Macromolecules

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Model Experiments Implicate a Benzoquinoneketene Intermediate in LCP Synthesis

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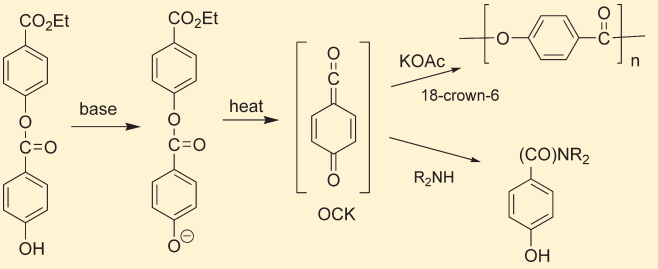
ABSTRACT: LCP synthesis from 4-hydroxybenzoic acid (HBA) and comonomers involves the formation of phenolic anion end groups at the later stages of polymerization. Model reactions show that these end groups can undergo cleavage to form 4-oxo-2,5-cyclohexadienylideneketene OCK (a benzoquinoneketene intermediate) with loss of a resonance-stabilized phenolic anion. With base, ethyl 4-(4′-hydroxybenzoyloxy)-benzoate formed ethyl 4-hydroxybenzoate and poly-HBA, while ethyl 4-(4′-methoxybenzoyloxy)benzoate did not react under the same conditions, indicating an E1cB mechanism involving OCK as an intermediate. Attempted trapping of the OCK intermediate using cycloadditions failed, but it was successfully trapped with secondary amines. These results make it likely that LCP synthesis occurs at least partly via OCK. It is a ubiquitous intermediate in LCP polymerization and characterization.



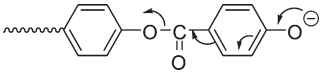
INTRODUCTION

4-Hydroxybenzoic acid (HBA) is an essential component of high-tech liquid crystalline polymers (LCP's). Its structure leads to all para-linked aromatic polyesters whose rodlike structures give rise to thermotropic liquid crystal character. The homopolymer is intractable, but certain copolymers have excellent physical properties and still permit processing and molding.[1−3] The copolymerizations with terephthalic acid and hydroquinone are performed by acetylating the *p*-hydroxyl group of the monomers, followed by thermal polymerization at ∼300 °C. At the beginning the polymerization proceeds via the expected acidolysis mechanism (Scheme 1). As the polymerization proceeds, decarboxylation of the carboxylic acid end groups leads to phenyl ester ends, while ketene loss from the acetate end groups forms phenolic ends. These two new end groups can combine, catalyzed by sodium or potassium acetate, to evolve phenol and the molecular weight continues to increase during the later stages.[4,5]

There are still many open questions regarding this high-temperature polymerization. The mass spectra of these copolymers showed evidence of stretches of homo-HBA,[6] and it has been an open question if these homopolymer stretches were formed during the polymerization or due to scrambling of 120 Da mass units during cationic mass spectral structure determinations.[7] In addition, the loss of 120 amu in the MS-MS of anions from HBA oligomers was noted.[8] 4-Oxo-2,5-cyclohexadienylideneketene (OCK) was proposed to be responsible for both these observations. OCK may also be an intermediate in the radical chain decomposition of acetate groups to form the phenolic end groups.[9] Though unstable under ordinary conditions, OCK has been studied spectrally in an argon matrix.[10]

In a separate physical organic chemistry investigation, Cevasco et al.[11] studied the reaction of 2,4-dinitrophenyl 4-hydroxybenzoate with aniline in alkaline conditions; on the basis of sophisticated kinetic measurements, they concluded that more anilide was formed than expected. The reaction proceeded by two different pathways, as shown in Scheme 2: the usual attack of aniline at the carbonyl group via a tetrahedral intermediate led to the expected anilide ($B_{Ac}2$ mechanism), but aniline also acted as a base, forming the phenolic anion which eliminates OCK; the latter reacts with aniline to form the anilide (E1cB elimination).

