

Polyethers Containing Coumarin Dimer Components in the Main Chain. I. Synthesis by Photopolymerization of 7,7'-(Polymethylenedioxy)dicoumarins

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ABSTRACT: Eight 7,7'-(polymethylenedioxy)dicoumarins were successfully synthesized by solution condensation of 7-hydroxycoumarin (umbelliferone) or 7-hydroxy-4-methylcoumarin (4-methylumbelliferone) with various dibromoalkanes. Upon benzophenone-sensitized irradiation with 350 nm light in dichloromethane, the terminal coumarin chromophores dimerize to form polyethers containing coumarin dimer components in the main chain. The configurations of the coumarin dimer linkages were characterized by $^1\text{H-NMR}$ spectra. For unsubstituted dicoumarins, the resulting polyethers consist mainly of *syn* and *anti* head-to-head coumarin dimer linkages. However, the configurations are *syn* and *anti* head-to-tail for those from 4-methyl-substituted dicoumarins. The highest reduced viscosity is 0.23 dL/g obtained with polyether from 7,7'-(decamethylenedioxy)dicoumarin. The photopolymerization in dichloromethane obeys zero order and first order with respect to coumarin chromophore and benzophenone, respectively. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1749–1758, 1997

Key words: 7,7'-(polymethylenedioxy)dicoumarin; photopolymerization; coumarin dimer; polyether; cyclobutane

INTRODUCTION

Coumarin is a compound existing in many plants. Its novel applications in many fields have been recently explored, such as in new photoresist materials and hydrogels containing pendant coumarin moieties which readily photodimerize upon irradiating with long wavelength UV light (>310 nm).¹ In the area of biochemistry, coumarinyl derivatives can also be used as a probe in detecting the effect of lipase² and as chiral stationary phases with high chiral recognition ability to racemates containing an aromatic moiety.^{3,4} Besides, as a result of high strain on its six–four–six fused

rings, coumarin dimers are susceptible to nucleophilic lactone-opening, photochemical, and thermal reactions.^{5,6} Recently, 7-hydroxycoumarin (umbelliferone) was investigated to elucidate the role of 7-hydroxyl groups on the above characteristic properties.⁷

In spite of the photopolymerization of dicoumarins that was successfully demonstrated by De Schryver and Leenders in a patent,⁸ discussions on the structure of photopolymerized products and the variation of viscosities under different conditions have not been undertaken yet. Upon irradiating with 350 nm light, coumarin will form, theoretically, four types of dimers via $[2 + 2]$ photochemical reactions: *syn* head-to-head, *syn* head-to-tail, *anti* head-to-head, and *anti* head-to-tail coumarin dimer. The four types of dimer can be synthesized in suitable reaction conditions, and their structures have already been characterized from $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectral analysis by exam-

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ining the variation of chemical shifts for different types of cyclobutyl protons.^{9–12} For 7,7'-coumarinyl polymethylene dicarboxylates with terminal coumarin chromophores, it is found that many factors such as the length of methylene unit, substituents of lactone, solvent polarity, and amount of photosensitizer influence the structure of coumarin dimer products.¹³ Moreover, the configuration of coumarin dimer groups linked on the polymer main chain can be identified readily as low molecular weight coumarin dimers.

In this work, we attempted to synthesize new polyethers containing coumarin dimer linkages in the main chains by photopolymerization of dioxycoumarins derived from 7-hydroxycoumarin (umbelliferone) or 7-hydroxy-4-methylcoumarin (4-methylumbelliferone). Moreover, the structures of the coumarin dimer components are characterized by ¹H-NMR spectral analysis, and the photopolymerization in solution kinetics was also investigated briefly.

EXPERIMENTAL

Materials

7-Hydroxycoumarin (umbelliferone) and 7-hydroxy-4-methylcoumarin (4-methylumbelliferone) were purchased from the Tokyo Kasei Kogyo Co. and used as received. 1,6-Dibromohexane and 1,8-dibromooctane were purchased from Fluka and Merck, respectively, and used without further purification. 1,10-Dibromodecane and 1,12-dibromododecane were from the Tokyo Kasei Kogyo Co. and used as received. Other chemicals were pure reagents and used as received. All the solvents were purified just before use by conventional methods.

Measurement

The viscosities of polymers were measured at 25°C using an Ostwald viscometer; the concentration was 0.25 g/dL in tetrahydrofuran (THF). Melting points were determined by a Fargo MP-ID and were uncorrected. Ultraviolet spectra were measured using an UV-visible spectrophotometer, Model UV-160A, from Shimadzu. ¹H-NMR spectra were obtained using a Bruker 200 MHz FT-NMR spectrometer with tetramethylsilane as the internal standard. Infrared spectra (KBr pellets) were recorded using an FTIR spectrophotometer, Model VALOR-III, from Japan Spectroscopic Co.

Elemental analyses were determined by a Heraeus CHN-O-Rapid elemental analyzer.

Irradiation Equipment

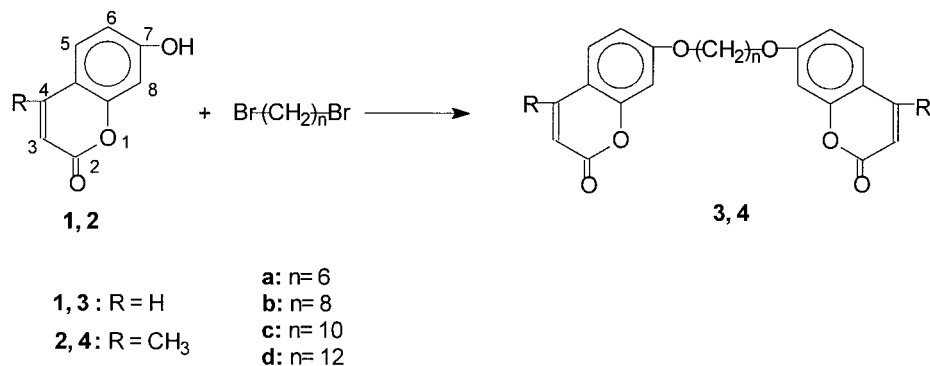
A photochemical chamber reactor, Model RPR-100, from Rayonet, was used in all photopolymerization experiments. This reactor was equipped with 16 lamps having $\lambda_{\text{max}} = 350$ nm. The power was about 400 W and the temperature inside the reaction chamber varied between 35 and 40°C. The quartz tube filled with dicoumarins was erected at the center of the chamber reactor during photopolymerization.

