propoxide (1 drop, 0.01 g) was added, and the heterogeneous mixture was heated under nitrogen to 200 °C for 2 h. A mechanical stirrer was fitted to the flask and vacuum (0.3 Torr) was applied. After 80 min, the polymer was a brown, solid crystalline mass. The polymer was insoluble in DMF and Me_2SO and was soluble in 1,1,1,3,3,3-hexafluoro-2-propanol. The inherent viscosity in HFIP at 25 °C was 0.23, the polymer had a glass transition temperature of 27 °C and a crystalline melting point of 62 °C: UV (HFIP, nm) 234 (13 900). Anal. Calcd: C, 68.3; H, 7.5; N, 9.5. Found: C, 65.8; H, 7.5; N, 8.8.

Synthesis of Methyl 4-(Hydroxyethyl)oxybenzoate. Into a flask were placed 4-(hydroxyethyl)oxybenzoic acid, methanol (200 mL) and sulfuric acid (1 mL). The suspension became homogenous when heated under reflux. After the solution was heated for 5.75 h, it was cooled and poured into toluene (100 mL). Water (150 mL) was added and the organic layer was separated. The aqueous layer was extracted with toluene (3 × 100 mL), and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent yielded a white solid which was recrystallized from CCl_4. White crystals (12.8 g, 59%), mp 65–66 °C, were obtained. Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.2; H, 6.2. Found: C, 68.3; H, 11.0.

Copolymerization of DEQ with Methyl 12-Hydroxydodecanoate. Into a 10-mL polymerization vessel were placed DEQ (1.00 g, 3.5 mmol), methyl 12-hydroxydodecanoate (0.80 g, 3.5 mmol) and benzophenone (1.0 g). The flask was flushed with nitrogen for several minutes and then placed into a 160 °C oil bath. The dodecanoate and the solvent melted, resulting in a yellow suspension. Dibutyltin diacetate (1 drop, 0.01 g) was added, and the suspension was stirred for 18 h at 150–160 °C. As the same temperature was maintained, vacuum was applied (0.7 Torr) and the stirring was continued for an additional 32 h. The partially solid mass was cooled and collected. The crude polymer was triturated with methanol for 3 days and filtered, resulting in the recovery of 1.45 g of light brown-yellow product. The polymer was soluble in HFIP, 1:1 phenol/chlorobenzene, pyridine, hot Me_2SO, and hot *N*-methylpyrrolidinone, forming bright-yellow solutions. The inherent viscosity, 0.32, was determined with a 0.5% solution in phenol/chlorobenzene (1:1) at 25 °C and the melting point was determined by DSC under an inert atmosphere. Anal. Calcd for 1:1 copolymer: C, 68.8; H, 7.8; N, 9.3. Found after drying at room temperature: C, 66.0; H, 7.6; N, 9.2. Found after drying at 100 °C (above T_m): C, 67.6; H, 8.2; N, 7.3.

General Procedure. In order to obtain a series of polymers with varied inherent viscosities, the above procedure was modified as follows: The reagents were mixed in the polymerization vessel and the vessel was flushed with nitrogen, as before. The first stage was constant for all polymerizations and was begun by placing the flask in a 150 °C oil bath. When a yellow suspension was obtained, dibutyltin diacetate (1 drop, 0.01 g) was added and the mixture was stirred at 150 °C. By allowing the second state to proceed for 15.5 or 63.5 h, after workup as before, one obtains polymer with inherent viscosities of 0.16 and 0.45, respectively (1/1 phenol/chlorobenzene, 25 °C).

The copolymerizations of DEQ/2-HEOB and DAQ/12-HDE were performed by utilizing the benzophenone technique described above.

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Synthesis of Polyesters Containing a Nonrandomly Placed Highly Polar Repeat Unit

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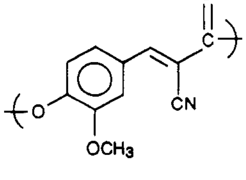
ABSTRACT: Three novel monomers containing the *p*-oxy-α-cyanocinnamate structure were synthesized from ω-hydroxyalkoxy-substituted benzaldehydes and methyl cyanoacetate. These ω-hydroxy-α-cyanoester monomers show a high degree of electron delocalization. Copolyesters were synthesized by copolymerization of these monomers with methyl 12-hydroxydodecanoate by the standard two-stage, high-temperature polyesterification procedure. The copolyesters, incorporating dipolar units all pointing in the same direction, are soluble and solution- and melt-processable.

Introduction

We recently synthesized a series of AB copolyesters with a highly dipolar quinodimethane repeat unit, with all the dipoles pointing in the same direction along the polymer chain.[1] These polymers were not readily soluble in common solvents like dichloromethane and were not meltable, hence were not readily processable. Accordingly, in this work we have synthesized copolyesters with somewhat less dipolar repeats units in order to achieve processability. The group we selected is the *p*-oxy-α-cyanocinnamate unit



Several monomers containing this unit were synthesized and then homo- and copolymerized. The resulting polymers were then characterized.

