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Kinetics of the Bulk Polymerization of Aromatic Diacids and Diacetates

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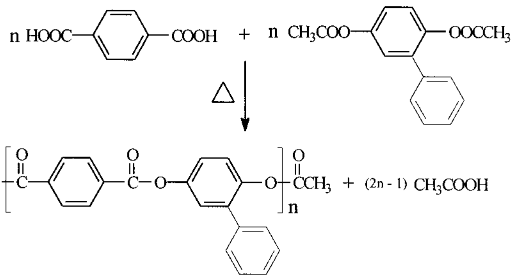
ABSTRACT: The acidolysis kinetics of the initial stage in the bulk polymerization of aromatic diacids (AA-type monomers) with aromatic diacetates (BB-type monomers) were investigated by a newly developed gas chromatography (GC) method. The model reactions of *p*-*tert*-butylbenzoic acid (ptBuBA) with either hydroquinone diacetate (HQD) or *p*-acetylaminophenol (APAP) follow second-order kinetics in these homogeneous conditions. HQD and APAP have approximately equal reactivity. The polycondensation of terephthalic acid (TA) with HQD, TA with 2-phenylhydroquinone diacetate (PhHQD), and TA with HQD and with 2,6-naphthalenedicarboxylic acid (NDA), follow pseudo-first-order kinetics. These reactions are heterogeneous. The polymerization of TA/PhHQD is the fastest, whereas the polymerization of TA/HQD is slower than that of TA/HQD/NDA. We propose that the solubility of the 1:1 dimer plays a crucial role in determining the polymerization rate, and that the mechanism changes from acidolysis to a dehydration esterification in the later stage of the AA/BB polymerization. The reaction rate constants and activation energies were obtained for all model reactions and polymerizations.

Introduction

The discovery of thermotropic liquid crystal polymers (LCPs) by Jackson-Kuhfuss[1] in 1973 led to extensive research in industry and academia on LCPs science and technology during the last 20 years. Today, thermotropic LCPs are enjoying a vigorous growth due to their many applications. The thermotropic LCP industry is a $100 billion/year business, with a yearly double-digit growth rate anticipated to last well into the next decade.

Thermotropic main-chain LCPs (MCLCPs) occupy a unique position among the thermotropic LCPs because of their attractive properties, such as high strength, excellent modulus and impact properties, flame retardant effect, resistance to a wide variety of aggressive chemicals, and unique processability.[2] Several synthetic routes have been explored for the preparation of thermotropic LCPs.[3,4] The acidolysis, an ester exchange reaction between acetoxyaryl groups and the carboxylic acid group with the elimination of acetic acid, is extensively used to prepare MCLCPs, such as the polyester from 4-acetoxybenzoic acid (ABA)/6-acetoxy-2-naphthoic acid (ANA), terephthalic acid (TA)/2-phenylhydroquinone diacetate (PhHQD), and 4,4′-biphenol/TA/4-hydroxybenzoic acid (HBA)/isophthalic acid (IA). Two kinds of monomers are currently being used in the synthesis of polyesters by acidolysis. The first ones are AB monomers that have both a carboxylic acid and an acetate functional group. In this denotation, A means a carboxylic acid functional group, and B an acetoxy functional group. Typical AB monomers are ABA and ANA. A second series of monomers are AA and BB monomers that have two carboxylic acid functional groups, such as TA, or two acetoxy functional groups, such as PhHQD. AB, AA/BB, and AA/BB/AB monomer systems are currently employed to commercially prepare MCLCPs.

The acidolysis kinetics have been extensively investigated for different AB polymerization systems: ABA,[5−7] ABA/ANA,[7,8] and PET [poly (ethylene terephthalate)]/ABA.[9] However, the acidolyis kinetics of AA/BB polymerizations have only been reported for the polymerization of bisphenol-A diacetate with IA[10] and, very recently, for TA with HQD (hydroquinone diacetate).[11] The AA/BB polymerization is one of the important ways to synthesize industrially important thermotropic MCLCPs, such as the polymer of TA and PhHQD. Therefore, the investigation of the acidolysis kinetics in the AA/BB acidolysis polymerization is of great interest.