In these reactions of 2,4-dinitrophenyl 4-hydroxybenzoate, the 2,4-dinitrophenoxide anion provided an excellent leaving group. It occurred to us that in alkaline conditions the phenolic end groups in polymers from HBA are similarly constructed for OCK formation, with the leaving group now being the polymeric phenoxide anion stabilized by a 4-aryloxycarbonyl group. We report on our study with model compounds to evaluate the possibility that OCK elimination occurs under LCP polymerization conditions from phenoxide ends of 4-hydroxybenzoic acid units:



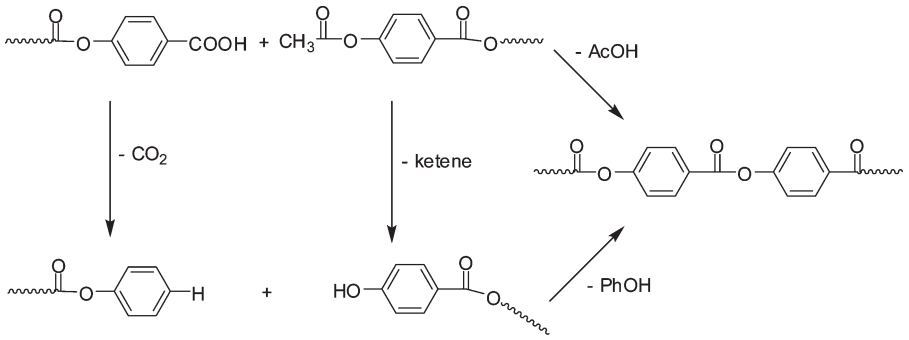
RESULTS AND DISCUSSION

Synthesis of Model Compounds. Ethyl 4-(4′-hydroxybenzoyloxy)benzoate **1** (hydroxyl dimer) was selected as a model for

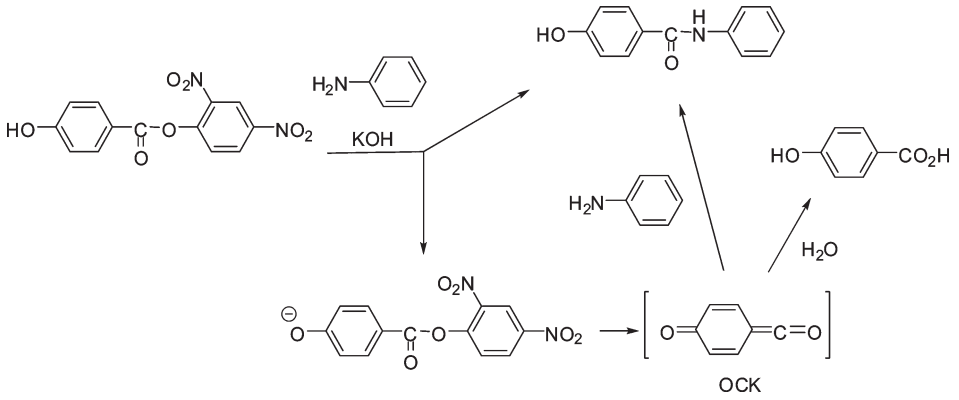
Received: May 13, 2011
Revised: June 13, 2011
Published: June 27, 2011

dx.doi.org/10.1021/ma201105q | *Macromolecules* 2011, 44, 5586–5589

Scheme 1. Change of Mechanism in LCP Polymerization



Scheme 2. Reaction of 2,4-Dinitrophenyl 4-Hydroxybenzoate with Aniline in Basic Conditions[11]