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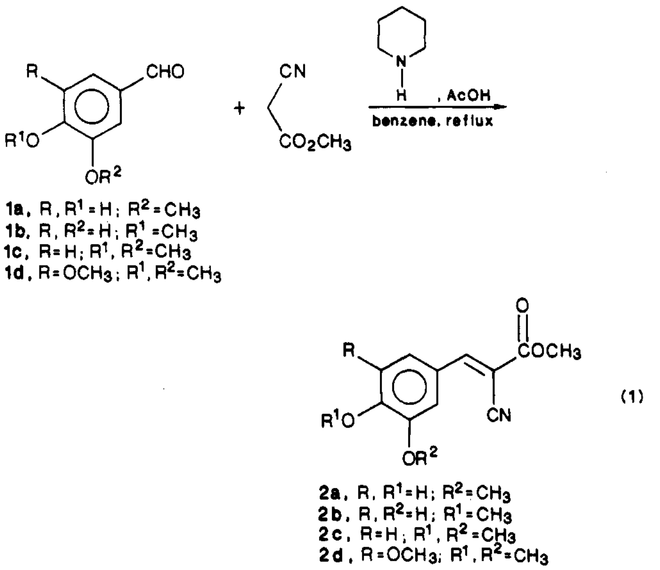
Table I
Physical and Spectral Data of Synthetic Intermediates

aldehyde	product	mp	yield, %	abs max, nm	mol abs ε
1a	2a	158–160	88	358	22 100
1b	2b	157–158	76	355	19 100
1c	2c	124–125	89	362	23 500
1d	2d	112–114	85	363	13 600
3	4	145–146	88	354	19 000
	5	140–142	22	306	15 000
6a	7a	73–75	60	274, 306	13 000, 10 000
6a	7b	51–54	89	na	na
6b	7c	75–78	28	274, 306	10 500, 8 200

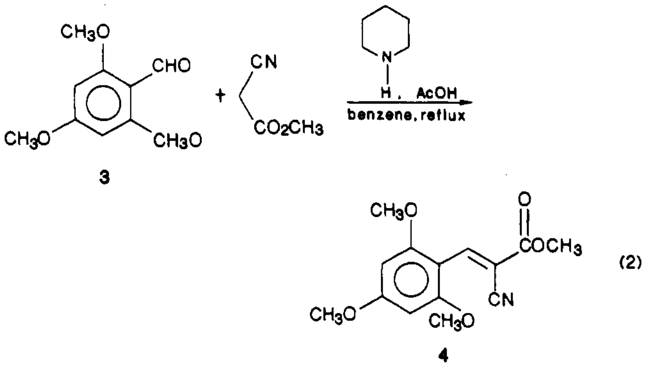
Results

Model Compound Synthesis and Properties. A series of model compounds was synthesized to ensure the viability of the Knoevenagel condensation between substituted benzaldehydes and methyl cyanoacetate.[2]



1a, R, R^1 = H; R^2 = CH_3
1b, R, R^2 = H; R^1 = CH_3
1c, R = H; R^1, R^2 = CH_3
1d, R = OCH_3; R^1, R^2 = CH_3

2a, R, R^1 = H; R^2 = CH_3
2b, R, R^2 = H; R^1 = CH_3
2c, R = H; R^1, R^2 = CH_3
2d, R = OCH_3; R^1, R^2 = CH_3



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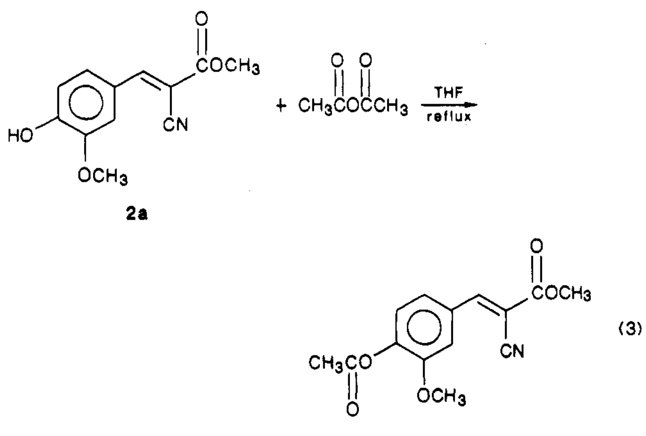
As seen in Table I, the model condensation reaction proceeded smoothly with a wide variety of substituted benzaldehydes yielding crystalline products. Both 200-MHz ^1H and 50-MHz ^{13}C NMR spectra indicate the presence of a single isomer of these cyanocinnamate derivatives. On the basis of our earlier experience with trisubstituted olefins,[3] we know that the ester group will be trans to the phenyl group. The cyanocinnamate derivatives are thus present as the *E* geometric isomer.

