Photoinduced Synthesis of Oligoesters

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Received April 5, 2006; Revised Manuscript Received June 10, 2006

ABSTRACT: For the first time, a true step-growth polymerization, i.e, polyesterification, was achieved by a photochemical means. Thus, heterobifunctional monomers, namely benzodioxinone and naphthodioxinone compounds possessing both chromophoric and aliphatic hydroxyl groups in the structure (HDPD and HDNP, respectively), were synthesized by a ring closure and subsequent etherification processes and characterized. Photolysis of these compounds in CH_2Cl_2 at $\lambda_{inc} = 300$ nm yielded oligoesters with narrow molecular weight distribution. In the case of HDNP, photolysis can be performed at higher wavelengths, e.g., at $\lambda_{inc} = 350$ nm, because of the extended absorption introduced by the naphthalene ring. The structure of the photochemically formed oligoester was confirmed by FT-IR and ^{1}H NMR spectral measurements.

Introduction

Photoinitiated polymerization is usually referred to as a chain process that is initiated by light and both the initiating species and the growing chain ends are radicals[1,2] and cations,[3,4] and in some cases, anions.[5−10] However, the corresponding polycondensation process in which a macromolecule is obtained by a step-growth addition of low-molecular-weight materials, referred to as photopolymerization, has been scarcely dealt with. In most cases,[11−15] the photopolymerization process is based on the dimerization of the nonconjugated olefins through singlet and triplet excited states and the obtained macromolecules do not represent the classical polycondensate structure such as those of polyesters, polyamides, and polyurethanes. The only attempt[16] in this direction concerns in situ polyurethane formation upon photolysis of alkoxypyridinium end groups in the presence of toluene diisocyanate. Hydrogen abstraction of alkoxy radicals generated from the decomposition of the pyridinium ions results in the formation of hydroxyl groups capable of reacting with the isocyanates present in the solution (Scheme 1).

However, the process could not be controlled, and as the irradiation proceeded, an insoluble network was formed. This behavior was attributed to the formation of allophanate and biuret linkages from an isocyanate function and the previously formed urethane linkage because hydroxyl functions were available only when the pyridinium ions decomposed by light.

Recently, Yokozawa and co-workers[17,18] have presented a new technique allowing a level of control over molecular weight and polydispersity in polycondensation reactions. Their technique is based on the conversion of a polycondensation reaction into a chain-growth reaction by promoting growth only at the reactive end of the polymer chains through the use of monomers, initiators, and selected reaction conditions.

It was recently reported[19] that functionalized salicylate esters can be readily prepared by a photochemical acylation process by using benzodioxinones in the presence of alcohols and phenols (Scheme 2). The reaction occurs under neutral conditions and is tolerant to a wide range of sterically hindered alcohols.

On the basis of above information, it seemed appropriate to design and synthesize benzodioxinones with hydroxyl functional groups and to test their photochemical behavior. In this report, we wish to present a new route to synthesize polyesters by photolysis of benzodioxinones bearing hydroxyl functions. Moreover, we will show that the irradiation wavelength can be extended to a higher region by introducing polynuclear aromatic compounds into dioxinone ring structure as in the case of naphthodioxinones.

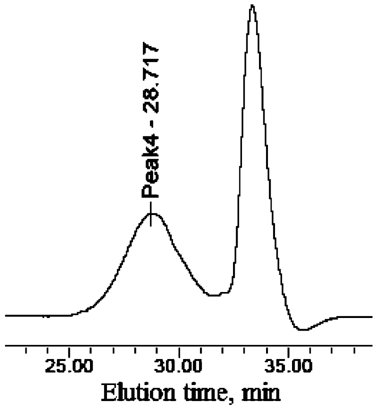
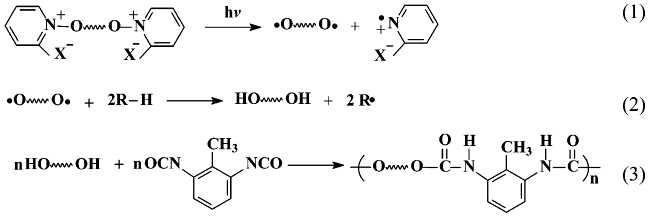


Figure 1. GPC trace of oligoester obtained by the photolysis of HDPD (Table 2, run 1).