The measurement of the amount of evolved acetic acid is the most obvious way to study acidolysis kinetics. Physical and chemical methods have been developed to monitor the evolution of acetic acid, including the determination of weight[5] or volume[6] of acetic acid and the titration of acetic acid trapped in water[10] or in an aqueous sodium hydroxide solution.[7] In this work, a much more simple, more reproducible, and more precise method based on the measurement of acetic acid by gas chromatography (GC) was developed. The AA/BB acidolysis systems described in this paper are the reactions of *p*-*tert*-butylbenzoic acid (ptBuBA) with either HQD or *p*-acetylaminophenol (APAP), and the polymerizations of TA/PhHQD, (industrial system), TA/HQD and TA/HQD/2,6-naphthalenedicarboxylic acid (NDA). The reactivities of HQD and APAP were investigated in their reactions with TA in bulk. The bulk polymerization rate

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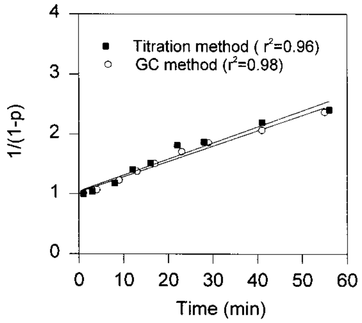
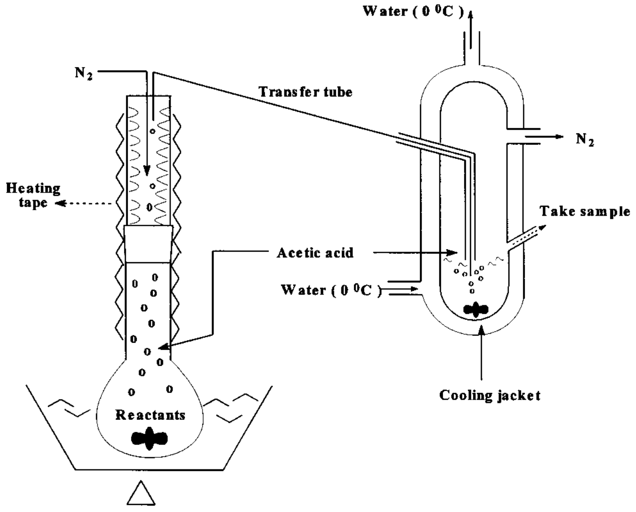


Figure 1. Comparison of the titration with GC methods for the kinetic study of the bulk copolymerization of ABA and ANA ($[ABA]_0/[ANA]_0$ = 73/27 mol/mol) at 250 °C.

Scheme 1. Setup for the Kinetic Studies of AA/BB Polymerization



of TA/PhHQD, TA/HQD, and TA/HQD/NDA was also investigated at higher temperatures ranging from 280 to 320 °C. The corresponding kinetic equations, reaction rate constants, and activation energies were obtained. In addition, a mechanism for the AA/BB polymerization is proposed.

Experimental Section

Materials. HQD (98%, Aldrich), ptBuBA (99%, Aldrich), and APAP (98%, TCI), PhHQD (99% from our GC measurement, Acros), TA (98%, Aldrich), and NDA (98%, TCI) were used as received.

GC Method for Kinetic Study. To use GC analysis for the measurement of evolved acetic acid, a new system was developed to trap the evolved acetic acid, as shown in Scheme 1. The nitrogen purge line from the bulk polymerization was led through a trap at 0 °C containing 26 mL of toluene and 0.1 mL of benzene as internal standard. Samples were taken from the trap at different polymerization times and the concentration of acetic acid was measured by GC. The GC method was compared with the titration method for the copolymerization of ABA and ANA, which was conducted at 250 °C for 60 min on a 9.3 g scale (ABA/ANA = 73/27, mol/mol) in bulk. The corresponding $1/(1 - p)$ (p means the extent of polymerization) values versus polymerization times are plotted in Figure 1. This plot shows that the correlation coefficient for the straight line from the GC measurement is higher than that from titration measurement. The same polymerization was carried out twice in the same conditions, and the same results were obtained. Therefore, we can conclude that the GC method is more precise, simpler, and more reproducible than the titration method.

The trapping efficiency for the collection of acetic acid was tested in a trap with toluene at 0 °C by placing a known amount of acetic acid into the polymerization vessel. The system was immersed into a hot oil bath, and the distilled acetic acid was bubbled through the cold trap containing toluene via a nitrogen purge. The trapping efficiency, calculated by weighing the amount of trapped acetic acid, was 97% at 0 °C.