Syntheses of 7,7'-(Polymethylenedioxy)dicoumarins (3, 4) (Scheme 1)

The dicoumarins **3a–d** (or **4a–d**) were prepared by solution condensation of 7-hydroxycoumarin (or 7-hydroxy-4-methylcoumarin) with various α,ω -dibromoalkanes using potassium carbonate (K_2CO_3) as the neutralizing agent. For example, 7-hydroxycoumarin (**1**: 0.503 g, 3.1 mmol) and K_2CO_3 (0.857 g, 6.2 mmol) were suspended in 10 mL acetone and the mixture was warmed up slowly to 50°C. Then, 10 mL of an acetone solution containing 1.3 mmol of α,ω -dibromoalkane was added dropwise. The solution was then refluxed for 8 h under gentle stirring. The residue, after evaporation of acetone, was shaken successively with a 300 mL 0.07N NaOH aqueous solution and 200 mL distilled water. The crude product was dried at 60°C for 24 h under reduced pressure. For dicoumarins **3a** and **4a**, the crude product was recrystallized twice in *N,N*-dimethylformamide (DMF) to obtain white needlelike crystals, whereas for other dicoumarins **3b–3d** and **4b–4d**, the crude products were separated by column chromatography (silica gel: 70–230 μm) using dichloromethane as the eluent. The solvent was evaporated off and the white powder products were dried *in vacuo* at room temperature.

3a

White needlelike crystal, yield 82.1%, mp = 165°C. IR(KBr) ν 2950 [$-(\text{CH}_2)_6-$], 1720 (lactone), 1118 cm^{-1} (Ph—O—R). ¹H-NMR (DMSO-*d*₆) δ 1.48–1.76 [m, 8H, $-(\text{CH}_2)_4-$], 4.04–4.10 (t, 4H, $-\text{O}-\text{CH}_2-$), 6.24–6.29 (d, 2H, $\text{CH}=\text{CH}-\text{CO}$), 6.89–6.95 (m, 4H, aromatic proton), 7.58–7.62 (d, 2H, aromatic proton), 7.94–7.99 ppm (d, 2H, Ar— $\text{CH}=\text{CH}$).



Scheme 1

ANAL: Calcd for C₂₄H₂₂O₆: C, 70.93%; H, 5.46%.
 Found: C, 70.95%; H, 5.46%.

3b

White powder, yield = 69.3%, mp 153°C. IR(KBr) ν 2945 [-(CH₂)₈-], 1710 (lactone), 1130 cm⁻¹ (Ph-O-R). ¹H-NMR (DMSO-*d*₆) δ 1.36–1.72 [m, 12H, -(CH₂)₆-], 4.02–4.09 (t, 4H, -O-CH₂-), 6.24–6.29 (d, 2H, CH=CH-CO), 6.89–6.97 (m, 4H, aromatic proton), 7.58–7.62 (d, 2H, aromatic proton), 7.94–7.99 ppm (d, 2H, Ar-CH=CH).

ANAL: Calcd for C₂₆H₂₆O₆: C, 71.88%; H, 6.03%.
 Found: C, 71.65%; H, 6.03%.

3c

White powder, yield = 64.9%, mp 140°C. IR(KBr) ν 2930 [-(CH₂)₁₀-], 1735 (lactone), 1130 cm⁻¹ (Ph-O-R). ¹H-NMR (DMSO-*d*₆) δ 1.30–1.72 [m, 16H, -(CH₂)₈-], 4.02–4.09 (t, 4H, -O-CH₂-), 6.25–6.29 (d, 12H, CH=CH-CO), 6.90–6.97 (m, 4H, aromatic proton), 7.59–7.63 (d, 2H, aromatic proton), 7.95–8.00 ppm (d, 2H, Ar-CH=CH).

ANAL: Calcd for C₂₈H₃₀O₆: C, 72.71%; H, 6.54%.
 Found: C, 72.80%; H, 6.55%.

3d

White powder, yield = 77.3%, mp = 146–147°C. IR(KBr) ν 2945 [-(CH₂)₁₂-], 1720 (lactone), 1130 cm⁻¹ (Ph-O-R). ¹H-NMR (DMSO-*d*₆) δ 1.25–1.701 [m, 20H, -(CH₂)₂₀-], 4.01–4.08 (t, 4H, -O-CH₂-), 6.23–6.28 (d, 2H, CH=CH-CO), 6.89–6.94 (m, 4H, aromatic proton), 7.58–7.62 (d, 2H, aromatic proton), 7.94–7.99 ppm (d, 2H, Ar-CH=CH).

ANAL: Calcd for C₃₀H₃₄O₆: C, 73.45%; H, 6.99%.
 Found: C, 73.54%; H, 6.92%.

4a

White needlelike crystal, yield = 80.2%, mp = 171°C. IR(KBr) ν 2945 [-(CH₂)₆-], 1740 (lactone), 1135 cm⁻¹ (Ph-O-R). ¹H-NMR (DMSO-*d*₆) δ 1.48–1.80 [m, 8H, -(CH₂)₄-], 2.38 (s, 6H, Ar-CH₃), 4.07 (t, 4H, -O-CH₂-), 6.18 (s, 2H, CH=CH-CO), 6.92–6.95 (m, 4H, aromatic proton), 7.63–7.67 ppm (d, 4H, aromatic proton).