Scheme 1. Photoinduced Polyurethane Formation



Experimental Section

Materials. Unless otherwise noted, commercially available materials were used without further purification. 2,6-Dihydroxybenzoic acid (%97, Acros), ethylene glycol dimethyl ether (%99.5, Fluka), thionyl chloride (%99.5 Acros), *N*4,*N*4-dimethylpyridin-4-amine (DMAP, 99%, Acros), benzophenone (≥99%, Aldrich), 3,7-dihydroxy-2-naphthoic acid (≥95.0%, Fluka), 3-bromo-1-propanol (%97, Aldrich), trifluoroacetic anhydride (99+%, Acros), trifluoroacetic acid (99.5%, Acros), potasium carbonate (99.99%, Aldrich),

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10.1021/ma0607721 CCC: $33.50

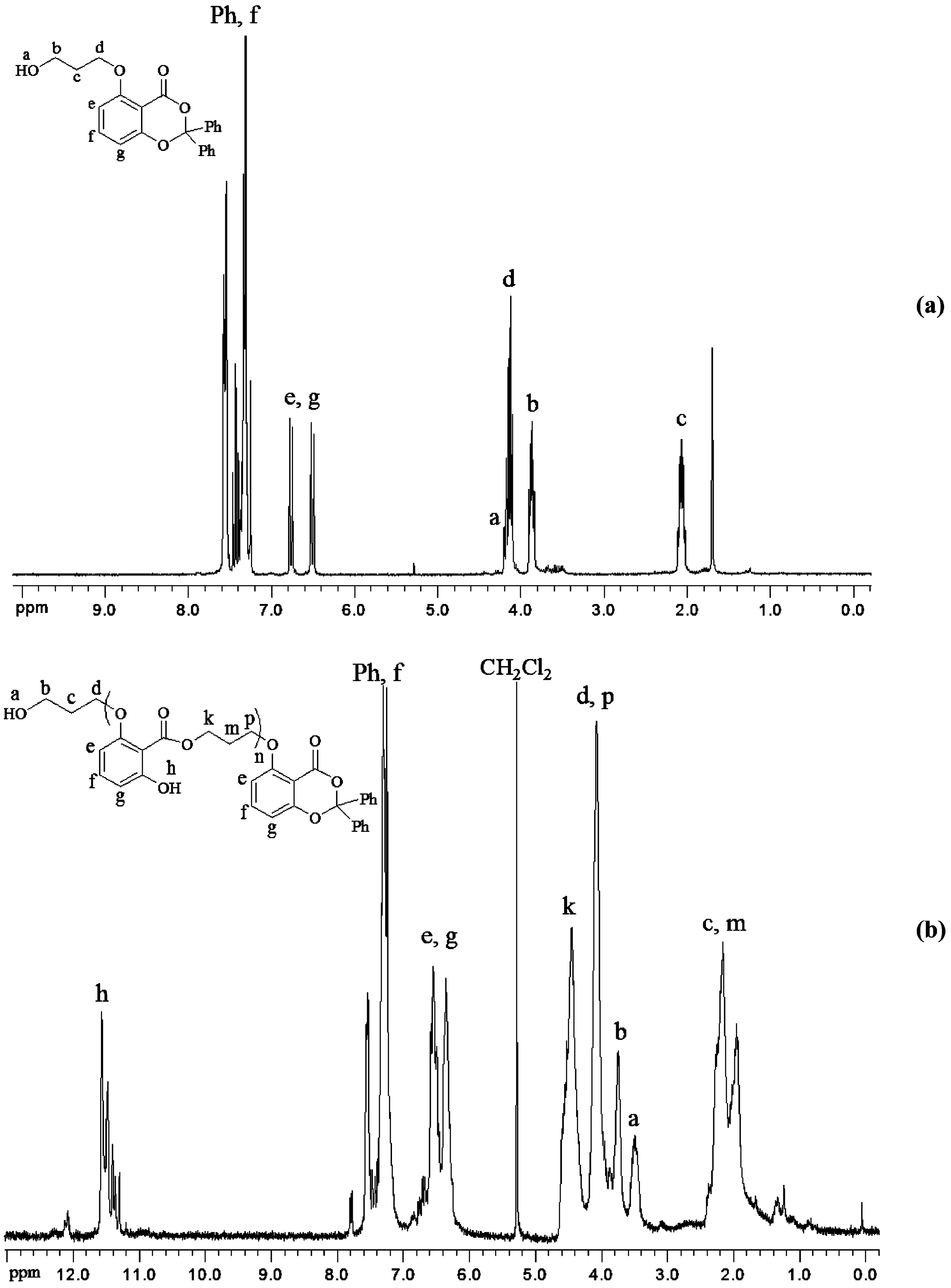


Figure 2. ^{1}H NMR spectra of HDPD (a) and the corresponding oligoester obtained by photolysis (Table 2, run 1) (b) in $CDCl_3$.

sodium sulfate anhydrous (≥99.0%, Aldrich) and silicagel 60 (Merck, 0.040−0.063 mm) were used as received. All solvents were of HPLC or ACS grade. Solvents used for moisture sensitive operations were distilled from drying reagents under a nitrogen atmosphere: Et_2O and THF from sodium benzophenone ketyl, benzene and toluene from sodium, CH_2Cl_2 from CaH_2, acetone over 4 Å molecular sieves.

Synthesis of 5-Hydroxy-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one (1). The precursor compound was synthesized according to the literature procedure.[20] Thus, to a flask containing 2,6-dihydroxybenzoic acid (5.0 g, 16 mmol) and DMAP (0.192 g, 1.6 mmol), ethylene glycol dimethyl ether (20 mL) and benzophenone (4.37 g, 24 mmol) were added. This solution was cooled to 0 °C under N_2, followed by the dropwise addition of thionyl chloride (1.74 mL, 24 mmol). The reaction was brought to room temperature and stirred for 18 h, after which the volatiles were removed via N_2 flushing while under vacuum. When the volume was reduced by approximately 50%, the remaining solution was purified by flash chromatography (5/95, EtOAc/Hex) and afforded 3.6 g (35%).

5-(3-Hydroxypropoxy)-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one (HDPD) (2). A solution of above-obtained benzodioxinone, **1** (0.5 g, 1.6 mmol), and anhydrous potassium carbonate (2 g) in acetone (15 mL) were stirred for 2 h. After that time, 3-bromo-1-propanol (0.4 mL, 4.8 mmol) was added, and the mixture was

