 g of acetic acid into the polymerization vessel. The system is immersed into a hot oil bath and the distilled acetic acid is bubbled through the trapping solution via the nitrogen purge. The amount of trapped acetic acid was measured by titration with the solution of sodium hydroxide. The corresponding efficiencies in various media are given as follows: The efficiency of water is 96% at 200 °C, 98% for ethanol at 300 °C, and 100% for 0.95 M NaOH at 200 and 300 °C, respectively. It indicates that the solution of sodium hydroxide is the most efficient medium. Therefore, 0.95 M NaOH was used as the trapping medium to measure the concentration of evolved acetic acid by back-titrating aliquots of the NaOH trapping solution.

Measurement of Acetic Acid. The progress of polymerizations was followed by measuring the concentration of evolved acetic acid trapped in the solution of sodium hydroxide at different times. The amount of acetic acid produced at a given time was determined by removing an aliquot of the trapping solution and back-titrating the sample. In order to calculate the amount of evolved acetic acid, the volume of the trapping solution must be recorded immediately prior to removing the aliquot. It is essential that the trapping solution be in a graduated cylinder so that an accurate measurement of the total volume can be obtained. The calculations for the evolved acetic acid are described below. The total number of moles of acetic acid ($N_{\mathrm{mAcOH(total)}}$) produced in the polymerization at a given time can be obtained from eq 1, in which V

$$N_{\mathrm{mAcOH(total)}} = \frac{N_{\mathrm{mAcOH(current\ aliquot)}} \times V_{\mathrm{(trap\ before\ current\ aliquot)}}}{V_{\mathrm{current\ aliquot}}} \qquad (1)$$

denotes the volume, $V_{\mathrm{current\ aliquot}}$ is the volume of the current aliquot and $N_{\mathrm{mAcOH(current\ aliquot)}}$ is the number of moles of acetic acid in the current aliquot, which was calculated using eq 2,

$$\begin{aligned} N_{\mathrm{mAcOH(current\ aliquot)}} = {} & M_{\mathrm{NaOH(trap)}} V_{\mathrm{NaOH(current\ aliquot)}} + \\ & M_{\mathrm{NaOH(current\ titration)}} V_{\mathrm{NaOH(current\ titration)}} + \\ & M_{\mathrm{HCl(added\ in\ current\ aliquot)}} V_{\mathrm{HCl(added\ in\ current\ aliquot)}} \end{aligned} \qquad (2)$$

where M denotes the molarity, $M_{\mathrm{NaOH(trap)}}$ is the concentration of sodium hydroxide in the trap. The calculations of $M_{\mathrm{NaOH(trap)}}$ prior to the first sample and prior to each additional sample are given in eqs 3 and 4, respectively. In eq 4, the increase of volume from the acetic acid coming into the trap and the decrease of volume from the aliquot removed from the trap have been taken into account.

$$M_{\mathrm{NaOH(trap)}} = \frac{V_{\mathrm{trap\ initial}} M_{\mathrm{trap\ initial}}}{V_{\mathrm{trap\ before\ sampling}}} \qquad (3)$$

$$M_{\mathrm{NaOH(trap)}} = \frac{(V_1 M_{\mathrm{HCl}} - V_2 M_{\mathrm{titrating\ base}})(V_{\mathrm{trap\ before\ sampling}} - V_{\mathrm{previous\ aliquot}})}{V_{\mathrm{previous\ aliquot}} V_{\mathrm{trap\ before\ current\ aliquot}}} \qquad (4)$$

in which V_1 is the volume of HCl added in the back-titration of the previous sample and V_2 is the volume of the titration of the previous sample.

Table 1. Initial Concentration (mol/L) of ABA and ANA at Different Polymerization Temperature

	homopolymerization		copolymerization[a] ABA/ANA (mol %)	
temp (°C)	ABA	ANA	73/27	30/70
250	10.6	8.2	10.0	
275	10.5	8.2	9.9	8.9
300	10.4	8.1	9.8	

[a] Initial concentrations (mol/L) are for the mixture of ABA and ANA.