Measurement of Initial Concentration of Monomers in the Melt State. The initial concentration of monomer $[M]_0$ is needed to determine the reaction rate constants (k_{obs}). Several methods have been reported for the calculation of $[M]_0$ in the melt state. The value of $[M]_0$ was assumed to be 1 in the pure melt in Mathew's work[6] because the molar volume of monomer was not precisely known in the melt. Because of the difficult measurement at high temperature, the reaction mixture density used to calculate $[M]_0$ was assumed to be 1 g/mL by Hall and co-workers.[12] The group contribution method of Van Krevelen[13] was also used by Hall and co-workers[7] and Vulic and Schulpen[5] for the calculation of $[M]_0$. In the present work, the calculation of $[M]_0$ is based on the measurement of the reaction mixture volume in the melt state. The volume of monomers at 275 °C was measured in a graduated cylinder for a given amount of monomer. The volume values at 275 °C are as follows: 4.0 mL for 3.56 g of ptBuBA, 3.85 mL for 3.65 g of APAP, 4.05 mL for 3.88 g of HQD, and 2.70 mL for 2.70 g of PhHQD. It should be noted that the volumes of TA and NDA are negligible because these compounds do not melt at temperatures used in the polymerizations. The values of $[M]_0$ are taken as being the same at different temperatures ranging from 250 to 320 °C based on the very close value of $[M]_0$ at temperatures ranging from 250 to 300 °C in the homo- and copolymerization of ABA and ANA.[7]

Dehydration of ptBuBA with *p-tert*-Butylphenol. ptBuBA (3.56 g, 0.02 mol) and 3.00 g (0.02 mol) of *p-tert*-butylphenol were added to a reaction flask. The mixture was heated to 240 °C for 14 h. During the reaction, the mixture system is homogeneous. The mixture of compounds was analyzed by GC/mass spectroscopy (MS). ptBuBA: RT (8.33 min), *m/z* (178); *p-tert*-butylphenol: RT (6.91 min), *m/z* (150), and *p-tert*-butylphenyl/ptBuBa: RT (13.61 min), *m/z* (310).

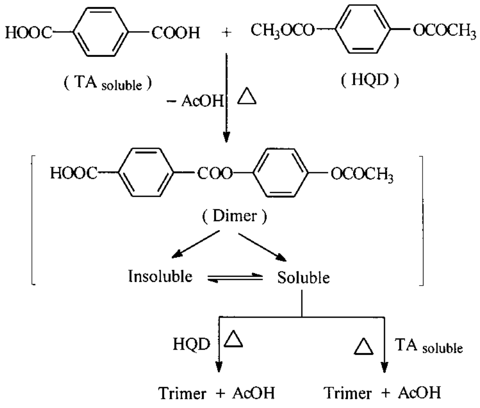
Attempted Decarboxylation of TA. The attempted decarboxylation of TA was carried out in a 50-mL round-bottomed flask with a long neck sealed with a rubber septum. A long needle was used to introduce a dry nitrogen stream. A narrow-bore Teflon tube, passed through the rubber septum, was used for the flow of gas phase. The gas stream was directed through a trap containing an aqueous solution of Ba(OH) $_2$ to collect carbon dioxide. The flask containing 1 g of TA was heated in a thermostated silicone oil bath under normal pressure at 330 °C for 3 h. No $BaCO_3$ white precipitate was observed in the trap. No benzoic acid was formed in the flask, as confirmed by GC/MS analysis.

Reaction of ptBuBA with Either HQD or APAP. The reactions of 7.13 g (40 mmol) of ptBuBA with either 3.88 g (20 mmol) of HQD or 3.86 g (20 mmol) of APAP were conducted in a 50-mL flask at temperatures ranging from 250 to 300 °C. The nitrogen purge line from the bulk reaction was led through a cold trap containing toluene at 0 °C. The flow rate of nitrogen was 12 mL/min. A heating tape was used to warm the reaction flask neck to assist in the immediate evolution of acetic acid produced in the reaction. The voltage control of the heating tape was set at 60 V. Acetic acid trapped in the toluene trap was measured by GC by taking samples from the trap at the different reaction times.

Polymerization of TA/PhHQD, TA/HQD, and TA/NDA/HQD. The polymerization of TA/PhHQD (10/10 mmol), TA/HQD (10/10 mmol) and TA/NDA/HQD (7/3/10 mmol), respectively, at temperatures ranging from 280 to 320 °C were carried out as already described for the reaction of ptBuBA with HQD.

Instrumentation. GC was performed with a Hewlett Packard model 5880. The column had a DB-5 stationary phase; 15 m × 0.53 mm i.d.; 1.5 μm film. The measurements were carried out at 70 °C. Proton nuclear magnetic resonance (^{1}H NMR) was conducted on a Bruker AM-250 at 250 MHz. GC/MS was performed on a Hewlett Packard GC/MS system equipped with a model 5890 GC and a model 5970 mass

Scheme 2. The Dimerization and Trimerization in the Initial Stage of Polymerization of TA with HQD



spectrometer connected to a RTE-6 data system. Separation was made on an HP Ultra-2 column (5% phenyl, methyl silicone OV-5, 25 m × 0.20 mm i.d, 0.3 μm film) with the following sequence: 70 °C for 1 min followed by a 20 °C/min gradient to 300 °C.