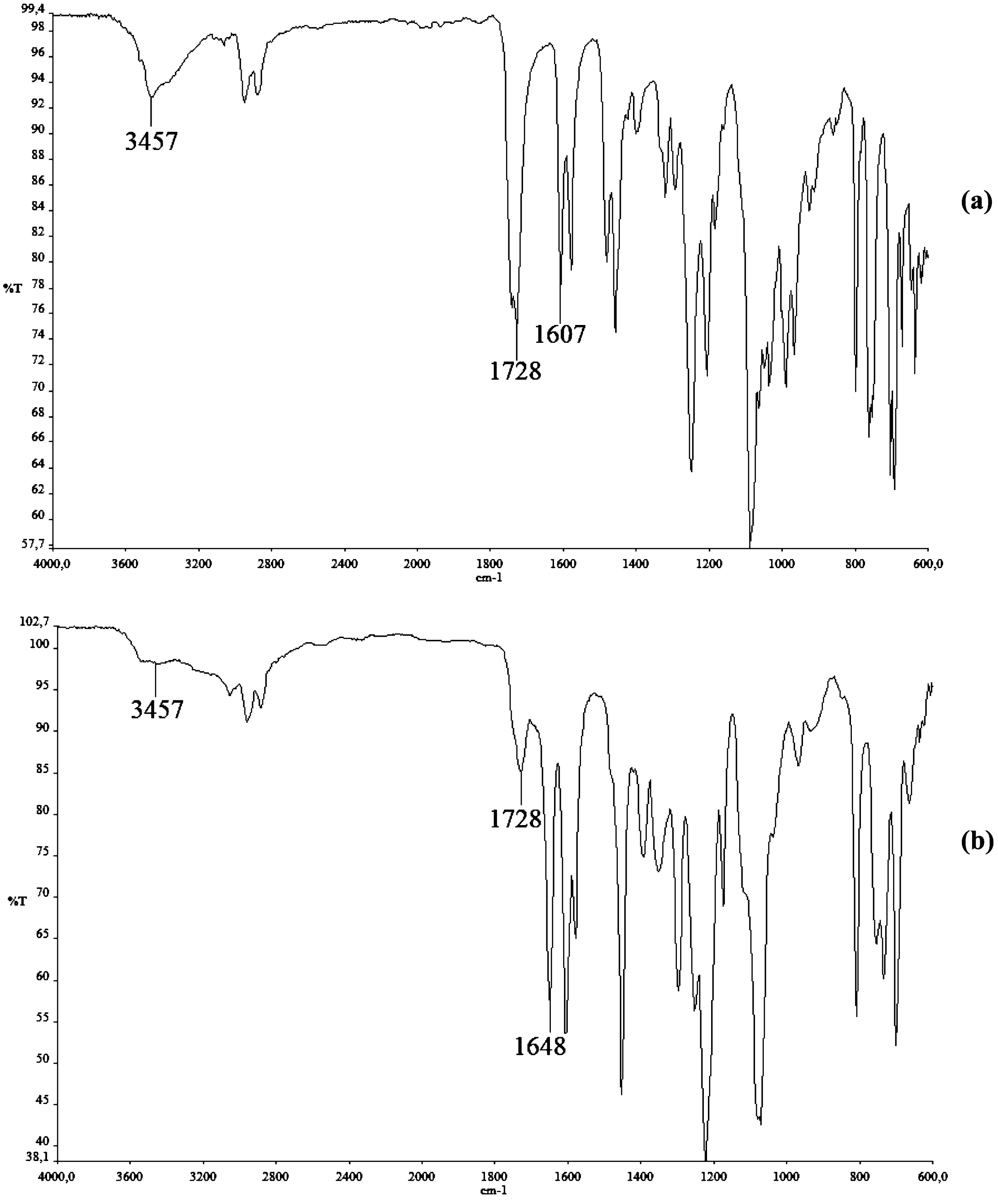
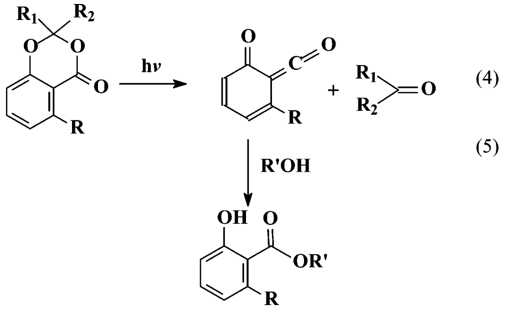


Figure 3. FT-IR spectra of of HDPD (a) and the corresponding oligoester obtained by photolysis (Table 2, run 1) (b).

Scheme 2. Salicylate Esters by Photoinduced Acylation



heated at reflux temperature for 4 h. Acetone was removed on the rotary evaporator, and the residue was diluted with diethyl ether, washed with water, then brine, and then dried over Na_2SO_4. After the volume was reduced to approximately 50%, remaining solution was purified by column chromatography (over silicagel 10% EtOAc−hexane) and afforded 0.470 g (80%) **2**, mp 155−158 °C.