Calculation of Initial Concentration of Monomer at High Temperature. The measurement of the slope in the plot of $1/(1 - p)$ versus time was used to determine the reaction rate constant. The value of the slope includes the initial concentration of monomer $[\mathrm{COOH}]_0$, as shown in eq 21. Therefore, the initial concentration of monomer was needed to calculate the reaction rate constant (k_{obs}).

Different methods have been used to calculate the initial concentration of monomer in the melt state. Vulic[12] used the group contribution method of Van Krevelen[16] to calculate the initial concentration of monomers at high temperature. Mathew[13] thought that the molar volume of monomer in the melt was not precisely known. As a result, he assumed that the initial concentration of monomer in the pure melt is 1. In our kinetic studies, the calculations of the initial concentration of monomers were also based on the method of Van Krevelen,[16] as described below.

The initial concentration of monomer can be calculated from eq 5, in which V is the molar volume in mL/mol, and as a

$$[\mathrm{COOH}]_0 = 1/V \qquad (5)$$

function of temperature it is expressed in eq 6, where E is the

$$V(T) = V(298) + E(T - 298) \qquad (E = 4.5 \times 10^{-4} \times V_{\mathrm{w}}) \quad (6)$$

molar thermal expansivity and V_{w} is the Van der Waals volume. T is the temperature in K. The $V(T)$ of the ABA monomer at different temperatures can be calculated from eq 7.

$$V(T) = 88.5 + 4.5 \times 10^{-4} \times 58.5(T - 298) \qquad (7)$$

In the case of ANA monomer, V_{w} of the ABA monomer was used instead of V_{w} of ANA because the latter is not known. The corresponding equation is given in eq 8. On the basis of

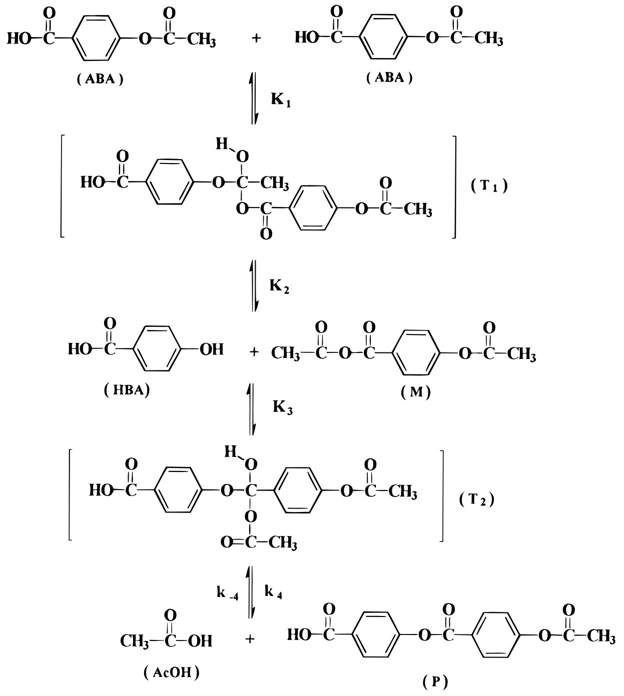
$$V(T) = 115.6 + 4.5 \times 10^{-4} \times 58.5(T - 298) \qquad (8)$$

eqs 5, 7, and 8, the initial concentrations of ABA and ANA in the bulk co- and homopolymerization at different temperatures were calculated as listed in Table 1.

Results and Discussion

Mechanism of Acidolysis Reaction in the Bulk Polymerization of ABA. Based on our previous work,[11] the mechanism of the acidolysis reaction in the bulk polymerization of ABA was proposed as shown in Scheme 1. In this mechanism, the first reaction is a nucleophilic addition of the carboxylic acid to the carbonyl group of the acetate, leading to the formation of a tetrahedral intermediate T_1 which can revert back to starting materials or form a mixed anhydride and HBA by elimination of the leaving group. The second reaction is the reaction of hydroxyl group on HBA with either the acyl or benzoyl group of the mixed anhydride. The former is a backward reaction, the latter gives another tetrahedral intermediate T_2. The growing chain P (low molecular weight product) can be formed by the forward reaction of the tetrahedral intermediate

Scheme 1. Mechanism of the Acidolysis Reaction in the Bulk Polymerization of ABA



T2. Although all of these reactions are reversible, the removal of acetic acid can be used as the driving force in the direction of the forward reaction which will lead to the formation of polymer.