Scheme 3. Syntheses of Hydroxyl Dimer 1 and Methoxyl Dimer 2

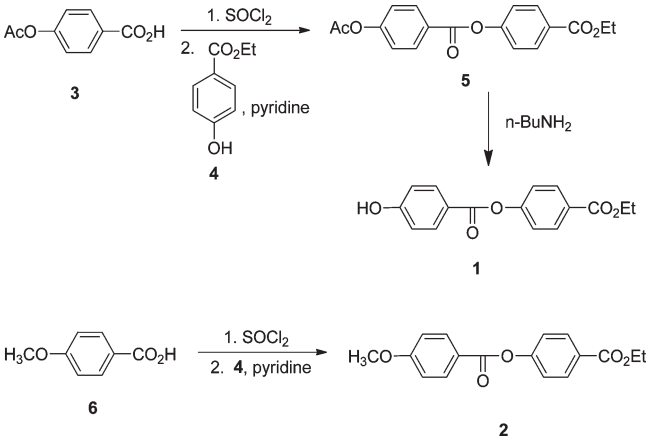


Table 1. Molecular Formulas of MS Anions Observed by ESI^{-}[a]

		mass		
anion	mol form	calcd	obsd	strength
BOH^{-}	$C_7H_5O_3$	137.024	137.026	m
$BOEt^{-}$	$C_9H_9O_3$	165.055	165.055	m
B_2OH^{-}	$C_{14}H_9O_5$	257.045	257.046	s
B_2OEt^{-}	$C_{16}H_{13}O_5$	285.076	285.077	s
B_3OH^{-2}	$C_{21}H_{13}O_7$	377.066	377.064	m
B_3OEt^{-}	$C_{23}H_{17}O_7$	405.097	405.096	m
B_4OH^{-}	$C_{28}H_{17}O_9$	497.087	497.091	w
B_4OEt^{-}	$C_{30}H_{21}O_9$	525.119	525.119	w

[a] B = OCK unit [$-p$-$OCH_6H_4(C{=}O)-$], e.g., BOH^{-} = p-HOC_6H_4-$(C{=}O)O^{-}$; s = strong, m = medium, w = weak.

an end group in the later stages of the LCP polymerization.[12] With the hydroxyl dimer, base could produce OCK by elimination; the methoxyl dimer, ethyl 4-(4′-methoxybenzoyloxy)-benzoate **2**, served as a control which would not be able to undergo this elimination. Dimers **1** and **2** were synthesized as shown in Scheme 3. 4-Acetoxybenzoic acid **3** was converted to the acid chloride and coupled with ethyl 4-hydroxybenzoate **4** to give ester **5**. The acetyl group of dimer **5** was cleanly removed by aminolysis with *n*-butylamine to give hydroxyl dimer **1**. The methoxyl dimer **2** was synthesized similarly from *p*-anisic acid **6**.

Model Reactions with Base. Reactions were performed with dimers **1** and **2** in attempts to implicate OCK as an intermediate in the reactions of hydroxyl dimer **1**. Hydroxyl dimer **1** was heated to 130 °C in the presence of potassium acetate and 18-crown-6 and stirred for 3 h, which are considerably milder conditions than the authentic LCP polymerization. Poly-HBA and ethyl 4-hydroxybenzoate **4** were the only products, as shown by mass spectra which defined the sizes of the oligomers

dx.doi.org/10.1021/ma201105q |*Macromolecules* 2011, 44, 5586–5589

as well as the end groups. Table 1 shows the anions observed in negative ESI and Table 2 the cations in positive ESI. Cyclics showed only in the cation spectra, since they have no protons acidic enough to give anions for the anion spectra. These linear and cyclic poly-HBA molecules are all presumed to be formed by oligomerization of OCK.

In contrast, the methoxyl dimer **2** was recovered unchanged under these conditions. This is strong evidence for OCK as an intermediate and shows that OCK molecules can combine to form oligomers.