Results and Discussion

Kinetic Treatment of Acidolysis Reaction in the AA/BB Polymerization. TA and NDA, the two diacids used in this study, are highly insoluble. Therefore, their polymerizations with HQD and PhHQD proceed heterogeneously, and this will affect the kinetics. The polymerization rate of this bimolecular reaction should be dependent on the concentration of acetoxy and carboxylic acid groups in the homogeneous liquid phase. Because HQD and PhHQD are part of the homogeneous phase, their concentration determines the initial concentration of acetoxy groups [CH_3COO]. The carboxylic acid group concentration, however, is not only dependent on the amount of dissolved TA, but also on dissolved oligomer in the liquid phase. In other words, [COOH] depends on the dimerization and trimerization reactions in the initial stages of the polymerization of TA with HQD, as shown in Scheme 2. The reaction rate is given as follows:

$$\frac{-\mathrm{d}[\mathrm{CH_3COO}]}{\mathrm{d}t} = k_1[\mathrm{TA_s}][\mathrm{HQD}] + k_2[\mathrm{dimer_s}][\mathrm{HQD}] + k_3[\mathrm{TA_s}][\mathrm{dimer_s}] \quad (1)$$

in which [HQD], [TA_s], and [$dimer_s$] are the concentrations of HQD, soluble TA, and soluble dimer, respectively, at the reaction time t. The concentration of soluble TA and soluble dimer is much lower than that of HQD; that is, $k_1[\mathrm{TA_s}][\mathrm{HQD}] + k_2[\mathrm{dimer_s}][\mathrm{HQD}] \gg k_3[\mathrm{dimer_s}][\mathrm{TA_s}]$, and the value of $k_3[\mathrm{dimer_s}][\mathrm{TA_s}]$ is negligible. Therefore, we can transform eq 1 as follows:

$$\frac{-\mathrm{d}[\mathrm{CH_3COO}]}{\mathrm{d}t} = k_1[\mathrm{TA_s}][\mathrm{HQD}] + k_2[\mathrm{dimer_s}][\mathrm{HQD}] \quad (2)$$

The concentration of soluble TA stays constant in the early stages of polymerization. The concentration of soluble dimer changes from zero at the start of the reaction to constant during the equilibrium of the soluble dimer with insoluble dimer after a very short time. We assume that the equilibrium is reached very rapidly. Therefore, we can treat the value of $k_1[\mathrm{TA_s}] + k_2[\mathrm{dimer_s}]$ as constant in the early stage of polymerization. Because the concentration of acetoxy groups is twice the concentration of HQD ([CH_3COO] = 2 [HQD]), eq 2 can be transformed into eq 3, which is a pseudo-first-order kinetic equation:

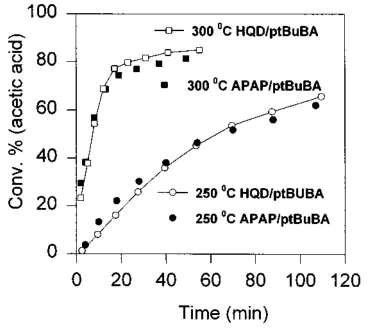


Figure 2. Conversion of the reaction of ptBuBA with either HQD or APAP at 250 and 300 °C as a function of time: $[\mathrm{ptBuBA}]_0/[\mathrm{HQD}]_0 = 2/1$ (mol/mol), $[\mathrm{ptBuBA}]_0/[\mathrm{APAP}]_0 = 2/1$ (mol/mol).

$$\frac{-\mathrm{d}[\mathrm{HQD}]}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{HQD}] \quad (3)$$

$$k_{\mathrm{obs}} = \frac{1}{2}(k_1[\mathrm{TA_s}] + k_2[\mathrm{dimer_s}])$$

If a straight line is obtained when ln [HQD] is plotted versus time, we can conclude that the reaction is a first-order reaction based on eq 4:

$$\ln\,[\mathrm{HQD}] = -k_{\mathrm{obs}}t + B \quad (4)$$

in which k_{obs} is the observed reaction rate constant and B is a constant. The concentration of HQD at any time can be determined experimentally, as shown in eq 5:

$$[\mathrm{HQD}] = \frac{N_{\mathrm{m\ AcOH(initial)}} - N_{\mathrm{m\ AcOH(total)}}}{2} \quad (5)$$

in which $N_{\mathrm{m\ AcOH\ (initial)}}$ and $N_{\mathrm{m\ AcOH\ (total)}}$ are the number of moles of acetic acid before the polymerization and at the polymerization time t, respectively.