*7-Hydroxy-2,2-diphenyl-4H-naphtho[2,3-d][1,3]dioxin-4-one (**3**).* To an ice-cold suspension of 3,7-dihydroxy-2-naphthoic acid (5.0 g, 24.5 mmol) in trifluoroacetic acid (23 mL) were added trifluoroacetic anhydride (18 mL) and benzophenone (6.68 g 49 mmol). The mixture was warmed slowly to room temperature and then stirred for 24 h. The mixture was then concentrated on the rotary evaporator, poured into a saturated solution of aqueous $NaHCO_3$, and extracted with three portions of diethyl ether. Collected extracts were washed with water and brine, dried ($MgSO_4$), and concentrated to leave yellow solids. Chromatography over silica using 10% EtOAc in hexane as the eluent afforded 1.6 g (18%) of **3** as yellow solid, mp 267−270 °C

*7-(3-Hydroxypropoxy)-2,2-diphenyl-4H-naphtho[2,3-d][1,3]dioxin-4-one (HDNP) (**4**).* A solution of above-obtained naphthodioxinone, **3** (0.15 g, 0.41 mmol), and anhydrous potassium carbonate (1 g) in acetone (15 mL) were stirred for 2 h at room temp. After that time, 3-bromo-1-propanol (0.1 mL, 1.2 mmol) was added, and the mixture was heated to reflux for 4 h. The mixture was then concentrated on the rotary evaporator then diluted with diethyl ether

Table 1. Spectral Characterization of Benzo- and Naphtho-dioxinone Derivatives

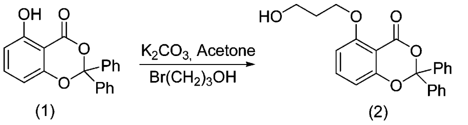
	^{1}H NMR		FT-IR	UV	
compound	group	δ (ppm)	%T (cm^{-1})	λ_{max} (nm)	ϵ_{max} (L mol^{-1}cm^{-1})
1	O*H*	10.13 (d, $J = 4.8$, 1H) 7.53−7.62 (m, 4H)	3240, 1694, 1633, 1587, 1471, 1342, 1225, 1110, 697	327	3295
	Ar-*H*	7.29−7.41 (m, 7H)			
	Ar-*H*	6.64 (d, $J = 8.4$, 1H)			
	Ar-*H*	6.54 (d, $J = 8.4$, 1H)			
2	Ar-*H*	7.57−7.26 (m, 11H)	3400, 2948, 2800, 1728, 1608, 1460, 1250, 1208, 1100, 705	320	4482
	Ar-*H*	6.78−6.74 (d, $J = 8.2$, 1H),			
	Ar-*H*	6.52−6.94 (d, $J = 8.3$, 1H)			
	O*H*	4.17 (s, 1H)			
	CH_2-CH_2-O	4.14−4.10 (t, $J = 5.6$, 2H)			
	CH_2-CH_2-OH	3.87−3.84 (t, $J = 6.1$, 2H)			
	HO−CH_2-CH_2−CH_2-O	2.11−2.02 (m, 2H)			
3	Ar-*H-1*	8.30 (s, 1H)	3462, 3065, 1717 1615, 1353, 1249, 1203, 1143, 760	386	2814
	Ar-*H*	7.69−7.12 (m, 14H)			
	O*H*	9.79 (s, 1H)			
4	Ar-*H-1*	8.29 (s, 1H)	3426, 3061, 2949, 2880, 1741, 1614, 1248, 1132,701	382	1678
	Ar-*H*	7.65−7.03 (m, 14H)			
	CH_2-CH_2-O	4.16−4.11 (t, $J = 6.0$, 2H)			
	CH_2-CH_2-OH	3.88−3.83 (t, $J = 5.9$, 2H)			
	O*H*	3.50 (br.s, 1H)			
	HO−CH_2-CH_2−CH_2-O	2.10−2.04 (m, 2H)			