The UV data for the model compounds (Table I) indicate that they are highly delocalized, but the dramatic shifts observed in the infrared spectra of the donor–acceptor quinodimethane monomers[1] are not present here. This indicates that the *p*-oxy-α-cyanocinnamate derivatives are not as highly polarized. Methyl *p*-hydroxy-*m*-methoxy-α-cyanocinnamate (**2a**) was acetylated to form **5**, a model for the polyester containing only α-cyano-

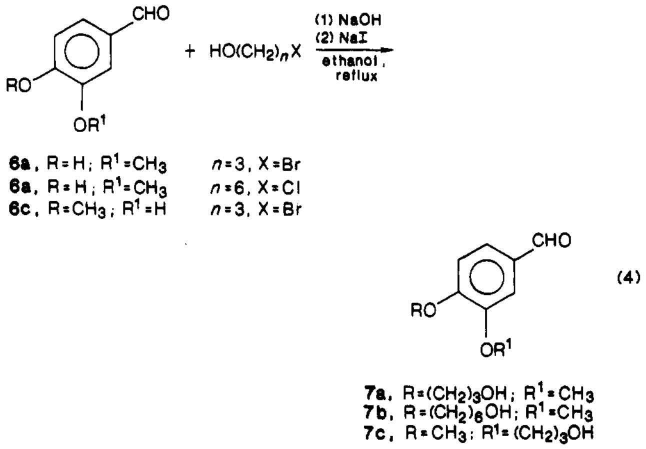


2a

5

cinnamate units, without spacers. Unfortunately, introduction of the acetate functionality results in a considerable hyprochromic shift of **5** relative to the hydroxy derivatives (**2a-d**, **4**). This is due to the fact that the acetoxy substituent is mildly electron-withdrawing and would therefore decrease the degree of polarization of the ring π-electrons with the cyano ester end of the molecule.

Synthesis of Monomers. In order to incorporate these dipolar moieties (**2a–d**, **4**) into a polymer chain in a nonrandom fashion, an AB-type functionality is required, such as ω-hydroxy-α-ester. Because the model studies proved that an ester substituent on the phenyl greatly decreased the dipolar character of the monomer and because a long alkyl chain would improve the processability of the polymer, 4-hydroxy-3-methoxybenzaldehyde and 3-hydroxy-4-methoxybenzaldehyde were converted to (ω-hydroxyalkyl)benzaldehyde derivatives (Table I).

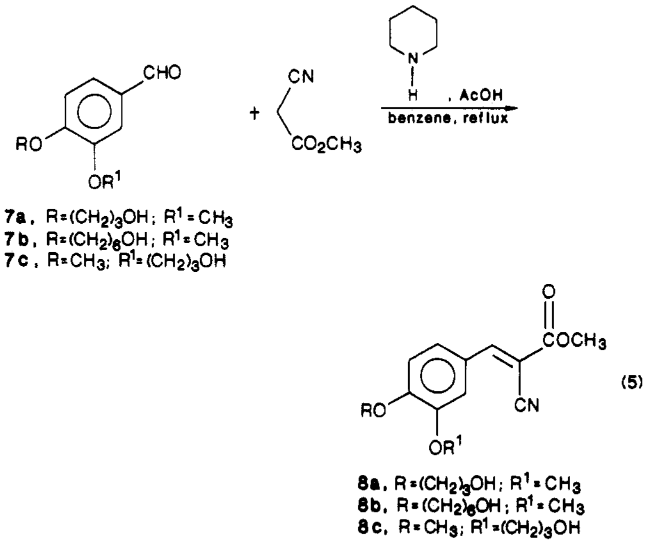


6a, R = H; R^1 = CH_3 n = 3, X = Br
6a, R = H; R^1 = CH_3 n = 6, X = Cl
6c, R = CH_3; R^1 = H n = 3, X = Br

7a, R = $(CH_2)_3OH$; R^1 = CH_3
7b, R = $(CH_2)_6OH$; R^1 = CH_3
7c, R = CH_3; R^1 = $(CH_2)_3OH$

With the procedure worked out for the model compounds, the chain-extended products were condensed with methyl cyanoacetate to form the desired polymerizable compounds (eq 5). The results are presented in Table I.

Polymer Synthesis and Characterization. Formation of polymers was accomplished with the standard two-stage, high-temperature polyesterification procedure in the presence of dibutyltin diacetate (Table II). Homopolymerization of **8a** yielded **9**, a hard, yellow, brittle compound that showed only slight solubility in organic solvents such as dichloromethane and acetone, which prevented characterization by size exclusion chromatography. In order to increase polymer solubility in dichloromethane, copolymers of **8a** and methyl 12-hydroxydodecanoate were synthesized. These polymers were quite soluble, and by varying the stage 2 reaction time, the average molecular weight could be controlled.