Trapping Experiments. To definitely show that OCK was involved, trapping experiments were designed. OCK resembles *p*-benzoquinone and appeared amenable to trapping by cycloaddition. The trapping agents tried were *N*-vinylcarbazole, *N,N*-dimethylisobutenylamine, diphenylisobenzofuran, 1-methoxycyclohexadiene, 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene, anthracene, and anthrone. In each case, the hydroxyl dimer was heated in the presence of the trapping reagent, potassium acetate, and 18-crown-6 to generate the required phenoxy anion. In no case was a cycloadduct from OCK characterized.

Accordingly, we returned to amines as traps. Since we wished to work in bulk to mimic polymerization conditions, dilute solutions as used by Cevasco were inappropriate.[11] To find conditions which exclude the direct displacement pathway, the amine reactions were run using the methoxyl dimer **2**: if no direct displacement ($B_{Ac}2$ mechanism) by an amine took place with methoxyl dimer **2**, it would not take place with hydroxyl dimer **1**. In fact, the methoxyl dimer **2** would react faster than the hydroxyl dimer **1** because *p*-methoxyl is less electron-donating than *p*-hydroxyl (Hammett $\sigma_{OCH3} = -0.12$, $\sigma_{OH} = -0.38$) and permits a more electophilic *p*-carbonyl group.

Heating *p*-anisidine with methoxyl dimer **2** at 120 °C for 3 h gave *N*-(*p*-methoxyphenyl)-*p*-methoxybenzamide by direct displacement, so *p*-anisidine was excluded as a trap. Day et al.[13] showed that secondary amines are much less reactive than primary amines in ester aminolysis. We tried *N*-methylpiperazine and *cis*-2,6-dimethylpiperidine, but again direct displacement occurred. However, the more hindered diethylamine and the less nucleophilic morpholine gave no direct displacement on methoxyl dimer **2**. Thus, these secondary amines should be unreactive to the ester group but are able to deprotonate the phenolic hydroxyl group. If OCK formed as an intermediate, it could then combine with the amine to form the corresponding amide.

Accordingly, these amines, acting as both base and trapping agents, were heated with hydroxyl dimer **1** (Scheme 5). The diethylamine reaction product was extracted three times with hot water, leaving a small amount of insoluble gum. The cooled water extracts were filtered to remove precipitated ethyl *p*-hydroxybenzoate, and the filtrate was rotary evaporated. The residue was a mixture of diethylamine, ethyl *p*-hydroxybenzoate, and the desired *p*-hydroxyamide **7a**. Morpholine gave analogous amide **7b**. No oligomers were found in these experiments. In separate control experiments, ethyl *p*-hydroxybenzoate was heated with these amines and recovered unchanged.

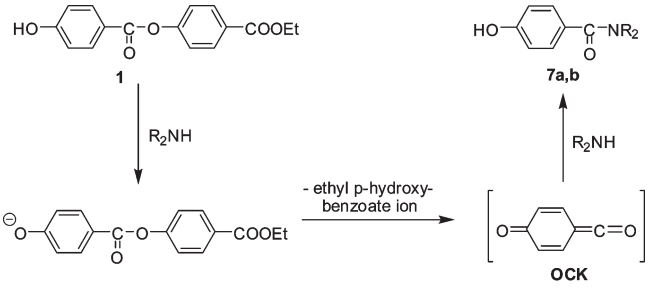
Exclusion of Self Condensation To Form Oligomers. We regard the HBA-oligomers as forming from polyadditions of OCK. However, one other possibility was considered: nucleophilic attack by the phenoxide anion on the acyl group of the hydroxyl dimer might occur, again with displacement of the stabilized *p*-ethoxycarbonylphenoxide anion. This would lead successively to trimer, tetramer, etc. To examine this possibility, model reactions were again employed. 4-Hydroxyacetophenone, simulating the anion of the hydroxyl dimer **1**, was allowed to react under our standard conditions with methoxyl dimer **2.** Only a very small extent of reaction occurred (less than 5%). Accordingly, this reaction can offer if anything only a minor route to the oligomeric poly-HBA.