Although the above mechanism of acidolysis reaction was proposed for the bulk polymerization of ABA, it can also be applied to the bulk homopolymerization of ANA and the bulk copolymerization of ABA and ANA.

Kinetic Treatment of Bulk Copolymerization of ABA and ANA. The bulk polymerization of ABA is a bimolecular second-order reaction, as seen in Scheme 1. If [COOH] denotes the concentration of acid groups, the reaction rate d[COOH]/dt is dependent on the concentrations of acid and acetoxyl groups in a homogeneous mixture. The corresponding reaction rate equations are given as follows:

$$\frac{-\mathrm{d[COOH]}}{\mathrm{d}t} = k_4[\mathrm{T_2}] - k_{-4}[\mathrm{P}][\mathrm{AcOH}] \qquad (9)$$

For [AcOH] = 0, eq 9 becomes

$$\frac{-\mathrm{d[COOH]}}{\mathrm{d}t} = k_4[\mathrm{T_2}] \qquad (10)$$

and the various equilibrium constants are

$$K_1 = \frac{[\mathrm{T_1}]}{[\mathrm{COOH}][\mathrm{OAc}]} \qquad (11)$$

$$K_2 = \frac{[\mathrm{HBA}][\mathrm{M}]}{[\mathrm{T_1}]} \qquad (12)$$

$$K_3 = \frac{[\mathrm{T_2}]}{[\mathrm{HBA}][\mathrm{M}]} \qquad (13)$$

Combining eqs 11−13, we get

$$\frac{-\mathrm{d[COOH]}}{\mathrm{d}t} = K_1K_2K_3k_4[\mathrm{COOH}][\mathrm{OAc}] \qquad (14)$$

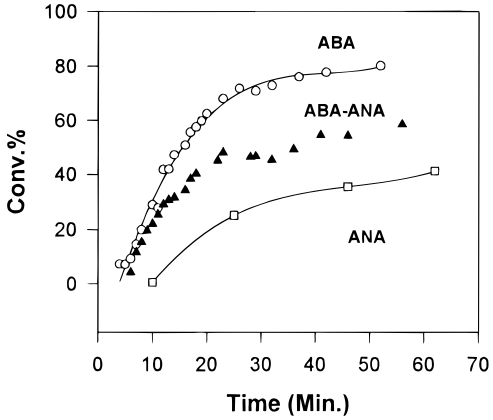


Figure 1. Conversion of co- and homopolymerization of ABA and ANA at 250 °C as a function of time. $[\mathrm{ABA}]_0/[\mathrm{ANA}]_0 = 73/27$ for the bulk copolymerization.

Because [COOH] = [OAc], eq 14 becomes

$$\frac{-\mathrm{d[COOH]}}{\mathrm{d}t} = K_1K_2K_3k_4[\mathrm{COOH}]^2 \qquad (15)$$

The extent of polymerization p is defined as

$$p = \frac{[\mathrm{COOH}]_0 - [\mathrm{COOH}]}{[\mathrm{COOH}]_0} \qquad (16)$$

Combination of eqs 15 and 16 gives

$$\frac{\mathrm{d}p}{\mathrm{d}t} = K_1K_2K_3k_4[\mathrm{COOH}]_0[1-p]^2 \qquad (17)$$

After integration of eq 17 from $t = 0$ to $t = t$

$$\frac{1}{[1-p]} = 1 + K_1K_2K_3k_4[\mathrm{COOH}]_0t \qquad (18)$$

The number average degree of polymerization (DP) and the reaction rate constant (k_{obs}) are defined as

$$\mathrm{DP} = \frac{[\mathrm{COOH}]_0}{[\mathrm{COOH}]} = \frac{1}{[1-p]} \qquad (19)$$

$$k_{\mathrm{obs}} = K_1K_2K_3k_4 \qquad (20)$$

In combination with eqs 18−20 they give

$$\mathrm{DP} = \frac{1}{[1-p]} = 1 + k_{\mathrm{obs}}[\mathrm{COOH}]_0t \qquad (21)$$

in which k_{obs} is the reaction rate constant, $[\mathrm{COOH}]_0$ is the initial concentration of monomer, and p is the fractional conversion. The reaction rate constant k_{obs} at a given reaction temperature is determined by plotting $1/(1-p)$ versus polymerization time.