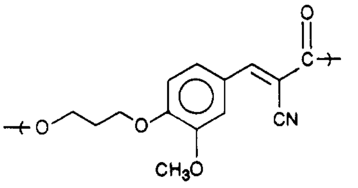


7a, R=$(CH_2)_3OH$; R^1=CH_3
7b, R=$(CH_2)_6OH$; R^1=CH_3
7c, R=CH_3; R^1=$(CH_2)_3OH$

(5)

8a, R=$(CH_2)_3OH$; R^1=CH_3
8b, R=$(CH_2)_6OH$; R^1=CH_3
8c, R=CH_3; R^1=$(CH_2)_3OH$

Additionally, as shown by polymer no. 8, large molar scaleup of the polymerization reaction could be accomplished with no adverse effects.



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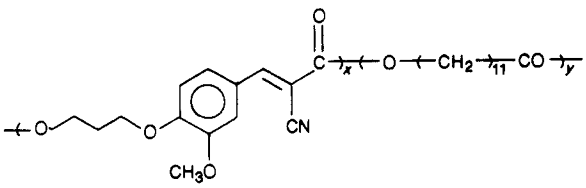

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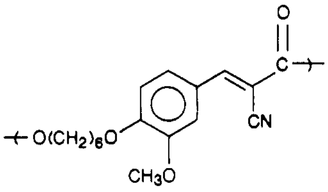

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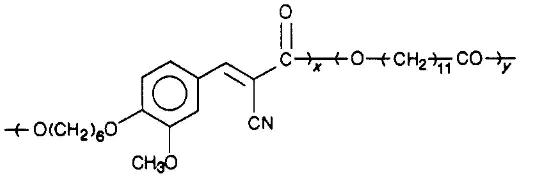

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To maximize the average number of dipolar moieties per polymer chain, various monomer ratios were studied. The 2:1 copolymer (**8a** to methyl 12-hydroxydodecanoate), no. 5, was easily soluble in dichloromethane and therefore, easily characterizable. However, the 3.67:1 copolymer, no. 9, was insoluble.

The desire to synthesize a soluble homopolymer led to the synthesis of **8c**, a monomer with a six-carbon alkyl chain. We hoped that the increase in alkyl chain length would result in a less crystalline polymer, which would therefore be more soluble. Unfortunately, homopolymer no. 6 of **8c** was insoluble in dichloromethane. A 3:1 copolymer, no. 7 of **8c** and methyl 12-hydroxydodecanoate, was also dichloromethane insoluble.

Solution-cast thin films were made from all of the soluble copolymers. These yellow, transparent films were flexible and amorphous. Upon heating, the films could be stretched to ≥300% their original length, yielding an oriented, crystalline polymer. As the polymer was oriented, it became cloudy in appearance. Under the polarizing microscope it was observed that the polymer lacked crystalline domains before orientation and possessed them after orientation.

Discussion

We have now synthesized two families of polymers containing a highly dipolar repeat unit. The previous polymers were based on a quinodimethane repeat unit and had high melting points and low solubilities.[1] Our presently reported *p*-oxy-α-cyanocinnamate polyesters are tractable, contain dipolar character, and can be cast from dichloromethane solutions into flexible, transparent thin films. Since these polymers can be oriented, causing crystal formation, they potentially possess good mechanical properties.

Experimental Section

General Method. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM Fx-200 spectrometer operating at 200 (^{1}H) and 50 MHz (^{13}C), respectively, on solutions in deuteriochloroform. Tetramethylsilane was used as the internal reference. IR spectra were measured on a Perkin-Elmer 983 infrared spectrophotometer. UV-vis spectra were recorded on a Perkin-Elmer 552 spectrophotometer. Molecular weights of polymers were estimated by gel permeation chromatography (columns, Du Pont Zorbax PSM-300S, Du Pont Zorbax PSM-60S, IBM 10-μm pore; detector, Spectra-Physics 8200 UV (254-nm) detector; eluent, chloroform). Elemental analyses were performed on MicAnal, Tucson, AZ. Melting points were recorded with a Mel-Temp melting point apparatus and are uncorrected.

Chain Extension Reaction between Substituted Aldehyde and ω-Haloalcohols (7a–c). With mild heating 0.030 mol of aldehyde was dissolved in 75 mL of absolute ethanol in a round-bottom flask fitted with a condenser. NaOH (1.2 g, 0.030 mol) was added, followed 15 min later by NaI (2.3 g, 0.015 mol). After an additional 15 min, 0.036 mol of the ω-haloalcohol was added and the mixture was heated under reflux. The reaction was followed by TLC, and upon completion (1–3 days) the solvent was removed with a rotary evaporator. The crude product was taken up in dichloromethane (100 mL) and washed with water (100 mL) and 5% aq NaOH (100 mL), and the organic layer was dried with magnesium sulfate. The solvent was removed under vacuum and the product was recrystallized from ethyl acetate/hexanes.

7a. Yield 60%; mp 73–75 °C; λ_{max} 274, 306 nm, ε 13 000, 10 000; IR (KBr) 3281, 1679 cm^{-1}; ^{1}H NMR (CDCl$_3$) 9.82 (d, 1 H), 7.42 (dd, 1 H), 7.38 (d, 1 H), 6.98 (d 1 H), 4.27 (t, 2 H), 3.90 (s, 3 H), 3.88 (t, 2 H), 3.02 (br, 1 H), 2.13 (quin, 2 H); ^{13}C NMR (CDCl$_3$) δ 191.1, 153.8, 149.7, 130.1, 126.8, 111.4, 109.1, 67.4, 60.3, 55.9, 31.6. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.56; H, 6.21.