ANAL: Calcd for C₂₆H₂₆O₆: C, 71.87%; H, 6.03%.
 Found: C, 71.79%; H, 6.02%.

4b

White powder, yield = 72.5%, mp = 185°C. IR(KBr) ν 2945 [-(CH₂)₈-], 1720 (lactone), 1145 cm⁻¹ (Ph-O-R). ¹H-NMR (DMSO-*d*₆) δ 1.37–1.72 [m, 12H, -(CH₂)₆-], 2.38 (s, 6H, Ar-CH₃), 4.03–4.09 (t, 4H, -O-CH₂-), 6.19 (d, 2H, CH=CH-CO), 6.92–6.95 (m, 4H, aromatic proton), 7.63–7.68 ppm (d, 2H, aromatic proton).

ANAL: Calcd for C₂₈H₃₀O₆: C, 72.71%; H, 6.54%.
 Found: C, 72.59%; H, 6.55%.

4c

White powder, yield = 71.4%, 135–136°C. IR(KBr) ν 2930 [-(CH₂)₁₀-], 1725 (lactone), 1145 cm⁻¹ (Ph-O-R). ¹H-NMR (DMSO-*d*₆) δ 1.29–1.71 [m, 16H, -(CH₂)₈-], 2.37 (s, 6H, Ar-CH₃), 4.02–4.08 (t, 4H, -O-CH₂-), 6.18–6.19 (d, 2H, CH=CH-CO), 6.92–6.95 (m, 4H, aromatic proton), 7.63–7.67 ppm (d, 2H, aromatic proton).

Table I Synthesis of Dicoumarins **3** and **4** from 7-Hydroxycoumarin and 7-Hydroxy-4-methylcoumarin, Respectively

Dicoumarins	n^a	R^b	mp (°C)	Yield (%)
3a	6	H	165	82.1
3b	8	H	153	69.3
3c	10	H	140	64.9
3d	12	H	146–147	77.3
4a	6	CH ₃	171	80.2
4b	8	CH ₃	185	72.5
4c	10	CH ₃	135–136	71.4
4d	12	CH ₃	154	56.5

^a n : number of methylene groups in dibromoalkanes.

^b 7-Hydroxycoumarin: $R = H$, 7-hydroxy-4-methylcoumarin: $R = CH_3$.

ANAL: Calcd for C₃₀H₃₄O₆: C, 73.45%; H, 6.99%.
Found: C, 73.61%; H, 7.03%.

4d

White powder, yield = 56.5%, mp = 154°C. IR(KBr) ν 2940 [—(CH₂)₁₂—], 1730 (lactone), 1150 cm⁻¹ (Ph—O—R). ¹H-NMR (DMSO-*d*₆) δ 1.26–1.71 (m, 20H, —(CH₂)₈—), 2.15 (s, 6H, Ar—CH₃), 4.02–4.08 (t, 4H, —O—CH₂—), 6.18 (s, 2H, CH=CH—CO), 6.91–6.95 (d, 4H, aromatic proton), 7.63–7.68 ppm (d, 2H, aromatic proton).

ANAL: Calcd for C₃₂H₃₈O₆: C, 74.11%; H, 7.38%.
Found: C, 74.25%; H, 7.30%.

Synthesis of Polyethers **5** and **6** by Photopolymerization (Scheme 2)

A solution of dicoumarin **3** or **4** (0.75 mmol) and benzophenone (0.48 mmol) in 30 mL dry dichloromethane, through which nitrogen was bubbled for 2 h to purge out the dissolved oxygen, was added into a quartz tube and irradiated with 350 nm UV light for 72 h. The yellowish solution was added dropwise into an excess of *n*-hexane or methanol, and the precipitates that appeared were collected by filtration and dried *in vacuo* at room temperature overnight.

The reaction conditions and yields of **3** and **4** are listed in Tables II together with the reduced viscosities of the resulted polyethers **5** and **6**. The ¹H-NMR spectral data of **5** and **6** are summarized in Table III.

Polyether 5a

Yellowish powder, yield = 74.2%, $\eta_{red} = 0.06$ dL/g (c 0.25 g/dL THF, 25°C). IR(KBr) ν 2930

[—(CH₂)₆—], 1745 (lactone), 1160 cm⁻¹ (Ph—O—R). ¹H-NMR (DMSO-*d*₆) δ 1.24–1.42 [m, 8H, —(CH₂)₄—], 3.75–3.9 (m, 4H, —O—CH₂—), 3.99–4.20 (m, 4H, cyclobutyl protons), 6.83–6.73 ppm (m, 6H, aromatic proton).

Polyether 5b

Yellowish powder, yield = 78.7%, $\eta_{red} = 0.11$ dL/g (c 0.25 g/dL THF, 25°C). IR(KBr) ν 2945 [—(CH₂)₈—], 1760 (lactone), 1160 cm⁻¹ (Ph—O—R). ¹H-NMR (CDCl₃) δ 1.25–1.71 [m, 12H, —(CH₂)₆—], 3.67–3.73 (m, 4H, —O—CH₂—), 3.94–4.14 (m, 4H, cyclobutyl protons), 6.38–6.70 ppm (m, 6H, aromatic proton).

