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A Change in Mechanism from Acidolysis to Phenolysis in the Bulk Copolymerization of 4-Acetoxybenzoic Acid and 6-Acetoxy-2-naphthoic Acid

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ABSTRACT: The polymerization reaction and its side reactions were investigated in the synthesis of 4-acetoxybenzoic acid (ABA) and 6-acetoxy-2-naphthoic acid (ANA) copolymers by the measurement of byproducts and polymer molecular weight and the study of polymer end groups and model reactions. A method was developed to isolate and collect the byproducts produced in the polymerization. These byproducts, acetic anhydride, phenol, phenyl acetate, ketene, and carbon dioxide, were detected using HPLC and GC/MS. The existence of acetoxy, carboxy, phenyl ester, and phenolic hydroxyl end groups on the polymer chain was confirmed by direct measurement of end groups and polymer molecular weight and by the study of model reactions, such as the decarboxylation of 4-(benzoyloxy)benzoic acid and the decomposition of ABA methyl ester. For the bulk copolymerization of ABA and ANA at temperatures ranging from 195 to 325 °C under nitrogen, the classical acidolysis mechanism changes to a phenolysis mechanism in the late stages of the polymerization.

Introduction

Liquid crystal polymers (LCPs), which are polymers exhibiting liquid crystal characteristics either in solution (lyotropic liquid crystal) or in the melt (thermotropic liquid crystal), have experienced an explosive growth in the last 20 years. This is primarily due to the fact that successful applications of LCPs have been developed, especially in electronic display and in nonlinear optical systems.[1,2]

Thermotropic LCPs can roughly be divided into thermotropic main chain LCPs and thermotropic side chain LCPs. Thermotropic main chain LCPs (MCLCPs), made of rigid groups within the polymer chain, occupy a unique position because of their well-known high mechanical strength and modulus, very good chemical resistance, and excellent dimensional stability.

At present, most applications of MCLCPs have involved the copolymer of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA). Commonly HBA/HNA copolymers are prepared in a two-step process. In the first step, HBA and HNA are converted into ABA and ANA by acetylation. In the second step, ABA and ANA monomers are polymerized in an autoclave under a nitrogen atmosphere from 195 to 325 °C, and then a vacuum is applied at 325 °C. The study of kinetics and mechanism for this highly successful LCP is of interest because knowledge of the correct rate equation and kinetic parameters and an understanding of the reaction mechanism will provide data to improve the polymer properties and to optimize the industrial process.

The kinetics of the bulk copolymerization of ABA and ANA at temperatures between 250 and 300 °C under nitrogen has been studied via the measurement of evolved acetic acid using titrimetry.[3] This copolymerization follows second-order reaction kinetics up to 70% conversion. Two kinetic regions were found in $1/(1 - p)$ vs time curves, in which p is the percent conversion. The first reaction constant is larger than the second one. The higher the polymerization temperature and the concentration of ABA, the earlier the appearance of the second kinetic region and the faster the polymerization reaction.

A detailed mechanism of the bulk copolymerization of ABA and ANA has not been described to date. But the reaction mechanism and side reactions of the homopolycondensation of ABA were investigated by Kricheldorf's group.[4] They claimed that in the crystalline state the condensation and transesterification led to the formation of high molecular weight polymer at temperatures above 280 °C, at which the oligomeric chains in the crystallites of oligomeric HBA have the necessary reactivity and segmental mobility for “living” character. On the basis of the investigation of the side reactions, such as the decarboxylation of ABA, Fries rearrangement, and the decomposition of acetoxy groups, they reported that “the polymerization of ABA above 300 °C is far from being a clean process.”[5]

The acidolysis reaction, namely the exchange reaction between acetoxyaryl groups and carboxylic acid group, has been investigated for the polyarylate synthesis. Two kinds of acidolysis mechanisms have been reported: a mechanism involving a four-membered ring transition state[6] and a mechanism involving an intermediate anhydride.[7−9] In 1961, a mixed anhydride mechanism was postulated by Temin[7] for the acidolysis in the study of the polymerization of bisphenol-A- diacetate with either adipic or sebacic acid. Sixteen years later, Ricke and co-workers proposed the same mechanism based on the detection of bisphenol and its monoacetate in the preparation of a copolyester from a preformed polyester, diacid, and diacetate.[8] In 1992, more evidence for an acidolysis mechanism involving a mixed anhydride was obtained by Hall's group in model studies.[9] The formation of *p*-*tert*-butylphenol, benzoic anhydride, and acetic benzoic anhydride was detected in the model reaction of *p*-*tert*-butylphenyl acetate with benzoic acid. These

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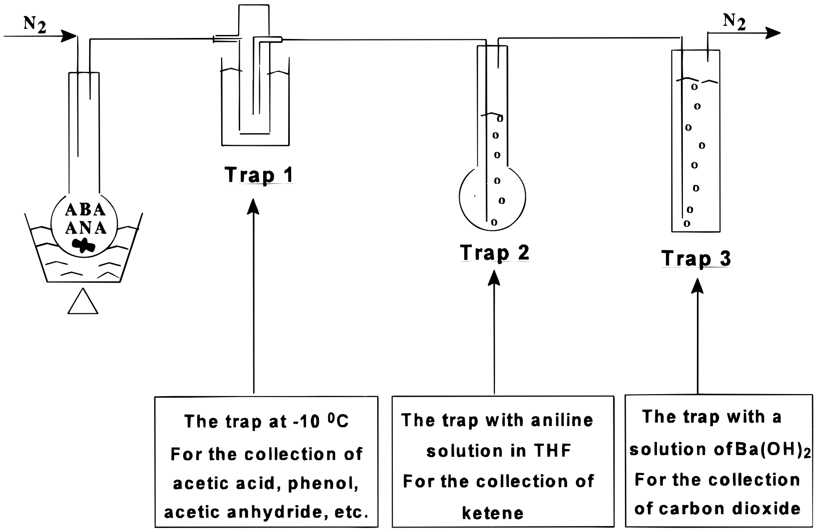
Scheme 1. Setup for Trapping the Byproducts Produced in the Bulk Copolymerization of ABA and ANA



results supported and confirmed the acidolysis mechanism involving an intermediate mixed anhydride.