Table 2. Molecular Formulas of MS Cations Observed by ESI^{+a}

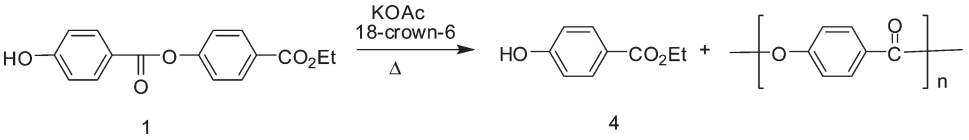
		mass		
cation	mol form	calcd	obsd	strength
$BOEtH_2^+$	$C_9H_{11}O_3$	167.071	167.070	m
B_2H^+	$C_{14}H_9O_4$	241.050	241.050	m
$B_2OH_3^+$	$C_{14}H_{11}O_5$	259.060	259.061	m
$B_2OEtH_2^+$	$C_{16}H_{15}O_5$	287.094	287.093	s
B_3H^+	$C_{21}H_{13}O_6$	361.071	361.072	m
$B_3OH_3^+$	$C_{21}H_{15}O_7$	379.081	379.080	w
$B_3OEtH_2^+$	$C_{23}H_{19}O_7$	407.113	407.113	m
B_4H^+	$C_{28}H_{17}O_8$	481.092	481.080	w
B_5H^+	$C_{35}H_{21}O_{10}$	601.113	601.101	w

[a] B = OCK unit [$-p$-$OCH_6H_4(C{=}O)-$], e.g., $BOEtH_2^+ = EtOC_6H_4C(OH)_2^+$; italics = cyclic; s = strong, m = medium, w = weak.

Scheme 5. E1cB Mechanism in the Aminolysis of Dimer 1 with Morpholine and Diethylamine



Scheme 4. Reaction of Hydroxyl Dimer 1 with Base



CONCLUSIONS

A model reaction of HBA dimer simulating LCP synthesis gave poly-HBA by an E1cB mechanism via the ketene intermediate OCK under very mild conditions. Cycloaddition trapping of OCK failed, but it was successfully trapped with secondary amines. Since LCP synthesis involves end groups like dimer **1** at much higher temperatures than were used in these model reactions, *these results indicate that LPC synthesis occurs partly via OCK*. Some OCK must distill out and some must add to phenoxide polymer ends, thus scrambling 4-hydroxybenzoic acid units in the polymer ends. The unstable substance OCK appears to be a ubiquitous intermediate in anionic, cationic, and free radical aspects of LCP synthesis and characterization.

EXPERIMENTAL SECTION

NMR and Mass Spectra. ^{1}H NMR spectra at 500 MHz and ^{13}C spectra at 125 MHz were recorded in $CDCl_3$ except where noted on a Bruker DRX 500 spectrometer. ESI mass spectra were obtained on a Bruker 9.4 T ApexQh FT-ICR instrument with electrospray ionization, both in the positive and negative ion modes.

Poly-HBA from Dimer 1. A mixture of dimer **1** (100 mg, 0.35 mmol), potassium acetate (2 mg, 0.0175 mmol), and 18-crown-6 (5 mg, 0.0175 mmol) was heated at 130 °C for 3 h. The resulting solid was triturated 3× with ether; the ether solutions contained ethyl 4-hydroxybenzoate **4**. The residue was shown to be HBA oligomers by NMR on a Bruker DRX 600 in hexafluoroisopropanol (HFIP) and by mass spectrometry. Both cyclic and linear oligomers formed as indicated in Tables 1 and 2.