7b. Yield 89%; mp 51–54 °C; IR (KBr) 3270, 1678 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 9.83 (d, 1 H), 7.44 (d, 1 H), 7.41 (s, 1 H), 6.96 (d, 1 H), 4.10 (t, 2 H), 3.92 (s, 3 H)8 3.66 (t, 2 H), 1.90 (q, 2 H), 1.61 (q, 2 H), 1.50 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 190.9, 154.0, 149.6, 129.7, 126.8, 111.2, 109.1, 68.9, 62.5, 55.9, 32.4, 28.7, 25.6, 25.4. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 64.95; H, 7.80.

7c. Yield 28%; mp 75–78 °C; λ_{max} 274, 306 nm, ε 10 500, 8200; IR (KBr) 3271, 1678 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 9.83 (d, 1 H), 7.43 (dd, 1 H), 7.39 (s, 1 H), 6.99 (d, 1 H), 4.28 (t, 2 H), 3.91 (s, 3 H), 3.88 (t, 2 H), 2.75 (br, 1 H), 2.13 (quin, 2 H); ^{13}C NMR (CDCl$_3$) δ 191.0, 153.7, 149.7, 130.1, 126.8, 111.4, 109.1, 67.5, 60.4, 55.9, 31.6. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.45; H, 6.75.

Condensation Reaction between Substituted Aldehyde and Methyl Cyanoacetate. In a round-bottom flask fitted with

Table II
Preparation and Physical Properties of Polyesters

run no.	stage 1, h	stage 2, h	monomer ratio[a]	polymer structure[b]	yield, %	MW[c]	calcd no. dipolar units[d]	solubility[e]
1	1	1	1:1	**10**	82	17 000	37	dichloromethane
2	1	2	1:1	**10**	85	22 000	48	dichloromethane
3	1	4	1:1	**10**	91	64 000	140	dichloromethane
4	1	0.67	*f*	**9**	100	na	na	*m*-cresol
5	1	2	2:1	**10**	91	17 000	47	dichloromethane
6	1	1.75	*g*	**11**	100	na	na	*m*-cresol
7	1	2	3:1[h]	**12**	80	na	na	*m*-cresol
8	2	0.75	1:1[i]	**10**	87	34 000	74	dichloromethane
9	2	2	3.67:1	**10**	93	na	na	*m*-cresol

[a] Unless otherwise stated, monomers are **8a** and methyl 12-hydroxydodecanoate, respectively. [b] See text for the general structures of the polymers. [c] Determined by GPC relative to polystyrene standards. [d] Number of cinnamate moieties per polymer chain. [e] All solubilities refer to 10% solutions by weight. [f] Homopolymer of **8a**. [g] Homopolymer of **8c**. [h] Monomers are **8c** and methyl 12-hydroxydodecanoate, respectively. [i] Polymerization scale was 5 times the standard amounts.

a Dean–Stark trap was placed the chain-extended aldehyde (0.030 mol) dissolved in benzene (75 mL). Methyl cyanoacetate (3.0 g, 0.030 mol) was then added, followed by the addition of a mixture of piperidine (1.2 mmol) and glacial acetic acid (6.3 mmol) in benzene (5 mL). The solution was heated under reflux until the theoretical amount of water had been collected. The solvent was then removed under vacuum with a rotary evaporator, and the crude product was recrystallized from ethyl acetate/hexanes.

2a. Yield 88%; mp 158–160 °C; $\lambda_{\max}$ 358 nm, ϵ 22 100; IR (KBr) 3389, 2223, 1731 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.16 (s, 1 H), 7.87 (d, 1 H), 7.42 (dd, 1 H), 7.01 (d, 1 H), 3.99 (s, 3 H), 3.92 (s, 3 H), 1.63 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 163.7, 155.2, 151.0, 146.8, 129.0, 124.2, 116.4, 114.9, 111.1, 98.5, 56.1, 53.2. Anal. Calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75; N, 6.01. Found: C, 61.85; H, 4.67, N, 5.96.

2b. Yield 76%; mp 157–158 °C; $\lambda_{\max}$ 355 nm, ϵ 19 100; IR (KBr) 3381, 2229, 1730 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.12 (s, 1 H), 7.67 (d, 1 H), 7.48 (dd, 1 H), 7.02 (d, 1 H), 3.94 (s, 3 H), 3.86 (s, 3 H); ^{13}C NMR (CDCl$_3$) δ 162.4, 153.7, 151.2, 145.4, 125.6, 123.8, 116.2, 114.7, 110.5, 98.0, 55.0, 51.9. Anal. Calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75; N, 6.01. Found: C, 61.65; H, 4.65; N, 6.03.