Kinetics of the Model Reaction of ptBuBA with HQD or APAP. HQD and APAP are important BB-type monomers for the synthesis of MCLCPs. Their reactivities were investigated in a kinetic study of their reactions with ptBuBA in the homogeneous state at temperatures ranging from 250 to 300 °C in bulk. The formation of acetic acid as a function of the reaction time is shown in Figure 2. The production rate of acetic acid is almost the same for both reactions, indicating that APAP and HQD have the same reactivity in the AA/BB polymerization at these temperatures. This result was confirmed by the investigation of the reactivity of acetoxy and acetamide functional groups of APAP with the monofunctional carboxylic acid ptBuBA. The reaction is shown in Scheme 3. After 7 min of reaction of ptBuBA with APAP at 290 °C, the ratio of the two peaks of unreacted acetamide and acetoxy function group, as measured by the integration in the ^{1}H NMR spectrum, is 59/54.

The kinetic treatment of the reaction of ptBuBA with HQD (2/1, mol/mol) is similar to the method described in a previous paper for the homopolymerization of ABA.[7] The kinetic equation for the homogeneous second-order reaction is shown in eq 6:

$$\frac{1}{M} = k_{\mathrm{obs}}t + B \quad (6)$$

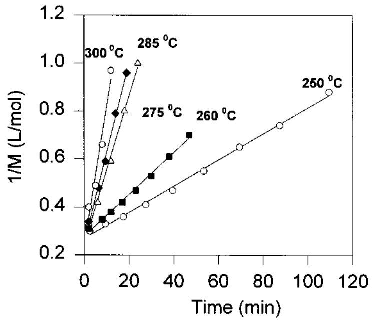


Figure 3. 1/[M] as a function of time in the bulk reaction of ptBuBA with HQD at different temperatures.

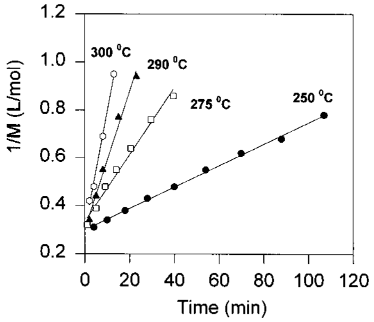
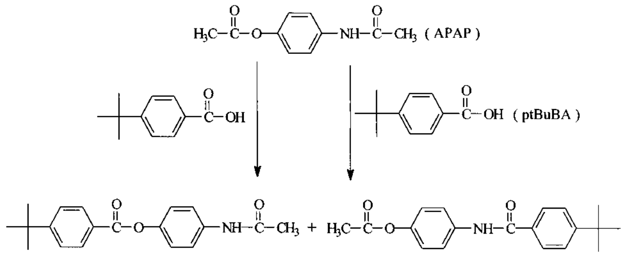


Figure 4. 1/[M] as a function of time in the bulk reaction of ptBuBA with APAP at different temperatures.

Scheme 3. The Reactions of ptBuBA with Acetoxyl and Acetamide Functional Groups of APAP



in which M is the molar concentration of the reactants at reaction time t, k_{obs} is the observed reaction rate constant, and B is a constant. The second-order plots of $1/M$ versus t are shown in Figure 3. Straight lines indicate that it is a second-order reaction at temperatures ranging from 250 to 300 °C. The reaction of ptBuBA with APAP (2/1, mol/mol) is also a second-order reaction, which was proven by the straight lines from the plots of $1/M$ versus t shown in Figure 4.

The reaction rate constants (k_{obs}) of both reactions obtained from the slope of the straight lines in Figure 3 and 4 were used to determine the activation energy (E_a) and the frequency factors (A) on the basis of eq 7:

$$\ln k_{obs} = \frac{-E_a}{RT} + \ln A \tag{7}$$

The Arrhenius plots of ln k_{obs} versus $10^3/T$ (k^{-1}) are shown in Figure 5. Values of E_a and ln A are listed in Table 1.

Kinetics of the Bulk Copolymerization of TA/HQD, TA/PhHQD, and TA/NDA/HQD. The kinetics of the bulk copolymerization of TA/HQD (1/1, mol/mol), TA/PhHQD (1/1, mol/mol), and TA/NDA/HQD (7/3/10, mol/mol/mol) were investigated in the heterogeneous state at temperatures ranging from 280 to 320 °C in bulk. The evolution of acetic acid (conversion of polymerization) as a function of polymerization time at 300 °C is shown in Figure 6, which shows that the polymerization of TA/PhHQD is the fastest and the polymerization of TA/NDA/HQD is faster than the polymerization of TA/HQD. The polymerization rate increases in the order: TA/HQD < TA/NDA/HQD < TA/PhHQD.