Table 2. Photopolymerization of HDPD and HDNP in CH_2Cl_2 at Room Temperature

run	monomer	[M] (mol·L^{-1})	λ_{inc} (nm)	time (h)	conversion (%)	M_n[a]	M_w/M_n[a]
1	HDPD	0.20	300	16	40	1445	1.03
2	HDPD	0.35	300	16	45	1354	1.01
3	HDPD	0.35	300	45	50	1482	1.01
4	HDPD	1.00	300	16	60	<900	-
5	HDNP	0.20	300	16	60	1333	1.01
6	HDNP	0.20	350	16	55	1312	1.01

[a] Determined by GPC according to polystyrene standards.

Scheme 3. Synthesis of HDPD



(6)

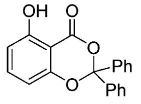
and washed with water and brine and then dried over Na_2SO_4. After the removal of approximately 50% of the solvent, it was purified by chromatography over silica gel (30% EtOAc−hexane) to give 0.15 g **4** (85%) as yellow solid, mp 127−130 °C

Photopolymerization. Typical procedure: A solution of benzodioxinone was put in a quartz tube and filled with dry nitrogen prior to irradiation from a Rayonet merry-go-round photoreactor equipped with 16 lamps emitting nominally at $\lambda = 300$ nm. At the end of irradiation for 12 h, polymers were precipitated in 10-fold excess hexane and dried in a vacuum. All the other polymerization reactions using different benzodioxinones were performed under identical conditions except that the Pyrex tubes and the lamps emitting nominally at $\lambda = 350$ nm were used for naphthodioxinones. Conversions for all samples were determined gravimetrically.

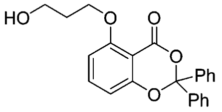
Characterization. ^{1}H NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard, using a Bruker AC250 (250.133 MHz) instrument. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) instrument equipped with a Waters styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0,3 mL/min and a Waters 410 differential refractometer detector.

Results and Discussion

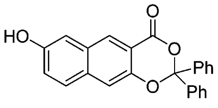
Synthesis. Monomers having both photochromic dioxinone and aliphatic hydroxyl functions were readily obtained via a two-step procedure. The structures of intermediates and products are given below:



(1)



(2) HDPD



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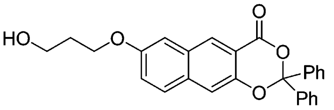


(4) HDNP

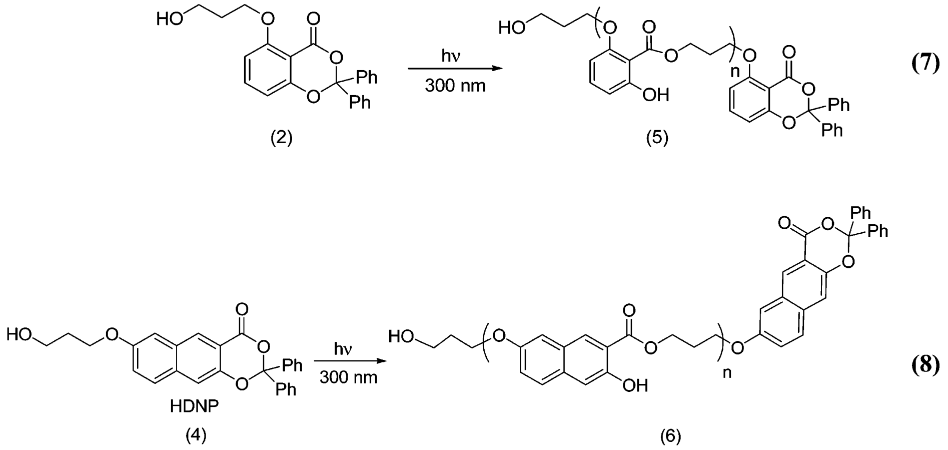
In the first step, hydroxydioxinone compounds (**1** and **3**) were synthesized by applying literature procedures using corresponding starting compounds.[20] Subsequent etherification with 3-bromo-1-propanol by using K_2CO_3 yielded the desired dioxinone-bearing aliphatic hydroxyl group (**2**, HDPD) as shown in Scheme 3. In the case of naphthodioxinone (**3**), the ring closure reaction in the first step using benzophenone and thionyl chloride was either not successful or the yield was too low. Therefore, the same reaction was performed by using trifluoroacetic acid and anhydride.[21] The subsequent etherification process yielded (HDNP) (**4**) in good yield.