Polyether 5c

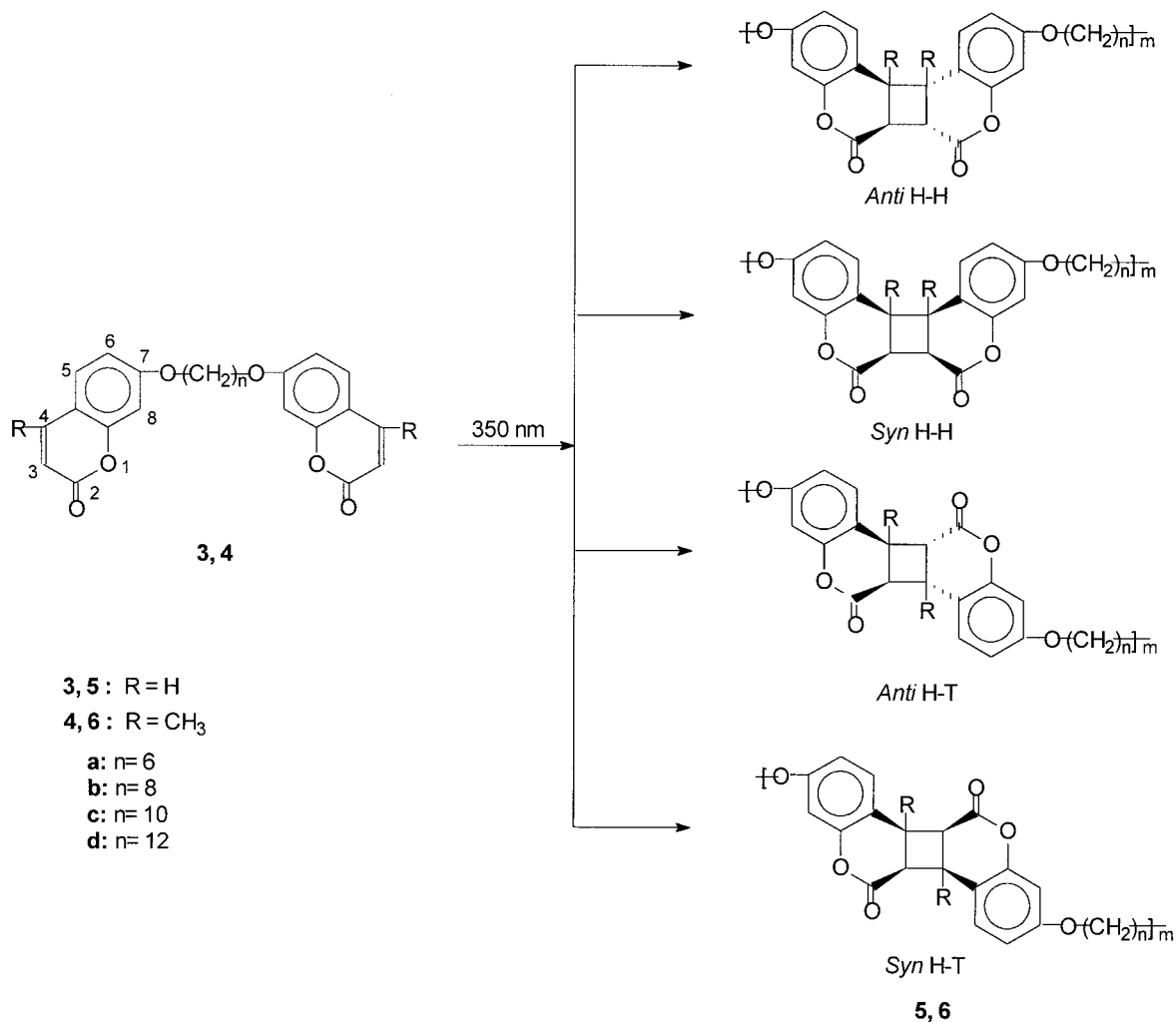
Yellowish powder, yield = 69.3%, $\eta_{red} = 0.22$ dL/g (c 0.25 g/dL THF, 25°C). IR(KBr) ν 2945 [—(CH₂)₁₀—], 1765 (lactone), 1165 cm⁻¹ (Ph—O—R). ¹H-NMR (CDCl₃/DMSO-*d*₆) δ 1.11–1.58 [m, 16H, —(CH₂)₈—], 3.68–3.87 (m, 4H, —O—CH₂—), 3.96–4.18 (m, 4H, cyclobutyl protons), 6.25–7.01 ppm (m, 6H, aromatic protons).

Polyether 5d

White powder, yield = 62.5%, $\eta_{red} = 0.23$ dL/g (c 0.25 g/dL THF, 25°C). IR(KBr) ν 2930 [—(CH₂)₁₂—], 1765 (lactone), 1160 cm⁻¹ (Ph—O—R). ¹H-NMR (CDCl₃) δ 1.22–1.78 (m, 20H, —(CH₂)₁₀—), 3.74–3.95 (m, 4H, —O—CH₂—), 4.01–4.16 (m, 4H, cyclobutyl protons), 6.39–6.99 ppm (m, 6H, aromatic protons).

Polyether 6a

Yellowish powder, yield = 55.9%, $\eta_{red} = 0.05$ dL/g (c 0.25 g/dL THF, 25°C). IR(KBr) ν 2945



Scheme 2

[—(CH₂)₆—], 1745 (lactone), 1164 cm⁻¹ (Ph—O—R). ¹H-NMR (DMSO-*d*₆) δ 1.07–1.73 [m, 14H, —(CH₂)₄— and cyclobutane —CH₃], 3.54–3.75 (m, 2H, cyclobutyl protons), 3.81–4.09 (m, 4H, —O—CH₂—), 6.00–7.32 ppm (m, 6H, aromatic protons).

Polyether 6b

Yellowish powder, yield = 65.9%, $\eta_{\text{red}} = 0.14$ dL/g (c 0.25 g/dL THF, 25°C). IR(KBr) ν 2930 [—(CH₂)₈—], 1765 (lactone), 1165 cm⁻¹ (Ph—O—R). ¹H-NMR (CDCl₃) δ 1.24–1.81 [m, 18H, —(CH₂)₆— and cyclobutane —CH₃], 3.36–3.75 (m, 2H, cyclobutyl protons), 3.77–3.99 (m, 4H, —O—CH₂—), 5.98–7.09 ppm (m, 6H, aromatic protons).