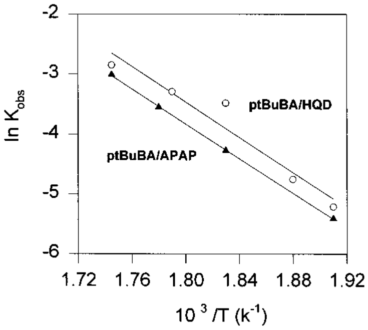


Figure 5. Arrhenius plots of the bulk reaction of ptBuBA with either HQD or APAP.

The first-order plots for the bulk copolymerizations of TA/PhHQD, TA/HQD, and TA/NDA/HQD at temperatures ranging from 280 and 320 °C are shown in Figures 7, 8, and 9, respectively. The straight lines demonstrate that these polymerizations are first-order reactions at these temperatures in the early stages. The reaction rate constants (k_{obs}) were measured from the slopes of the straight lines in Figures 7, 8, and 9, respectively, based on eq 4. Figure 10 shows the Arrhenius plots of ln k_{obs} versus $10^3/T$ (k^{-1}) for the measurement of the activation energy (E_a) and frequency factors (A). The values of k_{obs}, E_a, and ln A are presented in Table 1. To compare different reaction systems, the kinetic data for other model reactions and polymerizations are also listed in the same table.

Comparison of the Reactivity of the Different Monomer System. From the results shown in Table 1, we can draw several conclusions. First, the reaction rate constants increase with the increasing reaction temperature for all reactions and polymerizations. Second, the values of E_a and ln A for the reaction of ptBuBA with HQD are almost equal to those for the reaction of ptBuBA with APAP, indicating that the reactivities of the acetoxy and acetamide groups are very similar. In addition, their E_a and ln A values are also comparable with the values for the reaction of *p-tert*-butylphenyl acetate (ptBuPhOAc) with benzoic acid (BA),[12] and of ABA with ANA.[7] Consequently, we conclude that all these reaction rate constants are of the same order of magnitude. Third, at a given temperature, the polymerization rate increases in the order: TA/HQD < TA/NDA/HQD < TA/PhHQD. For example, the reaction rate constants for the polymerization of TA/PhHQD(1/1, mol/mol), TA/NDA/HQD (7/3/10, mol/mol/mol), and TA/HQD at 280 °C are 5.9, 5.6, and 3.7 (10^3 min^{-1}), respectively. The different reaction rates in these polymerizations are discussed next.

The initial rates of these polymerizations are mainly determined by the reactions of monomer with monomer and of monomer with dimer, as shown in eq 2. The concentration of soluble TA is assumed to be very similar in these systems. Therefore, we can conclude that the concentration of soluble dimer plays a decisive role in the determination of these polymerization rates. We believe that the dimer of TA and HQD is more insoluble than TA, whereas the dimers of TA/PhHQD and of NDA/HQD are more soluble than TA. We cannot measure the solubility directly and the aforementioned

Table 1. Reaction Rate Constants (k_{obs}),[a] Activation Energies (E_a),[b] and Frequency Factors (ln *A*) for Bulk Reaction

	T (°C)											
systems	250	265	275	280	285	290	300	310	315	320	E_a[b]	ln *A*
ptBuBA/HQD	5.4	8.7	31		37		58				29	23
ptBuBA/APAP	4.5		14			29	49				29	22
ABA/ANA[7]	4.9		13				43				25	19
ptBuPhOAc/BA[c]	3.5										29	
TA/PhHQD				5.9		7.9	19	40			44	35
TA/NDA/HQD				5.6			18		48		39	30
TA/HQD				3.7		7.0	15			32	35	27

[a] k_{obs} is reported in 10^3 L mol^{-1} min^{-1} from the reaction of HQD/ptBuBA to ptBuPhOAc/BA, and in 10^3 min^{-1} from the polymerization of PhHQD/TA to HQD/TA. [b] E_a is reported in kcal/mol. [c] Reaction was carried out in open system using diphenyl ether as solvent.[12]

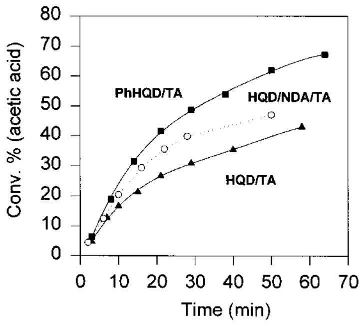


Figure 6. Conversion of the bulk copolymerization of TA/HQD, TA/PhHQD, and TA/NDA/HQD at 300 °C as a function of time: $[TA]_0/[HQD]_0 = 1/1$ (mol/mol), $[TA]_0/[PhHQD]_0 = 1/1$(mol/mol), and $[TA]_0/[NDA]_0/[HQD]_0 = 7/3/10$ (mol/mol/mol).