2c. Yield 89%; mp 124–125 °C; $\lambda_{\max}$ 362 nm, ϵ 23 500; IR (KBr) 2218, 1730 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.10 (s, 1 H), 7.75 (s, 1 H), 7.44 (dd, 1 H), 6.94 (d, 1 H), 3.96 (d, 3 H), 3.93 (d, 3 H), 3.91 (d, 3 H); ^{13}C NMR (CDCl$_3$) δ 163.1, 154.4, 153.4, 148.8, 127.7, 124.1, 116.0, 111.1, 110.6, 98.3, 55.8, 55.6, 52.8. Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.66. Found: C, 62.92; H, 5.19; N, 5.70.

2d. Yield 85%; mp 112–114 °C; $\lambda_{\max}$ 363 nm, ϵ 13 600; IR (KBr) 2217, 1731 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.15 (s, 1 H), 7.30 (s, 2 H), 3.96 (s, 3 H), 3.93 (s, 3 H), 3.92 (s, 6 H); ^{13}C NMR (CDCl$_3$) δ 163.0, 154.9, 153.1, 142.6, 126.3, 115.8, 108.4, 100.5, 60.9, 56.1, 53.2. Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.65; H, 5.45; N, 5.05. Found: C, 60.54; H, 5.40; N, 4.97.

4. Yield 88%; mp 145–146 °C; $\lambda_{\max}$ 362 nm, ϵ 19 000; IR (KBr) 2220, 1731 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.12 (s, 1 H), 7.29 (s, 2 H), 3.96 (s, 3 H), 3.93 (s, 3 H), 3.92 (s, 6 H); ^{13}C NMR (CDCl$_3$) δ 162.8, 154.6, 152.9, 142.4, 126.1, 115.7, 108.3, 100.3, 60.7, 55.9, 53.0. Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.65; H, 5.45; N, 5.05. Found: C, 60.85; H, 5.40; N, 5.02.

8a. Yield 93%; mp 150–151 °C; $\lambda_{\max}$ 363 nm, ϵ 23 300; IR (KBr) 3491, 2223, 1715 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.16 (s, 1 H), 7.80 (d, 1 H), 7.45 (dd, 1 H), 6.96 (d, 1 H), 4.29 (t, 2 H), 3.93 (s, 3 H), 3.92 (s, 3 H), 3.89 (t, 2 H), 2.13 (quin, 2 H); ^{13}C NMR (CDC)$_3$) δ 163.6, 154.9, 153.0, 149.4, 127.9, 124.6, 116.3, 111.9, 111.7, 98.9, 67.6, 60.6, 56.0, 53.2, 31.5. Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5,88; N, 4.81. Found: C, 61.84; H, 5.84; N, 4.78.

8b. Yield 93%; mp 91–93 °C; $\lambda_{\max}$ 365 nm, ϵ 23 700; IR (KBr) 3441, 2221, 1726 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.14 (s, 1 H), 7.78 (d, 1 H), 7.44 (dd, 1 H), 6.92 (d, 1 H), 4.10 (t, 2 H), 3.93 (s, 3 H), 3.91 (s, 3 H), 3.65 (t, 2 H), 2.32 (s, 1 H), 1.89 (m, 2 H), 1.61 (m, 2 H), 1.49 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 163.4, 154.8, 153.2, 149.2, 127.8, 124.0, 116.2, 111.6, 98.1, 68.7, 62.3, 55.8, 52.9, 32.3, 28.6, 25.5, 25.3. Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.67; H, 7.03; N, 4.17.

8c. Yield 77%; mp 151–154 °C; $\lambda_{\max}$ 363 nm, ϵ 22 000; IR (KBr) 3496, 2224, 1716 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.16 (s, 1 H), 7.79 (d, 1 H), 7.45 (dd, 1 H), 6.96 (d, 1 H), 4.29 (t, 2 H), 3.93 (s, 6 H), 3.89 (t, 2 H) 2.39 (br, 1 H), 2.13 (quin, 2 H), ^{13}C NMR (CDCl$_3$) δ 163.5, 154.9, 153.0, 149.4, 127.9, 124.6, 116.3, 111.8, 111.7, 98.8, 67.5, 60.5, 55.9, 53.2, 31.5. Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 60.82; H, 6.01; N, 4.44.

Acylation of 2a. **2a** (2.00 g, 0.00858 mol) was dissolved in 25 mL of dry THF in a three-necked round-bottom flask fitted with a condenser, exited to an oil bubbler, and with an addition funnel, fitted to allow a N_2 sweep. The addition funnel was charged with 0.90 mL (0.0096 mol) of acetic anhydride and 5 mL of dry THF, and a slow N_2 sweep was initiated. The anhydride solution was added over a 10-min period while the reaction flask was cooled in an ice bath. After 1 h the flask solution was heated to reflux for 4 h. The reaction mixture was cooled to room temperature and the solid present was filtered out and dissolved in 25 mL of $CHCl_3$. The organic solution was washed 2 times with 15 mL of a saturated $NaHCO_3$ solution and dried with $MgSO_4$, and the solvent was removed under vacuum with a rotary evaporator. The crude product was recrystallized from ethyl acetate/hexanes: yield 22%; mp 140–142 °C; $\lambda_{\max}$ 306 nm, ϵ 15 000; IR (KBr) 2223, 1758, 1731 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.20 (s, 1 H), 7.81 (d, 1 H), 7.46 (dd, 1 H), 7.16 (d, 1 H), 3.94 (s, 3 H), 3.90 (s, 3 H), 2.34 (s, 3 H). Anal. Calcd for $C_{14}H_{13}NO_5$: C, 61.09; H, 4.76; N, 5.09. Found: C, 60.99; H, 4.56; N, 5.03.