Polyether 6c

White powder, yield = 63.6%, $\eta_{\text{red}} = 0.15$ dL/g (c 0.25 g/dL THF, 25°C). IR(KBr) ν 2930 [—(CH₂)₁₀—], 1764 (lactone), 1165 cm⁻¹ (Ph—O—R). ¹H-NMR (CDCl₃/DMSO-*d*₆) δ 1.24–1.82 [m, 22H, —(CH₂)₈— and cyclobutane —CH₃], 3.36–3.75 (m, 2H, cyclobutyl protons), 3.74–4.03 (m, 4H, —O—CH₂—), 5.99–7.08 ppm (m, 6H, aromatic protons).

Polyether 6d

White powder, yield = 52.1%, $\eta_{\text{red}} = 0.19$ dL/g (c 0.25 g/dL THF, 25°C). IR(KBr) ν 2945 [—(CH₂)₆—], 1764 (lactone), 1170 cm⁻¹ (Ph—O—R). ¹H-NMR (CDCl₃/DMSO-*d*₆) δ 1.23–1.81 [m, 26H, —(CH₂)₁₀— and cyclobutane —CH₃], 3.36–3.69

Table II Irradiation of Dicoumarins **3** and **4** with 350 nm Light in CH₂Cl₂

	<i>n</i> ^a	<i>R</i> ^b	Dicoumarins Concn (<i>M</i>)	Benzophenone Concn (<i>M</i>)	Irradiation Time (h)	η_{red}^c (dL/g)	Yield (%)
5a	6	H	0.025	0.016	72	0.06	74.2
5b	8	H	0.025	0.016	72	0.11	78.7
5c	10	H	0.025	0.016	72	0.22	69.3
5d	12	H	0.025	0.016	72	0.23	62.5
6a	6	CH ₃	0.025	0.016	81	0.05	55.9
6b	8	CH ₃	0.025	0.016	81	0.14	65.9
6c	10	CH ₃	0.025	0.016	81	0.15	63.6
6d	12	CH ₃	0.025	0.016	81	0.19	52.1

^a *n*: number of methylene groups in dibromoalkanes.

^b Dicoumarins **5a–d** are derived from 7-hydroxycoumarin (*R* = H), whereas **6a–d** are derived from 7-hydroxy-4-methylcoumarin (*R* = CH₃).

^c Measured at 25°C in 0.25g/dL THF.

(m, 2H, cyclobutyl protons), 3.74–4.03 (m, 4H, —O—CH₂—), 6.03–7.07 ppm (m, 6H, aromatic protons).

RESULTS AND DISCUSSION

Synthesis of Dicoumarins (**3**, **4**) (Scheme 1)

The yield and melting point of dicoumarins **3** and **4** are summarized in Table I. The results are comparable to those reported by Leenders et al.⁹ For dicoumarins **3a–d** and 4-methyl-substituted **4a–d**, the yield are about 65–82% and 57–80%, re-

spectively. From the infrared spectra, the strong C—O—Ph stretching absorption bands in the region of 1118–1150 cm⁻¹ makes sure of the formation of ether linkages. Further characterizations have been confirmed by ¹H-NMR spectra and elemental analysis as shown in the Experimental section.

Synthesis of Polyethers **5** and **6**

The results of photopolymerization of the dicoumarins **3** and **4** in dichloromethane are summarized in Table II. The yields are about 63–79%

Table III Characteristic ¹H-NMR Spectra of Polyethers **5** and **6**

	Configuration of Photoproducts	Solvent	Cyclobutane Protons	Aromatic Protons
5a	syn H-H(41%) ^a	DMSO	4.17–4.20(d, 4H)	6.38–6.73(m, 6H, H ₅ , H ₆ , H ₈)
	anti H-H(59%)		3.99–4.06(d, 4H)	6.38–6.73(m, 6H, H ₅ , H ₆ , H ₈)
5b	syn H-H(54%)	CDCl ₃	4.08–4.14(m, 4H)	6.38–7.00(m, 6H, H ₅ , H ₆ , H ₈)
	anti H-H(46%)		3.94–4.03(m, 4H)	6.38–7.00(m, 6H, H ₅ , H ₆ , H ₈)
5c	syn H-H(27%)	CDCl ₃ /DMSO	4.08–4.14(m, 4H)	6.25–7.01(m, 6H, H ₅ , H ₆ , H ₈)
	anti H-H(73%)		3.96–4.03(m, 4H)	6.25–7.01(m, 6H, H ₅ , H ₆ , H ₈)
5d	syn H-H(45%)	CDCl ₃	4.13–4.16(d, 4H)	6.39–6.99(m, 6H, H ₅ , H ₆ , H ₈)
	anti H-H(55%)		4.01–4.04(d, 4H)	6.39–6.99(m, 6H, H ₅ , H ₆ , H ₈)
6a	syn H-T(48%)	DMSO	3.72(s, 2H)	6.01(d, 2H, H ₈), 6.34 (d, 2H, H ₆), 6.94 (d, 2H, H ₅)
	anti H-T(52%)		3.55(s, 2H)	6.66–6.83(m, 4H, H ₆ , H ₈), 7.28 (d, 2H, H ₅)
6b	syn H-T(48%)	CDCl ₃	3.69(s, 2H)	6.00(d, 2H, H ₈), 6.64 (d, 2H, H ₆), 7.03 (d, 2H, H ₅)
	anti H-T(52%)		3.39(s, 2H)	6.62–6.65(m, 4H, H ₆ , H ₈), 7.08 (d, 2H, H ₅)
6c	syn H-T(39%)	CDCl ₃ /DMSO	3.70(s, 2H)	6.02(d, 2H, H ₈), 6.63 (d, 2H, H ₆), 7.02 (d, 2H, H ₅)
	anti H-T(61%)		3.39(s, 2H)	6.75–6.81(m, 4H, H ₆ , H ₈), 7.08 (d, 2H, H ₅)
6d	syn H-T(25%)	CDCl ₃ /DMSO	3.67(s, 2H)	6.03(d, 2H, H ₈), 6.61 (d, 2H, H ₆), 7.02 (d, 2H, H ₅)
	anti H-T(75%)		3.40(s, 2H)	6.75–6.86(m, 4H, H ₆ , H ₈), 7.07 (d, 2H, H ₅)

^a The percents were calculated by the peak area of their ¹H-NMR spectra.