Side reactions leading to colored polyarylate in the acidolysis reaction were investigated by several groups. In the investigation of polyarylate model compounds by thermal decomposition, it was found that ketene produced by the decomposition of an acetate ester is one source of colored materials during the polyarylate synthesis.[10] Colored polyarylate resulting from a structural imperfection along the polymer backbone was reported by Dean.[11] He found that the formation of o-hydroxydibenzoylmethane in the polyarylate polymer chain led to color. On the basis of the analysis of standard poly-HBA samples prepared at 350 °C for 16 h and a rapid Fries rearrangement of the crystal molecular weight poly-HBA above 510 °C, Kricheldorf proposed that phenolic hydroxyl groups were formed from the thermal Fries rearrangement in the poly-HBA chains.[5] The phenolic hydroxyl groups are of the cause of the colored polyarylate.

The purpose of this work was to study the mechanism of the bulk copolymerization of ABA and ANA at temperatures ranging from 250 to 325 °C under nitrogen. The byproducts formed during the polymerization were isolated and detected. The nature of the end groups on the polymer chains was investigated by direct measurement of the end groups and the polymer molecular weight and by studying the model reactions. On the basis of these results, a change of mechanisms from acidolysis to phenolysis will be proposed in the bulk copolymerization of ABA and ANA.

Experimental Section

Materials. 4-(Benzoyloxy)benzoic acid (Indofine), 4-acetoxybenzoic acid methyl ester (Aldrich), phenyl *p*-hydroxybenzoate (97%, Pfaltz & Bauer, Inc), aniline (99.9%, Alfa Products) and THF (99.9%, Aldrich) were used as received. 4-Acetoxybenzoic acid (ABA) (Aldrich) was recrystallized from methanol. 6-Acetoxy-2-naphthoic acid (ANA) was prepared by the sodium hydroxide catalyzed reaction of 6-hydroxy-2-naphthoic acid (HNA) with acetic anhydride and then recrystallized from methanol.

Polymerization Procedures. The polymerization was conducted on a 9.3 g scale in bulk. The reactants were charged in a 73:27 molar ratio ABA:ANA. The copolymerizations were carried out at temperatures ranging from 250 to 325 °C for 4 or 5 h. The nitrogen purge line from the bulk polymerization was bubbled through a series of traps as shown in Scheme 1: a cold trap at −10 °C, a trap containing aniline solution in THF for the collection of ketene, and a trap containing aqueous barium hydroxide solution for the collection of carbon dioxide.

The Measurement of Trapping Efficiency of the Cold Trap. The formation of acetanilide by the reaction of ketene with aniline was used to identify ketene.[12] Because acetic anhydride would also react with aniline to form acetanilide, a cold trap at −10 °C (in Scheme l) was used to trap the evolved acetic anhydride (bp 139 °C) and to separate it from ketene (bp −56 °C). In order to know if the acetic anhydride and ketene could be separated, the trapping efficiency of the trap 1 was measured. A known amount of acetic anhydride was distilled through the cold trap at −10 °C, and the trapping efficiency was calculated by weighing the amount of trapped acetic anhydride. The trapping efficiency was 99.72% and 99.73% in two separate tests, indicating that acetic anhydride was almost completely trapped in trap 1. Ketene will pass through trap 1 and will be collected in trap 2, if present. Consequently, we can use these traps to identify ketene by its reaction with aniline. If a large amount of acetic anhydride were evolved, the formation of a very small trace of acetanilide could be ascribed to a trace of acetic anhydride reaching trap 2.

The Thermolysis of ABA Methyl Ester. The decomposition of ABA methyl ester was conducted in a 50 mL round bottom flask with a long neck connected with a short condenser. The condenser was 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 flow of gas phase. The gas stream was directed through a cold trap at −10 °C and through a trap containing a THF solution of aniline. The decomposition of ABA methyl ester was carried out at 325 °C for 2 h under normal pressure.

The Synthesis of 6-(Benzoyloxy)-2-naphthoic Acid. HNA (9.4 g, 0.05 mol) was dissolved in 20 g of a sodium hydroxide aqueous solution (20% by weight) and 9.4 mL of benzoyl chloride was added. The reaction mixture was shaken vigorously at 0 °C for 2 h. The white precipitate was filtered and then recrystallized from ethanol. The product was dried under vacuum. Its structure and purity was confirmed by ^1H NMR and GC/MS.

The Decarboxylation of 4-(Benzoyloxy)benzoic Acid and 6-(Benzoyloxy)-2-naphthoic Acid. The decarboxylation of 4-(benzoyloxy)benzoic acid and 6-(benzoyloxy)-2-naphthoic acid was carried out using the same setup as described for the thermolysis. The gas stream in this case was passed through a trap containing an aqueous solution of $Ba(OH)_2$ to collect carbon dioxide. The flask containing 4-(benzoyloxy)benzoic acid or 6-(benzoyloxy)-2-naphthoic acid was heated in a thermostated silicone oil bath under normal pressure at 325 °C for 2.5 and 3 h, respectively.