Methyl 12-Hydroxydodecanoate. 12-Hydroxydodecanoic acid (15.0 g, 0.0691 mol) was dissolved in 200 mL of methanol in a round-bottom flask fitted with a condenser. Sulfuric acid (2 mL) was added and refluxing initiated. After 24 h, refluxing was stopped and excess $NaHCO_3$ added to the reaction mixture. After the solid was filtered out, the methanol was stripped off with a rotary evaporator. Ether (75 mL) was added and the organic solution washed with 25 mL of a saturated $NaHCO_3$ solution. The organic layer was removed and the remaining aqueous layer extracted with 25 mL of ether. The combined ether layers were dried with $MgSO_4$ and then the ether was removed under vacuum by using a rotary evaporator. The crude product was recrystallized from hexanes: yield 100%; mp 29–31 °C; ^{1}H NMR (CDCl$_3$) δ 3.67 (s, 3 H), 3.62 (t, 2 H), 2.31 (t, 2 H), 2.17 (s, 1 H), 1.59 (m, 4 H), 1.28 (br s, 14 H); ^{13}C NMR (CDCl$_3$) δ 174.3, 62.7, 51.3, 33.9, 32.6, 29.4, 29.3, 29.1, 29.0, 25.6, 24.8. Anal. Calcd for $C_{13}H_{26}O_3$: C, 67.79; H, 11.38. Found: C, 67.39; H, 11.52.

Polymerization by the Two-Stage, High-Temperature Polyesterification Procedure. Into a polymerization flask flushed with nitrogen were placed the cinnamate derivative (2.6 mmol) and the comonomer (if used). A homogenous melt was achieved by heating the flask to 160 °C and dibutyltin diacetate (2 mol %) was added. The mixture was heated at 160 °C with a nitrogen purge and constant stirring for an approrpiate period (Table II). The second stage was begun by placing the solution under vacuum (0.2 Torr) with continued stirring. When the polymerization was complete, the yellow viscous mixture was cooled to room temperature and the product was dissolved in an appropriate solvent (dichloromethane or *m*-cresol). The products were purified by reprecipitation into methanol.

No. 1 (Table II). Yield 82%; mp ≈130–140 °C; MW 17 000; IR (KBr) 2218, 1731, 1715 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.14 (s), 7.79

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(br t), 7.45 (br s), 6.96 (q), 4.53 (t), 4.29 (t), 4.19 (t), 4.05 (t), 3.92 (d), 2.29 (br m), 1.75 (br t), 1.61 (br t), 1.28 (br s). Anal. Calcd for $C_{26}H_{35}NO_6$ (values for a hypothetical copolymer repeat unit): C, 68.25; H, 7.71; N, 3.06. Found: C, 68.00; H, 7.72; N, 3.26.

No. 2. Yield 85%; mp ≈130–140 °C; MW 22 000; IR (KBr) 2217, 1731, 1716 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.14 (s), 7.80 (br q), 7.44 (br s), 6.96 (q), 4.53 (br s), 4.29 (t), 4.19 (t), 4.05 (t), 3.92 (s), 2.28 (br m), 1.75 (br t), 1.61 (br t), 1.28 (br s). Anal. Calcd for $C_{26}H_{35}NO_6$ (values for a hypothetical copolymer repeat unit): C, 68.25; H, 7.71; N, 3.06. Found: C, 67.92; H, 7.77; N, 3.06.

No. 3. Yield 91%; mp ≈140–220 °C; MW 64 000; IR (KBr) 2219, 1730, 1714 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.14 (s), 7.80 (br d), 7.44 (br s), 6.96 (q), 4.53 (br t), 4.29 (br t), 4.19 (t), 4.05 (t), 3.92 (s), 2.29 (br m), 1.75 (br t), 1.61 (br t), 1.28 (br s). Anal. Calcd for $C_{26}H_{35}NO_6$ (values for a hypothetical copolymer repeat unit): C, 68.25; 7.71; N, 3.06. Found: C, 68.11; H, 7.81; N, 3.07.

No. 4. Yield 100%; mp ≈190 °C; IR (KBr) 2217, 1714 cm^{-1}; Anal. Calcd for $C_{14}H_{13}NO_4$ (values for the homopolymer repeat unit): C, 64.86; H, 5.05; N, 5.40. Found: C, 64.98; H, 5.65; N, 4.93.