Ethyl 4-(4′-Hydroxybenzoyloxy)benzoate 1. A solution of 4-acetoxybenzoic acid **3** (3.92 g, 21.7 mmol), thionyl chloride (8 mL, 109 mmol), and DMF (4 drops) was stirred under a stream of argon until excess thionyl chloride was removed (30 min). A solution of ethyl 4-hydroxybenzoate **4** (3.61 g, 21.7 mmol) in pyridine (5 mL) was added at 0 °C. After 2 h, the mixture was poured onto ice and warmed to room temperature. The mixture was filtered and washed with a solution of K_2CO_3 (8.92 g, mp 102−105 °C). The resulting powder was dissolved in *n*-butylamine (1.58 g, 21.7 mmol), stirred for 1 h, poured onto ice, and warmed to room temperature. The mixture was filtered, yielding **1**[12] (5.4 g, 87%, mp 164 °C). ^{1}H NMR: δ 1.406 (t, J = 7.3 Hz, CH_3), 4.394 (q, J = 7.3 Hz, CH_2), 6.929 (d, J = 9.0 Hz, H10), 7.283 (d, J = 9.0 Hz, H4), 8.102 (d, J = 8.5 Hz, H9), 8.119 (d, J = 8 Hz, H3). ^{13}C NMR: δ 14.32, 61.18, 115.53, 121.24, 121.79, 127.88, 131.14, 132.68, 154.69, 160.97, 161.71, 164.43.

Ethyl 4-(4-Methoxybenzoyloxy)benzoate 2. A solution of *p*-anisic acid **6** (1 g, 6.6 mmol), thionyl chloride (3 mL, 41 mmol), and DMF (2 drops) was stirred under a stream of argon until excess thionyl chloride was removed (30 min). A solution of ethyl 4-hydroxybenzoate **4** (1.09 g, 6.6 mmol) in pyridine (2 mL) was added at 0 °C. After 1 h, the mixture was poured onto ice and warmed to room temperature. The mixture was filtered, yielding **2**[12] (1.71 g, 86%, mp 92−94 °C). ^{1}H NMR: δ 1.405 (t, J = 7.3 Hz, CH_3), 3.905 (s, OCH_3), 4.381 (q, J = 7.3 Hz, CH_2), 6.994 (d, J = 9.0 Hz, H10), 7.288 (d, J = 8.5 Hz, H4), 8.120 (d, J = 9.0 Hz, H9), 8.154 (d, J = 9.0 Hz, H3). ^{13}C NMR: δ 14.34, 55.54, 61.05, 113.92, 121.37, 121.75, 127.92, 131.10, 132.38, 154.67, 164.09, 164.33, 165.89.

***N,N*-Diethyl-4-hydroxybenzamide 7a.** Dimer **1** (1 g, 3.4 mmol) was mixed with diethylamine (0.38 g, 5.2 mmol) at 120 °C for 3 h. The mixture was extracted 3× with hot water, leaving a viscous liquid. After cooling to room temperature, **5** was filtered off and the solvent was removed by rotary evaporation to give **7a** (26 mg, 8%, mp 132−135 °C). ^{1}H NMR: δ 1.145 (br s, CH_3), 1.235 (br s, CH_3), 3.320 (br s, CH_2), 3.557 (br s, CH_2), 6.768 (d, J = 8.0 Hz, OCCH), 7.417 (d, J = 8.5 Hz, OCCCH). ^{13}C NMR: δ 121.62, 127.74, 134.79, 134.79, 151.19, 169.13, 170.46.

(4-Hydroxyphenyl)(morpholino)methanone 7b. Dimer **1** (0.5 g, 1.7 mmol) was mixed with morpholine (0.23 g, 2.6 mmol) at 120 °C for 3 h. HBA was extracted 3× with hot water and rotary evaporated, leaving **4** and **7b** (184 mg, 52.3%, mp 115−120 °C). ^{1}H and ^{13}C NMR spectra as reported.[14]

ACKNOWLEDGMENT

We are indebted to Solvay Advanced Polymers, Alpharetta, GA, to University of Arizona/NASA Space Grant Program, and to Dr. Anne Padias and Samiul Ahad for help with the manuscript.

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