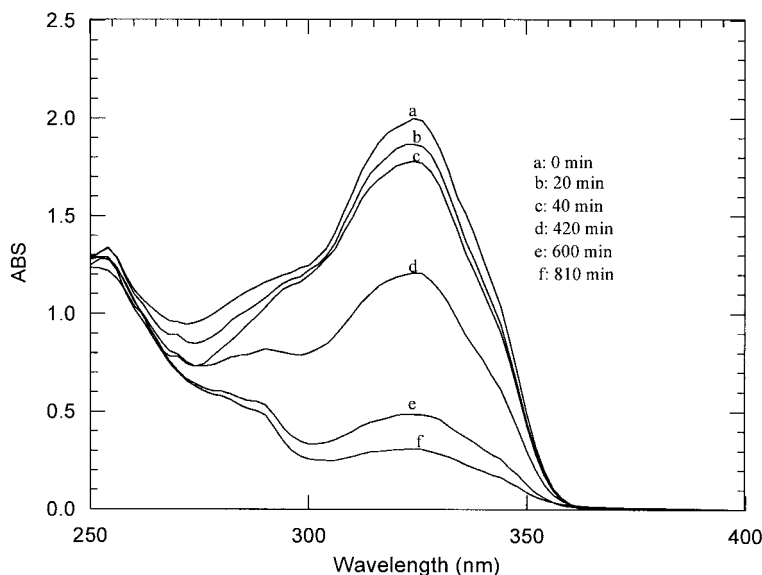


Figure 1 UV spectral variation of **3c** during irradiation with 350 nm light in CH_2Cl_2 .

and 52–66% for **3** and **4**, respectively. The reduced viscosities of polyethers **5** from **3** are between 0.06 and 0.23 dL/g and increase with number of methylene groups (n) in dicoumarins. Those of **6** from 4-methyl-substituted dicoumarins **4** are in the range of 0.05–0.19 dL/g and also show an increasing trend with increased n values. These results indicate that 4-methyl substitution lowers the yields and viscosities of the polyethers, which can be explained by the steric repulsion of the 4-methyl groups during photodimerization.

Structural Analysis of Polyethers **5** and **6**

Upon benzophenone-sensitized irradiation of the dicoumarins **3a–d** with 350 nm light, the characteristic chemical shifts of the $-\text{CH}=\text{CH}-$ (in lactone) at ca. $\delta 6.24\text{--}6.29$ ppm (H_3) and $\delta 7.94\text{--}8.00$ ppm (H_4) disappeared completely. For **4a–d**, the chemical shifts that disappeared are at ca. $\delta 6.18\text{--}6.19$ ppm (H_3). Dimerization of terminal coumarin chromophores can also be verified by a UV spectral change during irradiation as shown in Figure 1 in which the maximum absorptions at ca. 320 and 272 nm decrease continuously with irradiation time. Two reaction routes may compete to proceed: intramolecular and intermolecular reactions to form cyclomers and polymers, respectively. Each path may theoretically form four kinds of coumarin dimer structures: *syn* head-to-head, *syn* head-to-tail, *anti* head-to-head, and *anti* head-to-tail. Although the types of dimers for low molecular coumarinyl derivatives have been

widely discussed,^{9–11,14,15} structural analysis of the coumarin dimer chromophores linking on polymer chains has not been reported yet. The relationship between coumarin dimer structures and various reaction conditions would be interesting from academic and practical viewpoints.

The configurational assignments of photoproducts **5** and **6** are not conclusive from their IR and UV spectra. Dipole moment measurements and $^1\text{H-NMR}$ spectral analysis could be helpful for configurational assignment of the coumarin dimer.^{9,11,14–16} However, it is difficult to obtain the exact dipole moment of each segment of the polyether chains. Therefore, structural assignments of **5a–d** and **6a–d** were based on their $^1\text{H-NMR}$ (200 MHz) spectral data.

The chemical shift of cyclobutyl protons is an effective measure to distinguish *syn* forms from *anti* forms. After analyzing a large number of dimers from low molecular weight coumarin derivatives,^{9–11} it is found that for unsubstituted coumarin dimers the cyclobutyl protons of *syn* structures resonate around $\delta 4.0\text{--}4.21$ ppm, whereas those of *anti* structures resonate around $\delta 3.8\text{--}4.0$ ppm (in $\text{DMSO-}d_6$). This shielding is caused by the diamagnetic anisotropic effects of a carbonyl or phenyl nucleus in the *anti* configuration.^{9,15} For *syn* structures, it is convenient to characterize the head-to-head and head-to-tail structures by comparing the shifts of aromatic protons H_5 , H_6 , and H_8 with the same protons of model 3,4-dihydro-7-methoxycoumarin.⁹ For the model compound, the absorption of H_5 is found at $\delta 7.10$ ppm, H_6 at $\delta 6.67$