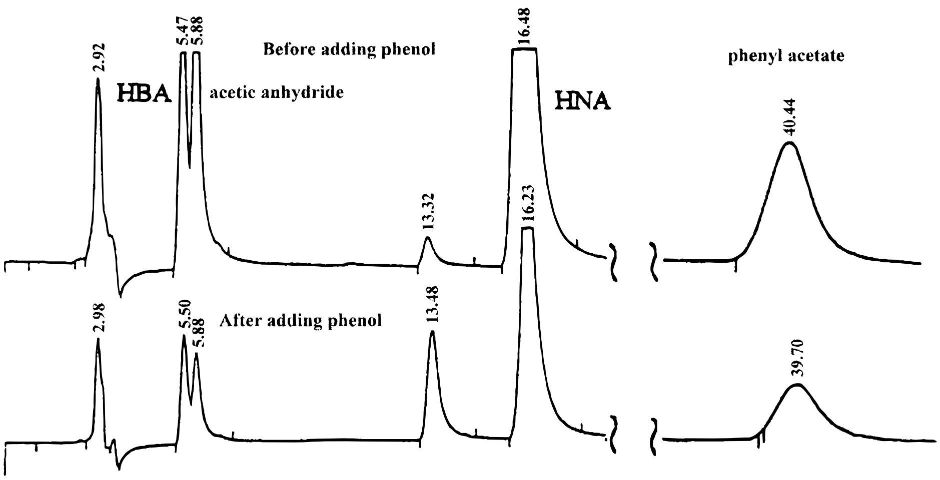


Figure 1. HPLC chromatogram of the distillate in trap 1 from the bulk copolymerization of ABA and ANA at 270 °C before and after adding phenol.

The Hydrolysis of Copolymers. ABA/ANA copolymer was purified using acetone in a Soxhlet extraction apparatus for 1 day, and then hydrolyzed in a solvent mixture of NaOH/H_2O/CH_3OH at 70 °C for 1 day. Before the measurement by GC/MS, aqueous hydrochloric acid was added to the solution of hydrolyzed copolymer until the pH reached 6–7.

The Measurement of the Converted Acetoxy End Group. Acetic anhydride and ketene are obtained from the acidolysis and the decomposition reaction of the acetoxy end group, respectively. In order to know how many acetoxy end groups were converted, acetic anhydride and ketene were collected in the trap containing the aniline solution in ethanol. The amount of acetic anhydride and ketene was calculated from the measurement of acetanilide formed by their reactions with aniline in the trap. The whole procedure is as follows: The trap containing aniline dissolved in ethanol was connected with the bulk copolymerizations of ABA and ANA (ABA:ANA = 73:27) by the nitrogen purge line. The copolymerization was carried out on a 10 g scale at a constant temperature in the range from 250 to 300 °C for 5 h. The trapped volatile products were concentrated by removing ethanol under vacuum. Aqueous sodium hydroxide was added until the solution was basic, and the organic layer was extracted using ether. This solution was concentrated and acidified with an aqueous hydrochloric acid solution. Acetanilide was isolated from the excess aniline by the extraction of this solution with chloroform. The amount of acetanilide was weighed. The corresponding amounts of the converted acetoxy end group were 2.6, 2.7, and 2.8% for the polymerization at 250, 275, and 300 °C, respectively.

Measurements. ^1H nuclear magnetic resonance (NMR) was performed on a Bruker AM-250 at 250 MHz. High-pressure liquid chromatograph (HPLC) was conducted on a Beckman Model 110A. The conditions of HPLC were as follows: column, 250 × 4.6 mm; packing, Nucleosil C18AB; mobile phase, acetonitrile/water + acetic acid; flow rate, 1 mL/min; and detector, UV at 254 nm. GC/MS was performed on a Hewlett-Packard GC/MS system equipped with a model 5890 GC and a model 5970 mass 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

The copolymerization of ABA and ANA, prepared from HBA and HNA by acetylation, is typically carried out at temperatures ranging from 190 to 325 °C under normal pressure and then at 325 °C under vacuum. This polymerization reaction and its side reactions were studied in detail in bulk at temperatures ranging from 195 to 325 °C under nitrogen, including the investigation of the model reactions, byproducts, polymer molecular weight, and the end groups on the polymer chains.

Isolation and Detection of Byproducts. Volatile byproducts form along with the polymer in the bulk copolymerization of ABA and ANA at temperatures ranging from 190 to 325 °C under nitrogen atmosphere. In order to isolate and identify these volatile byproducts, a setup consisting of three traps was designed and connected to the polymerization system as shown in Scheme 1. Trap 1 is a cold trap at −10 °C for the collection of the volatile byproducts with rather high boiling points, such as acetic acid and acetic anhydride. Trap 2 contains an aniline solution in THF and is desired to collect ketene. Trap 3 contains an aqueous solution of barium hydroxide for the collection of carbon dioxide. The copolymerization was run at 275 °C for 4 h under nitrogen, and the volatile byproducts were collected in these traps and analyzed by HPLC or GC/MS.

HPLC was used to analyze the distillate in trap 1. The intensity of the peak at 13.32 min increased by the addition of pure phenol to the distillate, as shown in Figure 1. This indicates that this peak is due to phenol. The confirmation of the identity of the peaks for acetic anhydride, phenyl acetate, HBA, and HNA was also performed by comparison with authentic standard compounds.

The content of trap 2 was concentrated and analyzed by GC/MS, and its GC chromatogram is presented in Figure 2. The peaks at 3.91 and 8.12 min are from aniline and butylated hydroxytoluene, respectively. The latter is used as a stabilizer in THF. The peak at 7.21 min has a molecular ion at 135 *m/z* as shown by its MS spectrum. The corresponding molecular ion and fragment ions are in very good agreement with those produced by authentic acetanilide. Therefore, we proved that acetanilide is formed in this trap and conclude that ketene is a byproduct from this copolymerization.