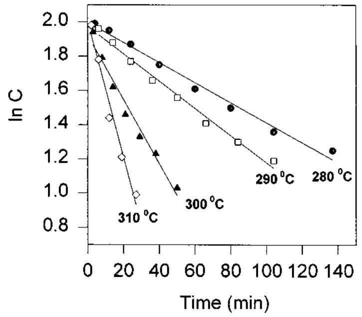


Figure 7. Plot of ln *C* as a function of time in the bulk copolymerization of TA and PhHQD at different temperatures: $[TA]_0/[PhHQD]_0 = 1/1$ (mol/mol).

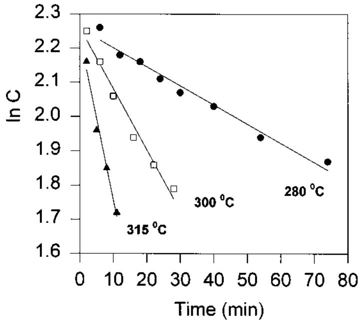


Figure 8. Plot of ln *C* as a function of time in the bulk copolymerization of TA, NDA, and HQD at different temperatures: $[TA]_0/[NDA]_0/[HQD]_0 = 7/3/10$ (mol/mol/mol).

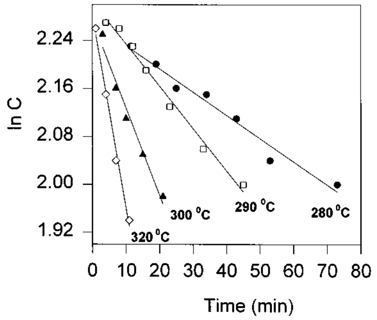


Figure 9. Plot of ln *C* as a function of time in the bulk copolymerization of TA and HQD at different temperatures: $[TA]_0/[HQD]_0 = 1/1$ (mol/mol).

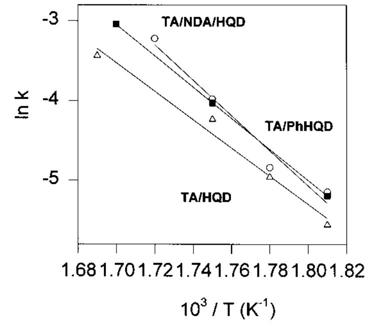


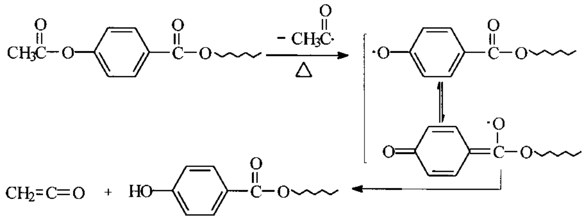
Figure 10. Arrhenius plots for the bulk copolymerization of TA/HQD, TA/PhHQD, and TA/NDA/HQD.

assumptions were deduced from the following facts and the analysis of molecular structure. The dimer and trimer derived from ABA, which are very similar to the TA/HQD oligomers, are more insoluble than ABA itself.[7] On the other hand, the dimer and trimer of TA with PhHQD are more soluble than TA because the polymerization visibly changes from heterogeneous to homogeneous during the polymerization. The chain packing of dimers from TA/PhHQD and NDA/HQD is frustrated by the presence of the phenyl group of PhHQD and the naphthalene moiety (nonlinear structure) of NDA. The polymerization mixture of TA/NDA/HQD contains 15% solubilizing NDA, whereas the polymerization of TA with PhHQD consists of 50% solubilizing PhHQD. Therefore, the concentration of soluble TA/PhHQD dimers is higher than that of soluble NDA/HQD dimers in the polymerization. Based on the observed polymerization rates, we can conclude that the higher the concentration of the soluble dimer, the faster the polymerization.

The polymerizations of TA/HQD, TA/PhHQD, and TA/NDA/HQD all follow first-order kinetics in the initial stages of the polymerization, as shown in Figures 7, 8, and 9, respectively. These first order kinetics are due to the constant concentration of the soluble TA or NDA and the concentration of their dimers in these heterogeneous polymerizations, as already discussed. However, the model reactions of ptBuBA with HQD or APAP are second-order reactions because all starting materials are soluble, and their concentrations change during the homogeneous reactions. In addition, the first-order reaction kinetics for these polymerizations indicate that the equilibrium of soluble dimers with insoluble dimers is reached very quickly in the initial stages, as already assumed. The reaction rate constants of the homogeneous reactions of HQD/ptBuBA and ptBuPhOAc/BA are larger than those of the heterogeneous polymerization from TA/PhHQD to TA/HQD, as shown in Table 1. Very recently, Mathew and co-workers[11] published a paper describing the bulk polymerization of TA and HQD. They assume second-order kinetics, which we find unsatisfactory because the heterogeneous nature of the polymerization.