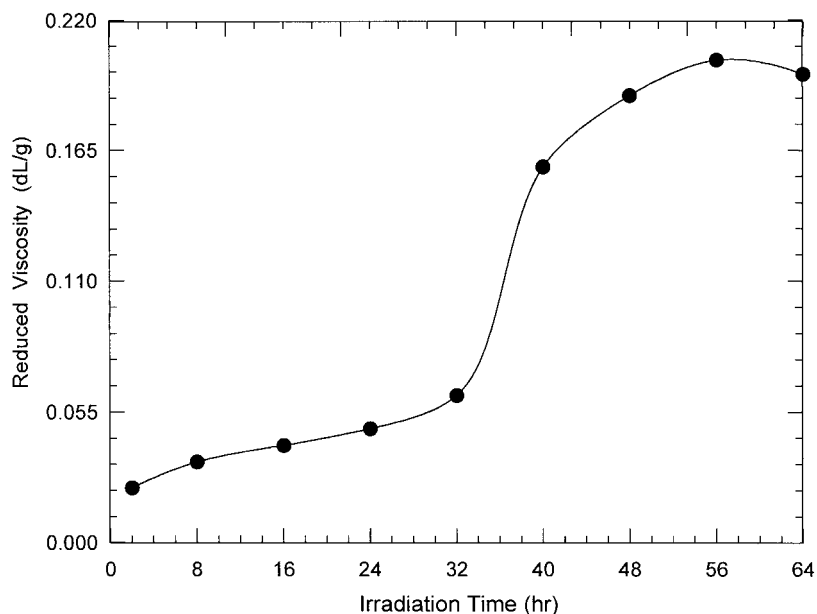


Figure 2 Viscosity variation of **5c** during irradiation of **3c** with 350 nm light in CH_2Cl_2 . The products used in the viscosity measurement were sampled from the reaction vessel by a syringe and precipitated in a large amount of methanol. Concentration: ca. 0.25 g/dL CH_2Cl_2 at 25°C.

ppm, and H_8 at $\delta 6.63$ ppm. If the *syn* head-to-tail is formed, H_5 and H_6 will be shifted slightly upfield, whereas H_8 will be shifted to a higher field by over 0.6 ppm. This strong shielding effect on H_8 is caused by diamagnetic anisotropy of a phenyl nucleus situated in front of the proton in the *syn* head-to-tail configuration.^{9,15} Such a strong selective shift does not exist for the H_8 ab-

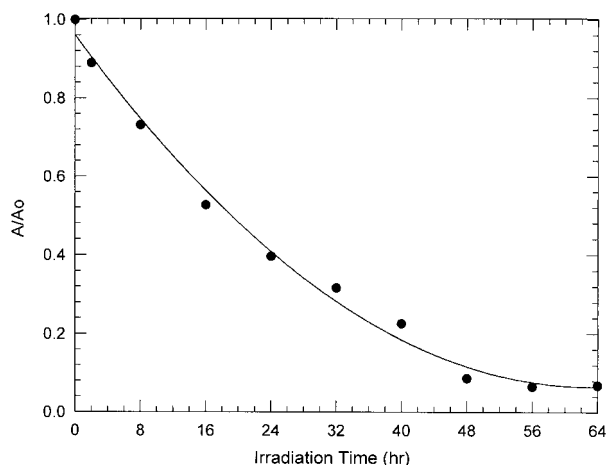


Figure 3 Absorption variation of **3c** during irradiation with 350 nm light in CH_2Cl_2 . A and A_0 represent UV absorption at 320 nm after and before irradiation, respectively.

sorption in the *syn* head-to-head configuration. The *anti* head-to-head and head-to-tail structures of several cyclobutanes have been characterized by the analysis of their ^{13}C —H satellite proton spectra.^{17,18} However, due to lack of these data, *anti* configurations of **5** and **6** are characterized by comparing them with those of low molecular derivatives obtained in similar conditions by Muthuramu and Ramamurthy.¹⁰

As depicted in Table III, for the photoproduct **5a**, two doublets of cyclobutyl protons appear at $\delta 4.02$ and $\delta 4.18$ ppm without an obvious upfield shift for H_8 , so the structure of **5a** is believed to be a mixture of *syn* head-to-head (41%) and *anti* head-to-head (59%). For **5b**, there are two set of peaks of cyclobutyl protons appearing at $\delta 4.08$ – 4.14 and $\delta 3.94$ – 4.03 . Because of no obvious upfield shift for H_8 , the configuration of **5b** should be a mixture of *syn* head-to-head (54%) and *anti* head-to-head (46%) structures. In the same way, **5c** and **5d** can also be easily specified as a mixture of *syn* head-to-head and *anti* head-to-head isomers as shown in Table III.

For low molecular weight 4-methyl-substituted coumarin dimers, *anti* dimers have their cyclobutyl protons at ca. $\delta 3.4$ ppm (in CDCl_3), whereas *syn* dimers have theirs at ca. $\delta 3.6$ ppm.¹¹ Similarly, this upfield shift of cyclobutyl protons is ex-

Table IV Initial Photopolymerization Rate of **3c**^a

Initial Conc of 3c ($\times 10^{-3}$ M)	Initial Concn of Benzophenone ($\times 10^{-3}$ M)	Initial Reaction Rate of 3c ($\times 10^{-8}$ M/min)
25	24	20.99
25	16	16.05
25	8	8.42
25	4	4.77
25	2	2.94
20	8	10.32
10	8	9.23
5	8	9.37
2.5	8	9.01
1.25	8	9.74

^a Irradiated in CH_2Cl_2 at 25°C with 350 nm light.

pected in the *anti* dimers due to the diamagnetic anisotropic effect of the carbonyl and phenyl nucleus situated in front of them.^{9,15} As shown in Table III, the signals of **6a** appear at $\delta 3.72$ and $\delta 3.55$ ppm and exhibit an obvious upfield shift of H_8 ($\delta 6.01$ ppm). It is identified to be a mixture of *syn* head-to-tail (48%) and *anti* head-to-tail (52%) isomers. The structures of **6b–6d** are also identified by the same method and are summarized in Table III.