The fractional conversion (p) can also be expressed as shown in eq 22. In fact, eq 22 was used to measure

$$p = \frac{N_{\mathrm{mAcOH(total)}}}{N_{\mathrm{mAcid(initial)}}} \times 100\% \qquad (22)$$

the value of the fractional conversion (p).

Kinetic Analysis of the Bulk Polymerization of ABA and ANA. The conversion of polymerization as a function of time was investigated in the bulk co- and homopolymerizations of ABA and ANA at 250 °C, as shown in Figure 1. It is obvious that the conversion of homopolymerization of ABA is the highest and that the

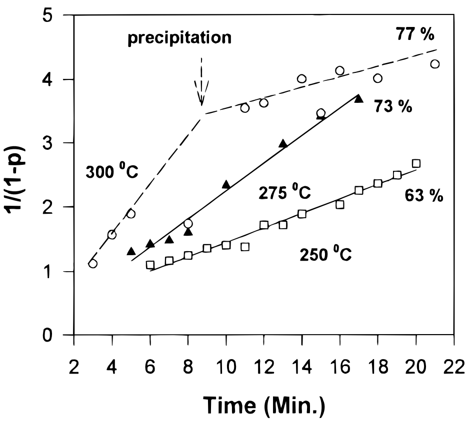


Figure 2. 1/(1 − p) as a function of time in the bulk homopolymerization of ABA at different temperatures.

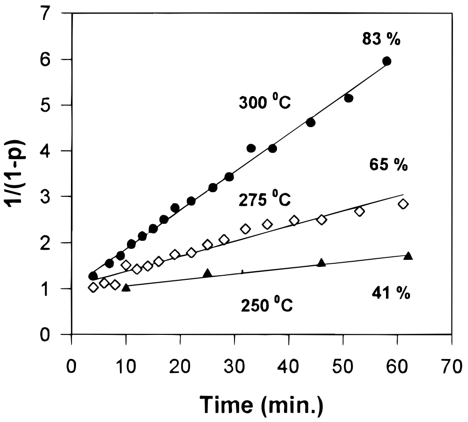


Figure 3. 1/(1 − p) as a function of time in the bulk polymerization of ANA at different temperatures.

conversion in the bulk copolymerization of ABA and ANA is higher than in the homopolymerization of ANA. These results demonstrate that the reaction rate decreases in the order of homopolymerization of ABA, copolymerization of ABA and ANA, and homopolymerization of ANA. This conclusion was confirmed by their reaction rate constants, as discussed below.

The bulk polymerizations of ABA were performed at different temperatures ranging from 250 to 300 °C and followed by the trapping method described in the Experimental Section. The plots of 1/(1 − p) versus polymerization time at 250, 275, and 300 °C are shown in Figure 2. The obtained straight lines indicate that in the early stages the bulk homopolymerization of ABA is a second-order reaction at these temperatures. These results are in good agreement with the expected results. There were no breaks in the time−conversion curve for the polymerization carried out for 20 min at 250 and 275 °C. A break was seen in a plot of 1/(1 − p) versus polymerization time at 300 °C. The corresponding DP is about 3.3, because the physical meaning of 1/(1 − p) is the number average degree of polymerization. At the time of the break in the curve (8 min), the bulk polymerization reaction turns from homogeneous to heterogeneous due to the early precipitation of ABA oligomer. The probable reason for the occurrence of the break is that the chain growth of the oligomer in a heterogeneous system takes place on the surface of the precipitate by stepwise addition of the monomer. Consequently, the mechanism of chain growth changes when the system changes from homogeneous to heterogeneous.