A $BaCO_3$ white precipitate was observed in trap 3, thereby demonstrating the formation of carbon dioxide during the copolymerization. More details about the extent and nature of the decarboxylation are described below.

End Groups of Polymer. It is known that acetoxy and carboxy end groups on the polymer chain are formed by the acidolysis mechanism in the bulk copolymerization of ABA and ANA at temperatures ranging from 195 to 325 °C under nitrogen. The question arises whether some polymer chains have other end groups.

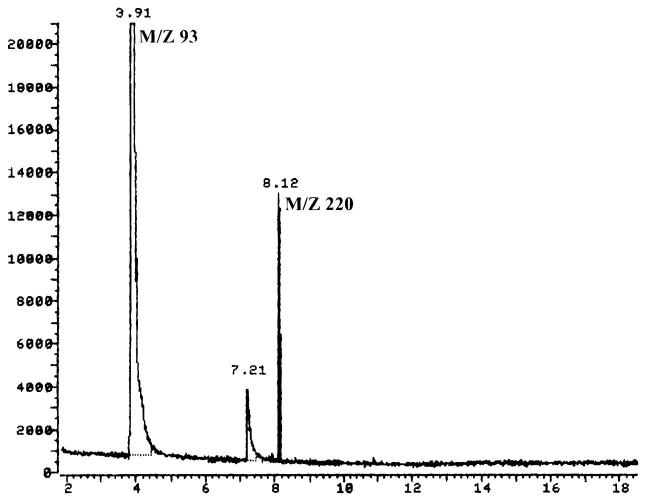


Figure 2. GC chromatogram of compounds in trap 2 from the bulk copolymerization of ABA and ANA at 270 °C.

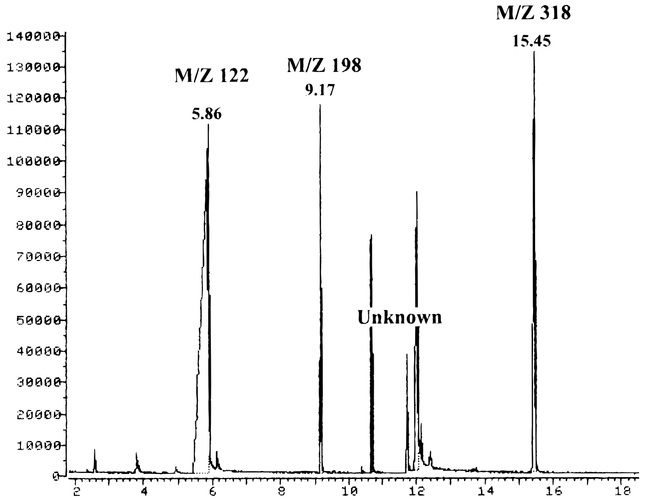
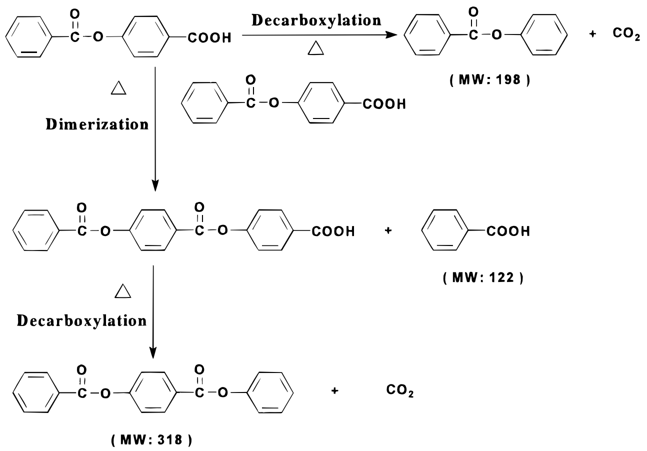


Figure 3. GC chromatogram of the acetone-soluble compounds in the thermolysis flask from the decarboxylation of 4-(benzoyloxy)benzoic acid at 325 °C.

Phenyl Ester End Group. Because it has been reported that the decarboxylation of HBA occurs almost quantitatively at 200 °C,[13] the stability of carboxy groups substituted on terminal phenyl and naphthalene rings on the ABA/ANA copolymer chain was investigated using model compounds.

4-(Benzoyloxy)benzoic acid was used as a model compound for a carboxy group substituted on a terminal phenyl group. The decarboxylation of this model compound was investigated by heating it at 325 °C for 2.5 h under nitrogen. Acetone-soluble compounds and an insoluble white solid were found as residues in the thermolysis flask. The chromatogram from GC/MS analysis of the acetone-soluble compounds is shown in Figure 3. The corresponding *m/z* values of the molecular ions were obtained from their MS spectra. Compounds with MW 122, 198, and 318 are formed as shown in Scheme 2. The compound of MW 122 corresponds to benzoic acid produced by the self-acidolysis of 4-(benzoyloxy)benzoic acid, and the compounds with MW 198 and 318 correspond to phenyl benzoate and phenyl 4-[(phenylcarbonyl)oxy]benzoate, obtained from the decarboxylation of 4-(benzoyloxy)benzoic acid and its dimer, respectively. The white insoluble solid is poly-HBA. These results indicate that the decarboxylation of 4-(benzoyloxy)benzoic acid and its dimer does take place at 325 °C. The formation of carbon dioxide was proven by the observation of a barium carbonate precipitate in the trap containing an aqueous barium hydroxide. On the basis of the measurement of the weight of $BaCO_3$ precipitate, the decarboxylation occurred to the extent of 5.3% by weight. Consequently, the decarboxylation of a carboxy group substituted on a terminal phenyl group on the ABA/ANA copolymer chain is expected to take place during the bulk copolymerization, leading to the formation of carbon dioxide and a phenyl ester end group.