From the structural assignments of **5** and **6**, clearly, the coumarin dimer structures are head-to-head for polyethers **5** and head-to-tail for 4-methyl-substituted polyethers **6**, which seems to be due to the steric hindrance of 4-methyl groups in lactone rings.

Viscosity Variation of **5** and **6**

There are two types of polymerization upon photoirradiation, i.e., photoinitiated polymerization and photopolymerization. Photoinitiated polymerization is defined as “a chain polymerization initiated by light,” whereas photopolymerization is a polymerization process in which all chain-propagating steps involve a photochemical reaction.¹⁹ From this statement, a photopolymerization should be considered as a multistep reaction, in contrast to the photoinitiated polymerization which is a chain process. Figure 2 shows the viscosity variation of **3c** with irradiation time, while Figure 3 indicates the concentration variation of coumarin groups during the irradiation process (the concentration is expressed as the ratio of absorption at 320 nm which corresponds to the $\pi-\pi^*$ transition of

coumarin chromophores). Clearly, high viscosity polyether forms only near the very end of the polymerization ($>92\%$ from Fig. 3). This is a curve like that of step polymerization and far different from the curve of chain polymerization. Therefore, it is confirmed that the polymerization is photopolymerization rather than a photoinitiated polymerization.

The influence of the methylene chain length (n) on the viscosities of photoproducts can be easily pointed out from Table II. For both **5** and **6**, the viscosity increases with the number of methylene groups in the dicoumarins. The viscosities increase from 0.06 and 0.05 dL/g to 0.23 and 0.19 dL/g for **5** and **6**, respectively, as n is increased from 6 to 12. These data suggest that the molecular weight increases with the number of methylene group, i.e., cyclization becomes gradually negligible when n is high. 4-Methyl substitution results in lower polymer yields and viscosities as mentioned above.

Kinetics of Photopolymerization

The initial reaction rates in Table IV are determined from the initial slope of the concentration vs. irradiation time plots. As shown in Figure 4, clearly, the initial reaction rate of **3c** bears no relation to the dicoumarin concentration, but it shows a linear dependence on the benzophenone concentration (Fig. 5). These results are coincident with the photopolymerization of 7,7'-coumarinyl polymethylene dicarboxylates reported previously,²⁰ in which the rate of polymerization has been derived as $d[C]/dt = k[B]$, where k is the

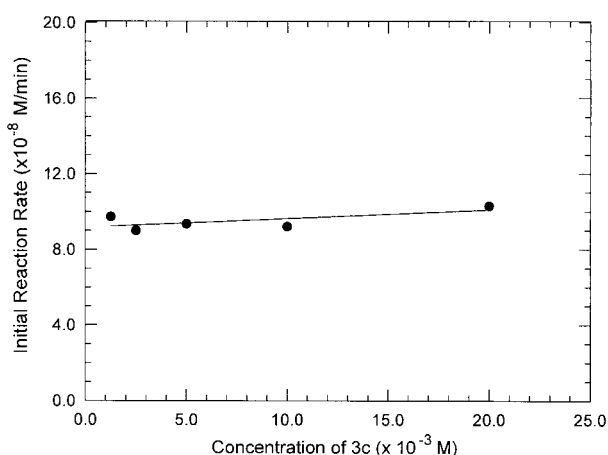


Figure 4 Initial reaction rate of **3c** under different concentrations. The concentration of benzophenone was kept constant at 8×10^{-3} M.

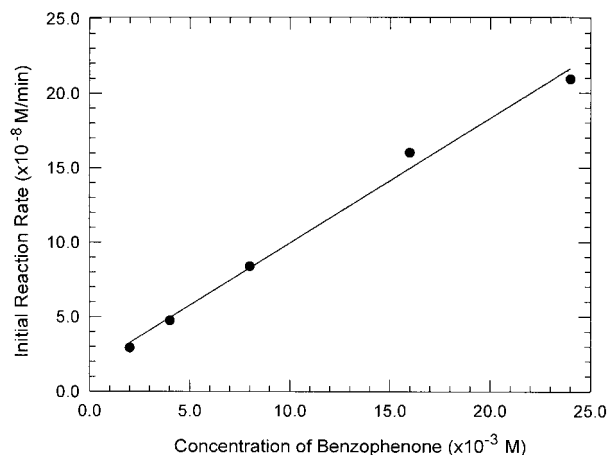


Figure 5 Initial reaction rate of **3c** vs. benzophenone concentration. The concentration of **3c** was kept constant at $2.5 \times 10^{-2} M$.

apparent rate constant and $[C]$ and $[B]$ are the concentrations of coumarin groups and benzophenone, respectively. The reaction mechanisms have been proposed and are believed to proceed via the triplet state in which benzophenone is the essential energy-transfer intermediate.

CONCLUSION

7-Hydroxycoumarin or 4-methyl-7-hydroxycoumarin were reacted in a solution with four α, ω -dibromoalkanes ($n = 6, 8, 10, 12$) to prepare eight 7,7'-(polymethylenedioxy)dicoumarins as monomers for photopolymerization. Upon irradiating with 350 nm light, the dicoumarins polymerize to form polyethers (through photodimerization of the coumarin chromophores) containing coumarin or 4-methylcoumarin dimer components in the main chain. The reduced viscosities are between 0.05 and 0.23 dL/g and increase with the n values, indicating that cyclization becomes gradually negligible when the length of the dicoumarins is increased. The highest reduced viscosity obtained is 0.23 dL/g from 7,7'-(decamethylenedioxy)dicoumarin. Polyethers **5a-d** contain mainly *syn* and *anti* head-to-head coumarin dimer components. However, for 4-methyl-substituted dicoumarins **4**, the resulting polyethers **6** contain mainly *syn* and *anti* head-to-tail structures, which

has been attributed to the steric hindrance of methyl groups. Photopolymerization of **3c** shows zero-order and first-order dependence on the concentration of coumarin groups and benzophenone, respectively.

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