The precipitation of ABA oligomer has also been observed by Kricheldorf[17] in the polymerization of ABA in solution and by Vulic[12] and by Mathew[13] in the bulk polymerization of ABA. The corresponding values of DP were different in these systems. In the polymerization of ABA conducted with solution, values of DP ranging from 6 to 8 were reported by Kricheldorf. In the bulk polymerization of ABA, Vulic only listed the approximate times of precipitation (break) at different temperatures. The time of precipitation and its DP were determined by the plots of 1/(1 − p) versus time in Mathew's paper. These data are summarized in Table 2.

Table 2 shows that the time of precipitation from ABA oligomer increases with the decrease of polymerization temperature. The precipitation of oligomer did not take place in the bulk polymerization of ABA carried out for 25 min below 280 °C, and this is in good agreement with our results. In the bulk polymerization of ABA at 300 °C, the precipitation time (4.5 min) obtained from Mathew's work is lower than that in our work (8 min) and lower than the value reported by Vulic (20 min), as shown in Table 2.

The effect of temperature on the bulk homopolymerization of ANA was also investigated from 250 to 300 °C. Figure 3 shows three plots of 1/(1 − p) versus time at 250, 275, and 300 °C, respectively. All plots were linear up to 60 min. Therefore, we conclude that the bulk homopolymerization of ANA followed second-order reaction kinetics. The break was not found in every polymerization, even if the polymerization was carried out up to 83% conversion (DP ≈ 6.2) at 300 °C for 60 min. This indicates that ANA oligomers are less likely to precipitate than ABA oligomers. In addition, the precipitation of ANA oligomer was reported by Economy[14] to occur after 100 min at 245 °C in the polymerization of ANA conducted in Therminol (a high-boiling aromatic hydrocarbon). This demonstrates that it takes a long time before the ANA oligomer precipitates.

The kinetics of the bulk copolymerization of ABA and ANA ($[ABA]_0/[ANA]_0$ = 73/27 mol %) were investigated at 250, 275, and 300 °C, respectively. Values of 1/(1 − p) versus copolymerization time at different polymerization temperatures were plotted in Figure 4. The bulk copolymerization of ABA and ANA followed second-order reaction kinetics, as confirmed by the straight lines in Figure 4. The break appears in the plot for the copolymerization of ABA and ANA at 300 °C. It demonstrates that the ABA−ANA co-oligomer also precipitates in the early stages of the polymerization

Table 2. Time of Precipitation (Break in Time−Conversion Curves) and the Corresponding DP in the Bulk Polymerization of ABA

	temp (°C)	time of the break (min)	DP
bulk of polymerization of ABA (Mathew)	250	not observed (up to 24 min)	
	270	not observed (up to 24 min)	
	300	4.5	1−1.5
	325	3.5	2−2.5
	350	3.0	3−3.5
bulk of polymerization of ABA (Vulic)	245	40	no data reported
	280	25	
	300	20	

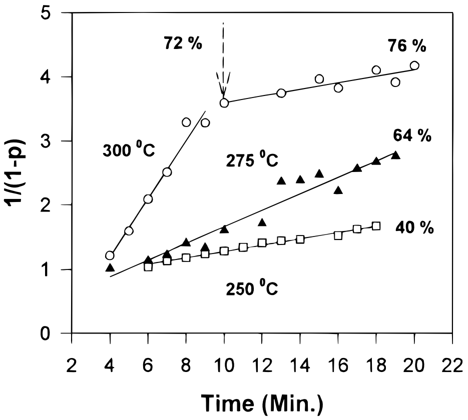


Figure 4. $1/(1 - p)$ as a function of time in the bulk copolymerization of ABA and ANA at different temperatures. $[\mathrm{ABA}]_0/[\mathrm{ANA}]_0 = 73/27$.