Scheme 2. The Decarboxylation of 4-(Benzoyloxy)benzoic Acid and Its Dimer

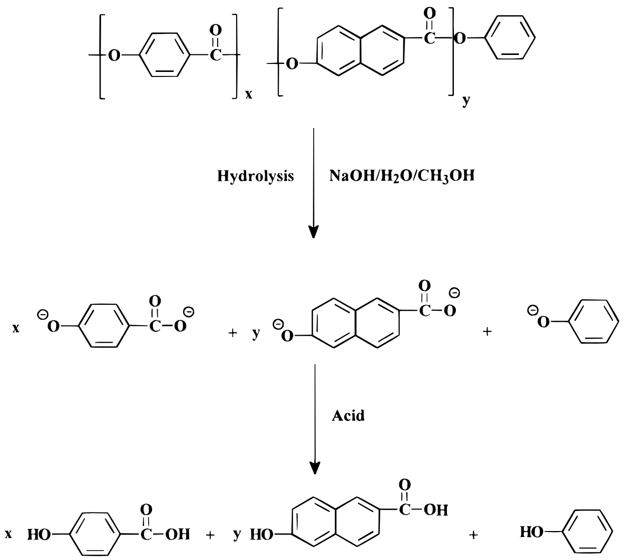


In a similar fashion, 6-(benzoyloxy)-2-naphthoic acid was used as a model compound for a carboxy group substituted on a terminal naphthyl group. The decarboxylation was carried out at 325 °C for 3 h. No white precipitate was observed in the trap with the barium hydroxide aqueous solution during the reaction, indicating that no carbon dioxide was formed. The corresponding compound of the decarboxylation, 6-(benzoyloxy)-2-naphthalene, was not found by GC/MS in the cold trap or in the decarboxylation flask. Therefore, we can conclude that this model compound does not decarboxylate under these conditions. Moreover, the fact that no carbon dioxide forms during the bulk copolymerization of ANA at 275 °C for 5 h confirms that 4-[(naphthylcarbonyl)oxy]-2-naphthoic acid does not decarboxylate.

On the basis of these results, we conclude that some polymer chains will have phenyl ester end group produced by the decarboxylation of a carboxy group substituted on a terminal phenyl end group, but no naphthyl ester end group. The total amount of carbon dioxide formed during the polymerization was calculated from the amount of barium carbonate: 64, 304, and 286 mg of barium carbonate were produced in the copolymerization of ABA and ANA for 5 h at 250, 275, and 300 °C, respectively. This corresponds to 0.58, 2.99, and 2.86 mol % of carboxy end groups being converted into the phenyl ester end groups. The extent of the decarboxylation of the carboxy groups increases 5-fold with an increase of the polymerization temperature from 250 to 275 °C, demonstrating that the temperature plays an important role in the decarboxylation of carboxy end groups. It should be noted that the concentration of the phenyl ester end groups might be lower than indicated by the calculation based on the barium carbonate precipitate, since some carbon dioxide will also be produced by the decarboxylation of HBA.

If the copolymer chains have a phenyl ester end group, then the hydrolysis of ABA/ANA copolymers

Scheme 3. Hydrolysis of ABA/ANA Copolymer Using $NaOH/H_2O/CH_3OH$



using $NaOH/H_2O/CH_3OH$ would result in some phenol being formed, as shown in Scheme 3. The corresponding hydrolysis solutions were analyzed using GC/MS. Phenol was detected in polymer samples made at 325 °C under nitrogen and at 325 °C under vacuum, as shown in the corresponding gas chromatogram (Figure 4). The small peak of phenol (MW 94) indicates the low concentration of phenol and therefore a low concentration of the phenyl ester end groups in the polymer.

The low concentration of phenyl ester end group can be explained as follows. Firstly, the higher the molecular weight of the copolymer, the lower the concentration of the end groups. Secondly, only some of the copolymer chains will have the phenyl ester end group. Finally, the concentration of the phenyl ester end groups will decrease due to the phenolysis reaction which occurs at this high temperature, as will be described below.

Phenolic Hydroxyl End Group. In the proposed acidolysis mechanism (Scheme 4), a phenolic hydroxyl and an intermediate mixed anhydride are formed from the tetrahedral intermediate T1. The latter is formed from the nucleophilic addition of the carboxylic acid to the carbonyl group of the acetate. The phenolic hydroxyl can react with the intermediate mixed anhydride in two ways. One leads to the ABA/ANA copolymer product and acetic acid through the tetrahedral intermediate T2. The other gives acetic anhydride and a symmetric anhydride, which will react with a phenolic hydroxyl group to form ABA/ANA copolymer product and carboxylic acid group. This reaction is supported by the fact that benzoic anhydride does not form anymore at the late stage of the model reaction of *p-tert*-butylphenyl acetate with benzoic acid,[9] but the reaction of *p-tert*-butylphenol with benzoic anhydride does take place.[9] This acidolysis mechanism shows that the phenolic hydroxyl end groups are formed along with acetic acid, acetic anhydride, carboxylic acid, and ester groups and obviously that they will be formed in an amount equal to that of acetic anhydride. Therefore, we conclude that the acidolysis is one of the sources of phenolic hydroxyl end groups.