The structures of the compounds were confirmed by spectral analysis. Spectral characteristics of the compounds are collected in Table 1. Notably, the naphthodioxinone derivative has absorption at about 380 nm, which enables performing the photopolymerization experiments at higher wavelengths where the potential interference of the absorption of the byproducts and polymers thus formed may be minimized.

Photopolymerization. HDPD and HDNP contain an aliphatic hydroxyl group and a benzodioxinone ring in the structure, and they are expected to yield polymers upon irradiation analogous to the photochemical behavior of benzodioxinonones in the presence of alcohols (Scheme 4).

The results of photopolymerization of both HDPD and HDNP under different experimental conditions are given in Table 2. As can be seen, in all cases, oligoesters with 3−8 repeating units and low polydispersities were formed. The oligomers exhibited monomodal molecular weight distribution, as can be

Scheme 4. Photopolymerization of HDPD and HDNP



seen from Figure 1, where the GPC trace recorded with the photolysis product of HDPD is presented (see for details Table 2, run 1). The extent of the polymerization was relatively low, and only dimers and trimers were produced when the monomer concentration was high, i.e., $[M] = 1$ mol L^{-1}.

This is in accordance with the experiments reported for the photochemical preparation of salicylate esters where the best yield was attained at 0.2 mol L^{-1} benzoxinone concentration. It should be pointed out that, although it was reported that phenols are good substrates for photoacylation reaction,[20] photolysis of the precursor compounds possessing phenolic hydroxyl groups did not yield oligomers under identical experimental conditions. These results can be attributed to the low nucleophilic character of the OH group present in the precursors **1** and **3**.

The structure of the polymers was confirmed by ^{1}H NMR and IR analysis. Figure 2 shows the ^{1}H NMR spectra of HDPD and the corresponding oligomer after photolysis.

^{1}H NMR spectra of HDPD and the photolysis product are shown in Figure 2a and b, respectively. The broadening of the peaks together with a new peak at about 4.50 ppm (a) appears in the spectrum (b), corresponding to the new vicinity (ester group) of the CH_2 protons, clearly indicates the polyester formation. Moreover, the free OH protons appearing at about 11 ppm in both spectra again confirms that phenolic hydroxyls do not take part in the condensation process.

IR spectral analysis of the oligomeric compound **5** also revealed the polycondensation reactions (Figure 3). As can be seen, the intensity of the carbonyl band at 1728 cm^{-1} corresponding to the dioxinone ring decreased and a new carbonyl band indicating intramolecular hydrogen bonding appeared at 1650 cm^{-1}. Additionally, broadening of the bands at about 3500 cm^{-1} belonging to both phenolic and aliphatic hydroxyl groups was noted.

Conclusion

In conclusion, we have demonstrated for the first time that polyester formation can be achieved by photochemical means using benzodioxinones structurally equipped with aliphatic hydroxyl groups. Although the chain growth is limited and only oligomers are formed, it is clear that the process is highly chemoselective and the products exhibit extremely narrow molecular weight distribution. At this point, further studies are necessary to confirm whether the control of the polydsipersity is due to the limited chain growth or the photochemical activation at the end of the growing chain in a manner similar to Yokozawa's concept. It appears that photopolymerization by using bisbenzodioxinones in the presence of diols can bring insight into such mechanistic details. Further studies in this line are now in progress together with the application of the process to the photochemical curing of water soluble hydroxyl containing polymers potentially useful for water-born curing and resist systems.

Acknowledgment. We thank Istanbul Technical University, Research Funds for financial support.

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MA0607721