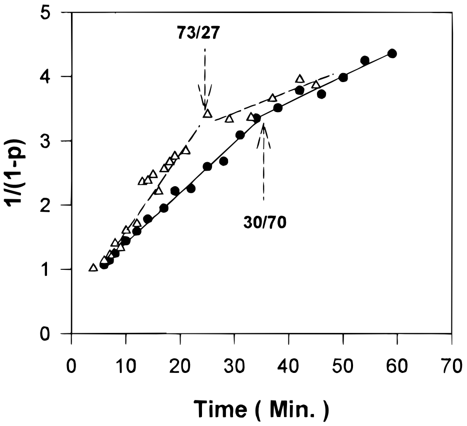


Figure 5. $1/(1 - p)$ as a function of time in the bulk copolymerization of ABA and ANA at 275 °C. The initial concentration of ABA and ANA is 73/27 and 30/70 (mol %).

at high temperature. This copolymerization also follows second-order kinetics as described by Economy.[14] In that work, the kinetics of the copolymerization of ABA and ANA ($[\mathrm{ABA}]_0$:$[\mathrm{ANA}]_0$ = 1:1) at 245 °C was investigated in an inert high-boiling hydrocarbon solvent (Therminol 66). The break in the plot of 1/monomer concentration versus time was not observed in this copolymerization carried out for 275 min (DP $\approx$ 2.5) at 245 °C.

The kinetics of the bulk copolymerization of ABA and ANA was studied by using different initial concentration ratios of ABA to ANA at 275 °C. These copolymerizations also follow second-order reaction kinetics, as shown in Figure 5. The breaks appear at 40 and 25 min in the copolymerization by using 30/70 and 73/27 of $[\mathrm{ABA}]_0/[\mathrm{ANA}]_0$, respectively. After Figures 2, 4, and 5 were compared, it was found that all breaks in the plots of $1/(1 - p)$ versus time take place at DP ranging from 3 to 4. The time at which the breaks occur varies with the initial concentration of ABA and temperatures used in the polymerizations. The time increases from 10 to 25 min when the temperature decreases from 300 to 275 °C in the bulk copolymerization with 73/27 of the initial concentration ratio of ABA to ANA. This result is consistent with the bulk polymerization of ABA as given before. The time of break increases from 8 to 10 min as the concentration of ABA decreases from 100% (homopolymerization of ABA) to 73% (copolymerization) at 300 °C, and the time of the breaks also increases from 25 to 40 min with the decrease of the concentration of ABA from 73% to 30% in the copolymerization at 275 °C.

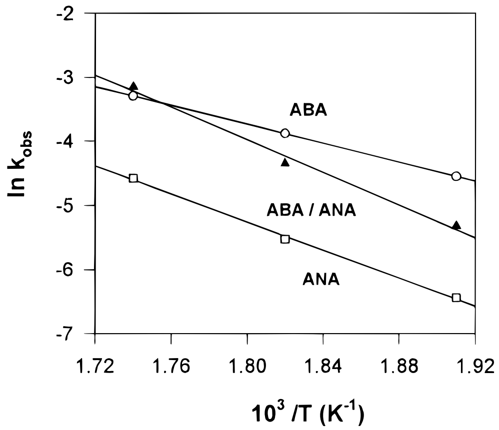


Figure 6. Arrhenius plots for the initial stage of the bulk co- and homopolymerization of ABA and ANA.

On the basis of the measurement of the initial slope in the plots of $1/(1 - p)$ versus time, the reaction rate constants for the bulk homo- and copolymerization of ABA and ANA were determined by using eq 21. The rate constants were used to make the Arrhenius plots shown in Figure 6. From the slope of the straight lines in Figure 6, the activation energy (E_a) and frequency factors (A) were calculated. The values of k_{obs}, E_a, and ln A are presented in Table 3. The reaction rate constants of other polymerization systems are also listed in the same table. We calculated the rate constants from the plots of $1/(1 - p)$ versus time presented in Mathew's paper,[13] and we normalized these values using $[\mathrm{COOH}]_0$ calculated according to the method of Van Krevelen.[16] The percent conversion vs time curves shown in Economy's paper[14] were also used by us to calculate the corresponding rate constants. Consequently, these values are approximate.