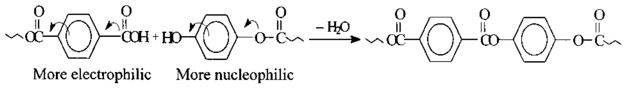
Mechanism of the AA/BB Polymerization. In an AB polymerization, such as the polymerization of ABA and ANA, a mechanism change from acidolysis in the early stages to phenolysis in the later stages of polymerization has been proposed in our previous work.[14] The phenolysis mechanism is responsible for the formation of high molecular weight of polymer in the later stages of this polymerization. The question arises as to what mechanism the AA/BB polymerization follows.

In the AB type polymerization of ABA and ANA, phenyl ester end groups are formed by the decarboxylation of carboxylic acid groups and phenolic hydroxyl end groups by the decomposition of acetoxy end groups and by acidolysis.[14] Decarboxylation of aromatic carboxylic acid groups is very well documented.[15] In the AB polymerization the decarboxylation is thought to be even more favored because of the electronic effects from the electron-donating substituent in the *para*-position based on the S_E2 mechanism. The decomposition of acetoxy end group is also favored because of the electronic-accepting *para*-substituent on the benzoic acetate.



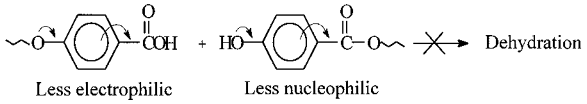
To achieve high molecular weight, these phenyl ester and phenolic hydroxyl end groups formed in side reactions have to be able to react. Indeed, we showed that phenolysis is a viable mechanism under these conditions.

In contrast, in the AA/BB polymerization, the decarboxylation of the carboxylic acid end group does not take place. This point is supported by the fact that TA heated at 330 °C for 3 h does not decarboxylate. The formation of carbon dioxide and benzoic acid was not observed. We propose that this lack of decarboxylation is due to the deactivating effect of an acceptor substituent in the *para*-position. Therefore, no phenyl ester end groups are formed. However, the phenolic hydroxy end groups are still formed by the decomposition of acetoxy end groups, although probably more slowly.[14] To achieve high molecular weight, a mechanism different from the phenolysis observed in the AB system has to be operational. The question arises if the phenolic hydroxy end groups are able to react with the remaining carboxylic acid end groups in a dehydration.



The proposed dehydration reaction of a phenolic hydroxy with a carboxylic acid end group in the AA/BB polymerization was investigated by using the model reaction of *p*-*tert*-butyl phenol with ptBuBA. The formation of *p*-*tert*-butylphenyl/ptBuBA was confirmed by GC/MS.

We previously showed that the dehydration of a phenolic hydroxy with a carboxylic acid group does not take place in the AB type polymerization of ABA and ANA. This statement was supported by the investigation of the model reaction of *p*-benzoyloxybenzoic acid with phenyl *p*-hydroxybenzoate.[14] So, why is there a difference between the AB type polymerization and the AA/BB type polymerization? The following argument can be made. The AB monomer has an electron-donating substituent *para* to the carboxylic acid end groups and an electron-accepting substituent *para* to the phenolic hydroxyl end groups, making the carbonyl carbon of carboxylic acid less electrophilic and the phenolic hydroxyl less nucleophilic.



No dehydration occurs. However, in the AA/BB polymerization, the carbonyl carbon of the carboxylic acid end groups is more electrophilic because of the electron-accepting substituent in the *para* position, and the phenolic hydroxyl is more nucleophilic because of the electron-donating substituent in the *para* position, as already shown. Therefore, we conclude that dehydration is a feasible reaction in this case.

Conclusions. The acidolysis kinetics in the initial stages of the AA/BB polymerization were investigated by a newly developed GC method. Highly reproducible results were obtained from the model reaction of ptBuBA with HQD or APAP and the polymerization of TA/PhHQD, TA/HQD, and TA/NDA/HQD at higher temperatures in bulk. Reaction temperature and dimer solubility have a pronounced influence on the reaction rate. The higher the solubility of oligomer, the faster the reactions. HQD and APAP have the same reactivity. The polymerization of TA/NDA/HQD (7/3/10, mol/mol/mol) is faster than polymerization of TA/HQD (1/1, mol/mol) but slower than TA/PhHQD (1/1, mol/mol). The model reactions follow second-order kinetics. The polymerizations of TA/HQD, TA/NDA/HQD and TA/PhHQD are pseudo-first-order reactions. A dehydration esterification is proposed for the later stage of AA/BB polymerization.

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