The formation of ketene and *p-tert*-butylphenol was noted by Hall's group in the decomposition of *p-tert*-butylphenyl acetate at temperatures ranging from 200 to 600 °C.[10] Kricheldorf also proposed that acetoxy end groups decompose to phenolic hydroxyl end groups on the basis of the detection of acetylating reagents (ketene or acetic anhydride) in the polymerization of ABA at temperatures between 300 and 400 °C.[5]

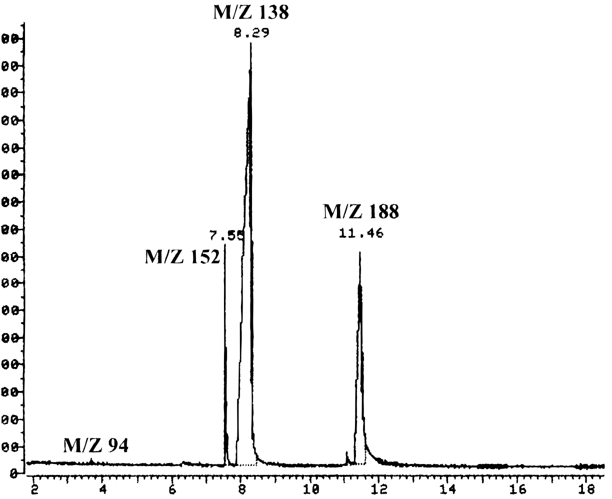
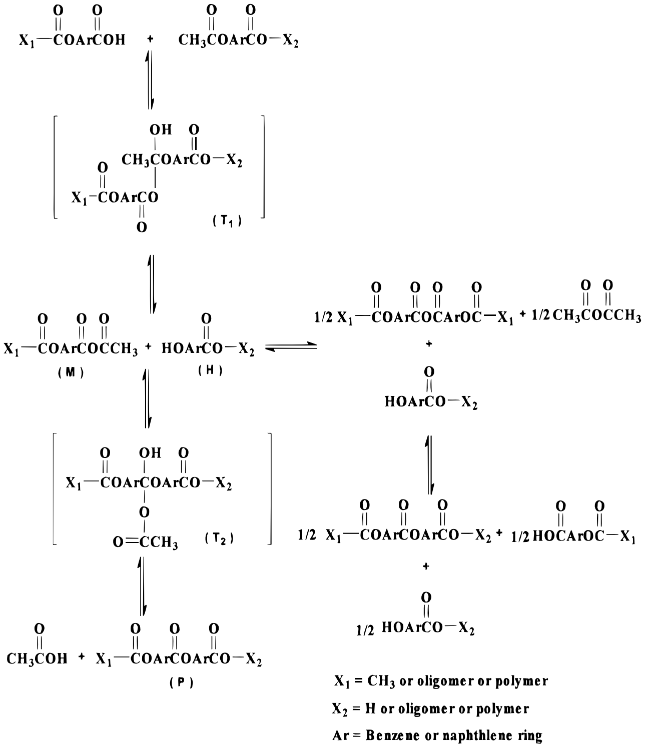


Figure 4. GC chromatogram of the hydrolyzed ABA/ANA copolymer by $NaOH/CH_3OH/H_2O$.

Scheme 4. Proposed Acidolysis Mechanism of the Synthesis of ABA/ANA Copolymer



We reexamined the stability of the acetoxy end group at polymerization temperatures such as 325 °C using a model compound. In order to simulate the structure of acetoxy end groups on the polymer chains, 4-acetoxybenzoic acid methyl ester (ABA methyl ester) was selected as the model compound. The decomposition of ABA methyl ester was carried out at 325 °C for 2 h. As described above, a trap containing an aniline in THF solution was used to trap ketene. Acetanilide was found in this trap, demonstrating the formation of ketene. The formation of ketene was also supported by the formation of HBA methyl ester, which was detected by GC/MS in the residue of the thermolysis flask (Figure 5). The

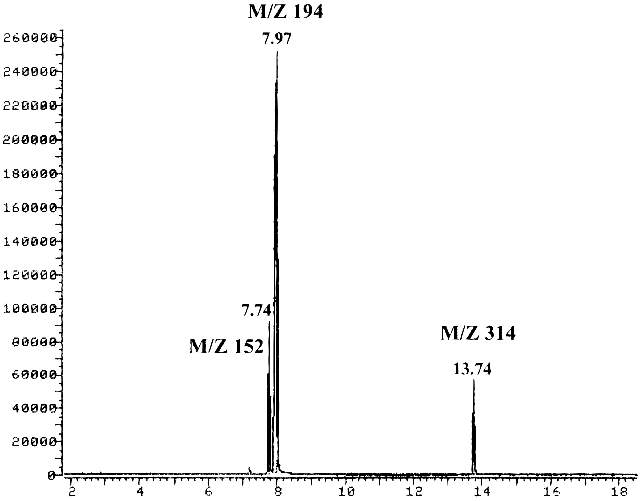


Figure 5. GC chromatogram of compounds in the flask from the decomposition of ABA methyl ester at 325 °C.

Table 1. Uncorrected Values of M_w, M_n, and M_w/M_n of ABA/ANA Polymers Obtained at Temperatures between 250 and 300 °C for 5 h

polymerization temp (°C)	M_w[a]	M_n		M_w/M_n	
		NaOD[b]	PFP[c]	NaOD	PFP
250	1400	1400	1300	1.00	1.20
270	7800	8000	5000	1.00	1.60
300	16200	24700[d]	10000	0.7	1.60

[a] Measured by viscosity method using the Mark−Houwink parameters. [b] Measured by hydrolyzing prepolymer with a mixture of NaOD, D_2O, and CD_3OD and determining the integration ratio of the aromatic peaks to the acetate peak in ^1H NMR. [c] Measured by dissolving prepolymers in pentafluorophenol using ^1H NMR and comparing the aromatic to acetate peak ratio. [d] Values subject to large error due to the small size of the end group peak.

peak at 7.74 min in Figure 5 has 152 *m/z* of molecular ion measured by MS. This molecular ion and fragment ions are ascribed to HBA methyl ester, proving that ABA methyl ester decomposes into ketene and HBA methyl ester. From this we can deduce that phenolic hydroxyl end group will also be produced by the decomposition of acetoxy end group of ABA/ANA polymers along with the loss of ketene.