No. 5. Yield 91%; mp (dec) 240 °C; IR (KBr) 2218, 1731 cm^{-1}. Anal. Calcd for $C_{40}H_{48}N_2O_{10}$ (values for a hypothetical copolymer repeat unit): C, 67.02; H, 6.75; N, 3.91. Found: C, 66.89; H, 6.96; N, 3.67.

No. 6. Yield 100%; mp (dec) ≈300–340 °C, IR (KBr) 2217, 1712 cm^{-1}.

No. 7. Yield 80%; mp (dec) ≈250 °C; IR (KBr) 2217, 1726 cm^{-1}; Anal. Calcd for $C_{63}H_{79}N_3O_{14}$ (values for a hypothetical copolymer repeat unit): C, 68.64; H, 7.22; N, 3.81. Found: C, 68.23; H, 6.88; N, 3.64.

No. 8. Yield 87%; mp ≈140–160 °C; MW 34 000; IR (KBr) 2217, 1731, 1715 cm^{-1}. Anal. Calcd for $C_{26}H_{35}NO_6$ (values for a hypothetical copolymer repeat unit): C, 68.25; H, 7.71; N, 3.06. Found: C, 68.02; H, 7.57; N, 3.04.

No. 9. Yield 93%; mp ≈180–185 °C; IR (KBr) 2217, 1729 cm^{-1}. Anal. Calcd for $C_{63.4}H_{69.7}N_{3.67}O_{16.7}$ (values for a hypothetical copolymer repeat unit): C, 66.21; H, 6.11; N, 4.47. Found: C, 65.41; H, 6.17; N, 4.29.

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Novel Polymerization Reaction: Double Cycloaddition of Sydnone and Bismaleimide

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ABSTRACT: A novel polymerization reaction of mesoionic sydnone and bismaleimide is described. This polymerization is based on the double 1,3-cycloaddition of sydnone to two maleimide functions to form carbon dioxide and 1,7-diazabicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic acid diimide (8), which are the recurring units of the polymer chain. A new class of polyimides has been synthesized by this reaction. These polyimides have good thermal stability and solubility.

Introduction

Since the first synthesis of sydnone in 1935 the chemistry of mesoionic heterocyclic compounds has been extensively explored.[1] However, despite the high reactivity of some of its members, the application of mesoionic compounds in the synthesis of macromolecules is extremely limited. Stille and Bedford[2] reported the reaction of disydnone with diene or diyne to form poly(pyrazoline) and poly(pyrazole), respectively, of low to moderate molecular weights. Rigby and Stark[3] described the reaction of some reactive olefins such as bismaleimide with tautomer of 1,3-oxazol-5-one, which is mesoionic 1,3-oxazolium-5-olate, to form insoluble materials. These materials are believed to be polyimides containing 7-azabicyclo[2.2.1]heptane units according to reaction of 1,3-oxazol-5-one and maleimide.[4]

It is now found that the double cycloaddition of sydnone to an equimolar amount of bismaleimide forms a new class of polyimides with a polycyclic structure and usually of high molecular weights. These polyimides have good thermal stability and are soluble in many organic solvents.

Results and Discussions

The 1,3-dipolar cycloaddition reaction of mesoionic sydnone (**1**) to olefinic double bonds is known to form initially an unstable 1:1 primary adduct, which eliminates carbon dioxide, followed either by 1,3-proton shift to become a Δ^2-pyrazoline or by further elimination of a neutral molecule to form a pyrazole derivative as the final stable products.[5] Only in the reaction of 3-phenylsydnone and acenaphthylene, in addition to the normal product pyrazoline, is a bis adduct formed in low yield.[6] This bis adduct is the result of double cycloaddition of sydnone to two molecules of the olefin after elimination of carbon dioxide. Similarly, in the reaction of sydnone with cyclooctadiene or butadienes, such double cycloaddition occurs intramolecularly to afford low to moderate yield of bis adducts.[7]

It is found that the reaction of 3-phenylsydnone (**1a**) and *N*-phenylmaleimide affords exclusively two isomeric bis adducts, 7-phenyl-1,7-diazabicyclo[2.2.1]heptane-2,3-*exo*-5,6-*exo*-tetracarboxylic acid bis(phenylimide) (**4**) and the corresponding -2,3-*endo*-5,6-*exo*- isomer **5** in practically quantitative yield.[8] Because of the high reactivity of maleimide as a dipolarophile toward azomethine–imine dipoles, such as intermediate **3**, the reaction of the latter with *N*-phenylmaleimide is much faster than its intramolecular rearrangement to the energetically unfavorable pyrazoline **6**, because **6** contains a highly strained double bond. Therefore, in this reaction, the products are exclusively **4** and **5** in 87:13 ratio when the reaction is carried out at 95 °C.

This bifunctional character of sydnone toward maleimide allows its reaction with bismaleimide to form polyimide. Such polymerization is demonstrated by the re-

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