From Table 3, the following conclusions can be drawn. First, at a given temperature (250 and 275 °C), the reaction rate increases with increasing initial ABA concentration. For example, 20.6, 13.0, 8.8, and 4.0 ($\times 10^3$ L mol^{-1} min^{-1}) were the reaction rate constants obtained for the homopolymerization of ABA (100% ABA), copolymerization of ABA and ANA (73% and 30% ABA), and homopolymerization of ANA (0% ABA), respectively. The rate constant in the bulk polymerization of ABA is greater than in the bulk polymerization of ANA. The bulk copolymerization has a rate constant which falls between the two homopolymerizations and is dependent on the monomer ratios. This result conflicts with Economy's data ($k_{\mathrm{ANA}} > k_{\mathrm{ABA}} > k_{(\mathrm{ABA/ANA:}\ 1/1)}$), as shown in Table 3. The difference between our work and Economy's work is that the polymerizations were carried out in different states. Our polymerizations were conducted in the melt state, while Economy's were performed in a solvent.

Second, in a given polymerization system (ABA, ANA, and ABA−ANA), the higher the temperature, the higher the reaction rate, as would be expected. This conclusion was confirmed by the rate constants at different temperatures from Mathew and Vulic, as given in Table 3.

Third, two kinetic regions separated by a break clearly appear in Figures 2, 4, and 5. All of the corresponding second reaction rate constants (k_{obs}') are smaller than the first reaction rate constants (k_{obs}). This means that the reaction in a homogeneous system is faster than in a heterogeneous system. This is not consistent with the values obtained by Mathew, as shown in Table 3, where the first rate constant is smaller than the second rate constant.

Table 3. Reaction Rate Constants,[a] Activation Energies[b] (E_a), and Frequency Factors (ln A) in the Polymerization of ABA and ANA and Related Polymerizations

	current					Vulic[12]				Mathew[13]					Economy[14]			Huang[11]	
	T (°C)	k_{obs}	k_{obs}'	E_a	ln A	T (°C)	k_1	E_a	ln A	T (°C)	k_1	k_2	E_a	ln A	T (°C)	k_1	k_2	T (°C)	k_1
ABA	250	10.6		14.6	9.5	245	3.2	25.6	14.0	250	1.8		18.6	14.0	245	2.5	4.5		
	275	20.6				280	11.9			275	4.2								
	300	37.0	6.5			300	22.6			300	8.8	29.9							
ANA	250	1.6		21.8	14.4										245	3.6	8.5		
	275	4.0																	
	300	10.3																	
$[ABA]_0$:$[ANA]_0$ (73:27)	250	4.9		25.2	18.9														
	275	13.0	3.2																
	300	42.7	5.2																
$[ABA]_0$:$[ANA]_0$ (30:70)	275	8.8	4.6																
$[ABA]_0$:$[ANA]_0$ (50:50)															245	1.5			
model reaction																		250	0.4

[a] The rate constants k are reported in 10 ^{3} L mol^{-1} min^{-1}. [b] The activation energy E_a is reported in kcal/mol.

Finally, although the polymerizations of ABA were carried out in the melt state in our current work, and in Mathew's and Vulic's work, the values of the rate constants and E_a were not in good agreement at a given temperature. The reason may be that different methods were used to measure the evolved acetic acid produced in the polymerization. In the previous kinetic studies in solution, the reaction rate constants for the different systems reported by Huang[11] and by Economy[14] were different as given in Table 3.

Conclusions

The kinetics of bulk co- and homopolymerization of ABA and ANA in the initial stage of acidolysis at different temperatures were investigated via the measurement of evolved acetic acid by titrimetry. All polymerizations are second-order up to 70% conversion.

Two kinetic regions were observed in the homopolymerization of ABA and copolymerization of ABA and ANA at 275 and 300 °C, and the first reaction rate constant (k_{obs}) is larger than the second one (k_{obs}'). The time of mechanism change corresponds to a phase transition from homogeneous to heterogeneous, resulting from the precipitation of oligomer, and is dependent on the temperature and initial concentration of ABA used in the polymerizations. The higher the temperature and the concentration of ABA, the earlier the phase transition takes place. The corresponding DP ranges from 3 to 4.

Polymerization temperature and the initial monomer concentration ratio have a pronounced influence on the reaction rate. The higher the concentration of ABA and temperature, the faster the reactions are. The rate constants and activation energies were obtained.

The mechanism for the formation of ABA/ANA copolymer with high molecular weight at high temperature is being investigated.

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