On the basis of the results above, we conclude that the phenolic hydroxyl end groups can be formed by the acidolysis reaction and by the decomposition of acetoxy end groups on the polymer chains in the bulk copolymerization of ABA and ANA at temperatures ranging from 195 to 325 °C.

Molecular Weight. The number-average molecular weight (M_n) of the polymer was calculated on the basis of the assumption that every polymer chain has one acetoxy end group by measuring the integration ratio of the aromatic peaks to the acetate peak in the ^1H NMR spectrum of the polymer. Two methods were used, either by hydrolyzing the copolymer in a mixture of NaOD, D_2O, and CD_3OD or by dissolving the polymer itself in pentafluorophenol. The weight-average molecular weights (M_w) of the copolymers were measured using the viscosity method. The values of M_w, M_n, and M_w/M_n of polymers are listed in Table 1. It shows that the calculated values of M_w/M_n based on these two methods are less than 2. It is well-known that, for a condensation polymer, the polydispersity will be equal to or larger than 2. Therefore we can assume that the M_n values determined for the copolymers were inflated and that some polymer chains do not have an acetoxy end group. In other words, some acetoxy end groups were converted to other end groups.

Table 2. Corrected Values of M_w, M_n, and M_w/M_n Based on the Loss of Acetoxy End Group of ABA/ANA Polymers Produced at Temperatures between 250 and 300 °C for 5 h

polymerization temp (°C)	M_w[a]	M_n		M_w/M_n	
		NaOD[b]	PFP[c]	NaOD	PFP
250	1400	1100	1000	1.30	1.40
270	7800	3200	2500	2.50	3.10
300	16200	4000	3300	4.00	4.90

[a] Measured by viscosity method using the Mark−Houwink parameters. [b] Same as Table 1, but corrected for loss of acetoxy end group. [c] Same as Table 1, but corrected for loss of acetoxy end group.

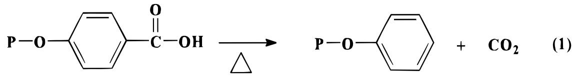
Phenolic hydroxyl end groups are produced during the acidolysis reaction and by the decomposition of acetoxy end groups as described before. The amount of acetoxy end groups converted to phenolic hydroxyl end groups equals the amount of acetic anhydride and ketene formed, which was calculated on the basis of the amount of acetanilide formed by the reaction of acetic anhydride and ketene with aniline in the trap. A total of 2.6, 2.7, and 2.8 mol % of acetoxy end groups were converted to phenolic hydroxyl end groups in the copolymerization of ABA and ANA for 5 h at 250, 275, and 300 °C, respectively. It indicates that most of phenolic hydroxyl end groups are formed during the acidolysis reaction of acetoxy groups. It should be noted that the actual amount of acetoxy end group converted to phenolic hydroxyl end groups will be higher than the observed amounts above. The reason is that the amount of acetanilide formed is lower than the actual amount of acetic anhydride and ketene due to their reactions with ethanol and/or phenol in the trap.

The inflated M_n values were corrected using the observed amount of acetoxy end groups converted to phenolic hydroxyl end groups, as shown in Table 2. In the case of the polymerization at 275 and 300 °C, the M_w/M_n values are now larger than 2, as expected for a polycondensation. For the polymerization at 250 °C, the M_w/M_n value is still smaller than 2, because the observed amount of acetoxy end groups converted to phenolic hydroxyl end groups is lower than the actual amount. Certainly, this argument also applies to the polymerizations at 275 and 300 °C. At both temperatures the occurrence of phenolysis, as described later, will also decrease the concentration of phenolic hydroxyl end group. The phenolysis leads to an increase of polymer molecular weight. As a result, it compensates for the inflation of polymer molecular weight calculated on the basis of the observed amount of acetoxy end group. This means that the M_n value calculated based on the observed amount of acetoxy end group is much closer to the M_n value based on the actual amount of acetoxy end group at 275 and 300 °C. Consequently, the M_w/M_n value is larger than 2 in the bulk copolycondensation of ABA and ANA at 275 and 300 °C for 5 h.

We can conclude that the molecular weight data also indicate that phenolic hydroxyl end groups occur at the polymer chain ends and that they arise from the acetoxy end groups.

Mechanisms of the Synthesis of ABA/ANA Copolymer in the Bulk State. On the basis of the detection of byproducts, the study of model reactions, and the investigation of the polymer end groups and polymer molecular weight, the mechanism of the bulk copolymerization of ABA and ANA at temperatures ranging from 190 to 325 °C under nitrogen is modified as described below.

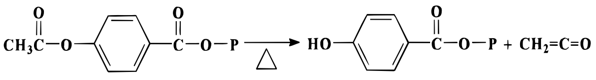
In the early stage of copolymerization, at relatively low temperatures, the reactions proceed through the acidolysis mechanism as described in Scheme 4. Acetic acid, acetic anhydride, HBA, HNA, and oligomer and polymer with phenolic hydroxyl end groups are present in the same polymerization system along with the monomers, oligomers, and polymer. As the acidolysis continues with the increase of the temperature, two kinds of side reactions occur. One is the decarboxylation of carboxy groups of HBA, oligomer, and polymer chain ends to form phenol and oligomers and polymers carrying phenyl ester end groups (reaction 1).



(1)

P = H or oligomer or polymer

The other is the decomposition of the acetoxy group on the monomer, oligomer, and polymer chain ends with the loss of ketene to produce HBA, HNA, and oligomers and polymers carrying phenolic hydroxyl end groups (reaction 2).



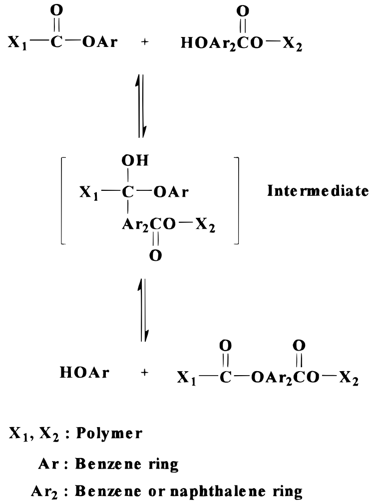
(2)

P= H or oligomer or polymer

All monomers will have reacted as the acidolysis and side reactions proceed. Consequently, only oligomers and polymers will exist in the polymerization system. They have two of the four possible end groups, namely mostly acetoxy and carboxy, but also some phenolic hydroxyl groups and phenyl esters. The reactivities of the different end groups are discussed below.

The acidolysis reaction involving acetoxy and carboxy end groups on the polymer chains will continue to form polymer. A phenyl ester end group can also react with a phenolic hydroxyl end group to give polymer, as shown by the fact that the phenolysis reaction can also be used to synthesize high polyester.[14,15] To our knowledge, the reaction of a phenyl ester end group with a acetoxy or a carboxy end group does not occur. The direct esterification of phenolic hydroxyl with carboxy end groups also does not take place on the basis of our investigation of the model reaction of 4-(benzoyloxy)benzoic acid with phenyl *p*-hydroxybenzoate. Water and the corresponding ester were not formed in this model reaction. However, transesterification and/or acidolysis do take place to produce HBA. This means that these reactions will form HBA and HNA in the copolymerization of ABA and ANA. Therefore, three reactions, acidolysis (formation of acetic acid), phenolysis (formation of phenol), and transesterification and/or acidolysis (formation of HBA and HNA), form polymers. The question arises as to which reaction is fastest. The evolution of acetic acid, phenol, and HBA and HNA play an important role in determining these reaction rates since these reactions are reversible. Especially at the beginning of the polymerization, the rate of acidolysis will be much higher than the others, as witnessed by the faster evolution of acetic acid (bp 117 °C) compared to phenol (bp 180 °C). Moreover, phenol probably plasticizes the polymer to some extent, while acetic acid does not. The transesterification and/or acidolysis leading to formation of HBA and HNA should be slower than phenolysis, since the driving force for HBA is its subsequent decarboxylation to phenol and carbon dioxide or its reaction with polymer.

Scheme 5. Proposed Phenolysis Mechanism of the Synthesis of ABA/ANA Copolymer in the Late Stage of Polymerization



As described above, the acidolysis of acetoxy with carboxy end groups on polymer chains takes place first. Consequently, the concentration of acetoxy and carboxy end groups decreases until the acetoxy and/or carboxy end group concentration approaches a very low level. The phenolic hydroxyl and phenyl ester end groups formed by side reactions begin to form in the early stages. The phenolysis reaction between them will start to occur as their concentrations build up and this reaction will eventually be responsible for the formation of high polymer with the evolution of phenol in the late stage of polymerization, as shown in Scheme 5.

On the basis of the measurement of the conversion of carboxy end groups to phenyl ester end groups and acetoxy end groups to phenolic hydroxyl end groups in the copolymerization of ABA and ANA for 5 h at 275 and 300 °C, the concentration of phenolic hydroxyl end groups is approximately equal to the concentration of the phenyl ester end groups. This means that all of the phenolic hydroxyl end groups will eventually react with phenyl ester end groups by phenolysis. The transesterification and/or acidolysis can be considered to be negligible. It should be noted that, if the concentration of the phenolic hydroxyl end groups is higher than that of phenyl ester end groups, the reaction of the remaining phenolic hydroxyl end groups will form high polymer by transesterification and/or acidolysis with the evolution of HBA and HNA (above). It means that, in the synthesis of polyarylate by the acidolysis route, the transesterification and/or acidolysis can also lead to high polymer in the late stages of polymerization without phenolysis reaction (no formation of the phenyl ester end group by the decarboxylation of carboxy end group).

The mechanisms proposed above can explain the following experimental facts. Firstly, they account for the formation of byproducts such as phenol, ketene, and carbon dioxide. Phenyl acetate can be obtained from the reaction of phenol with acetic anhydride in the cold trap. Secondly, the whole process of the synthesis of ABA/ANA copolymer from monomers to high polymer is explained, and the mechanism changes from acidolysis to phenolysis. Thirdly, the values of copolymer molecular weight polydispersity measured by ^{1}H NMR can be accounted for. Finally, the color-forming ABA/ANA copolymer can be explained as follows: phenolic hydroxyl end groups are formed by the acidolysis process and by the decomposition of acetoxy end group in the bulk polymerization of ABA and ANA at a temperature between 190 and 325 °C under nitrogen. The color of the polymer can be ascribed to the presence of the phenolic hydroxyl end groups, as described in the Introduction.[5,11]

Conclusions

Small molecules such as acetic anhydride, phenol, phenyl acetate, ketene, and carbon dioxide were found in the bulk copolymerization of ABA and ANA at temperatures ranging from 195 to 325 °C under nitrogen. The presence of phenolic hydroxyl and phenyl ester end groups was confirmed, besides the expected acetoxy and carboxy end groups. The acidolysis and phenolysis mechanisms are proposed in this copolymerization, and the acidolysis mechanism changes to the phenolysis mechanism in the late stage of copolymerization. These mechanisms explain the formation of not only the byproducts and high polymer but also the colored polymer.

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