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Photoresponsive Polyquinolines

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ABSTRACT: Photoresponsive polyquinolines containing isomerizable stilbene units were synthesized by polymerization reactions utilizing 4,4′-diacetylstilbene (**2**) as the bis(ketomethylene) monomer and 4,4′-diamino-3,3′-dibenzoylstilbene (**3**) as the bis(amino ketone) monomer. The diacetylstilbene monomer (**2**) was polymerized with 4,4′-diamino-3,3′-dibenzoyldiphenyl ether, 3,3′-dibenzoylbenzidine, and **3**. Monomer **3** also was polymerized with 4,4′-diacetyldiphenyl ether and 4,4′-diacetylbiphenyl. These polymers exhibited photoviscosity effects in dilute solution, ranging from a 2% to a 23% change in viscosity during irradiation. Photomechanical measurements showed that films of the polymer contracted by as much as 5% when irradiated above T_g. A smaller contraction was observed upon irradiation below T_g. In addition, the polymer obtained from **2** and 3,3′-dibenzoylbenzidine produced an anisotropic solution (10% (w/w) in *m*-cresol/di-*m*-cresyl phosphate).

Introduction

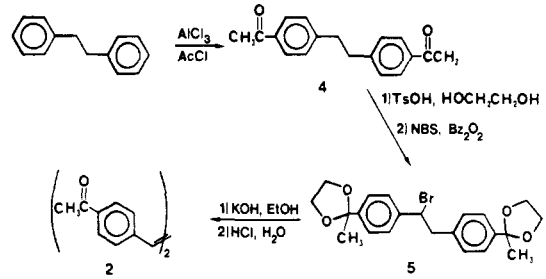
Since the concept of photoresponsive polymers was first suggested in 1967,[1] a variety of photoresponsive polymers have been studied.[2] The work was concentrated primarily on polymers incorporating azobenzene or spirobenzopyran residues as the photoresponsive units. While the azobenzene undergoes simple *E* to *Z* isomerization, the spirobenzopyran undergoes a reversible photoinduced rearrangement to a merocyanine. These chromophores have been incorporated into polymers in the main chain,[3,4] as pendant groups,[5-7] as cross-links,[6] or simply as additives.[6,8] Previous research has focused on flexible and semirigid polymers such as polyamides,[3,8] polyurethanes,[4,9] polyacrylates,[6,7] and polystyrenes.[5]

Numerous physical properties of photoresponsive polymers have been shown to be altered when the chromophoric units are isomerized. These properties include dilute solution viscosity,[3,7] conductivity,[3] pH,[3] and solubility.[5] In addition, polymer chain mobility has been probed by the trans–cis isomerization of azobenzene units in the polymer chain.[4,9-11]

A study of the photochemical behavior of 4,4′-disubstituted stilbenes indicated that they isomerized readily.[12] There are two examples in which stilbene has been incorporated into a polymer main chain. The quantum efficiency for stilbene isomerization in copolyamides has been measured.[13] The viscosity of a polyaramide containing stilbene units contained in the diamine monomer showed a decrease on irradiation and slowly recovered in the dark.[14] Unexpectedly, the same polymer in bulk relaxed instead of contracting on irradiation.

Although rigid rod polyquinolines demonstrate excellent thermal stability, high phase transition temperatures, and a high degree of crystallinity, they are relatively insoluble, even in acidic solvents such as sulfuric acid and trifluoromethanesulfonic acid.[15] This research was undertaken, therefore, to improve the processability of rigid rod polyquinolines by incorporating photoisomerizable (*E*)-stilbene units in the main chain. Irradiation of these polymers was expected to effect an *E* to *Z* isomerization converting the rigid rod polymer to a nonlinear one, thereby aiding in its dissolution. Thermal relaxation of the *Z* isomer could again generate the rigid rod after processing.

Scheme I
Synthesis of 4,4′-Diacetylstilbene (2)



Results and Discussion

Stilbene Monomers. Before proceeding with large-scale preparations of the stilbene monomers, we prepared a model compound (**1**) from 4,4′-diacetylstilbene (**2**) and *o*-aminobenzophenone. Synthesis of **1** under the same conditions as the polymerizations indicated that the stilbene monomers could be successfully polymerized without decomposition. Because of the mild electron-withdrawing character of the quinoline ring, isomerization of the stilbene unit in the polymer should proceed smoothly, re-

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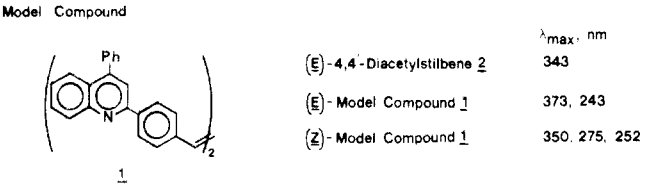
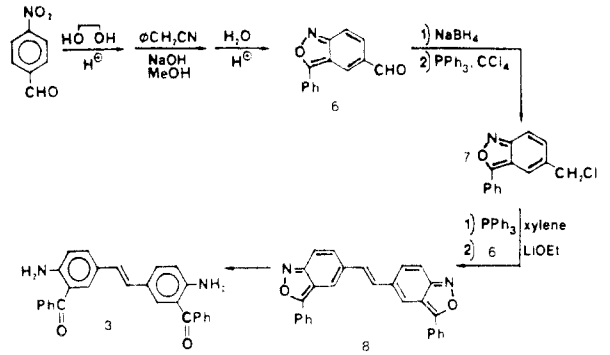


Figure 1. UV/visible maxima of 1.

Scheme II
Attempted Synthesis of
4,4′-Diamino-3,3′-dibenzoylstilbene (3)



gardless of solvent.[11] To confirm this isomerization, ultraviolet spectra were taken of the model compound before and after irradiation at 300 and 350 nm (Figure 1). The spectra indicate conclusively that isomerization does occur.

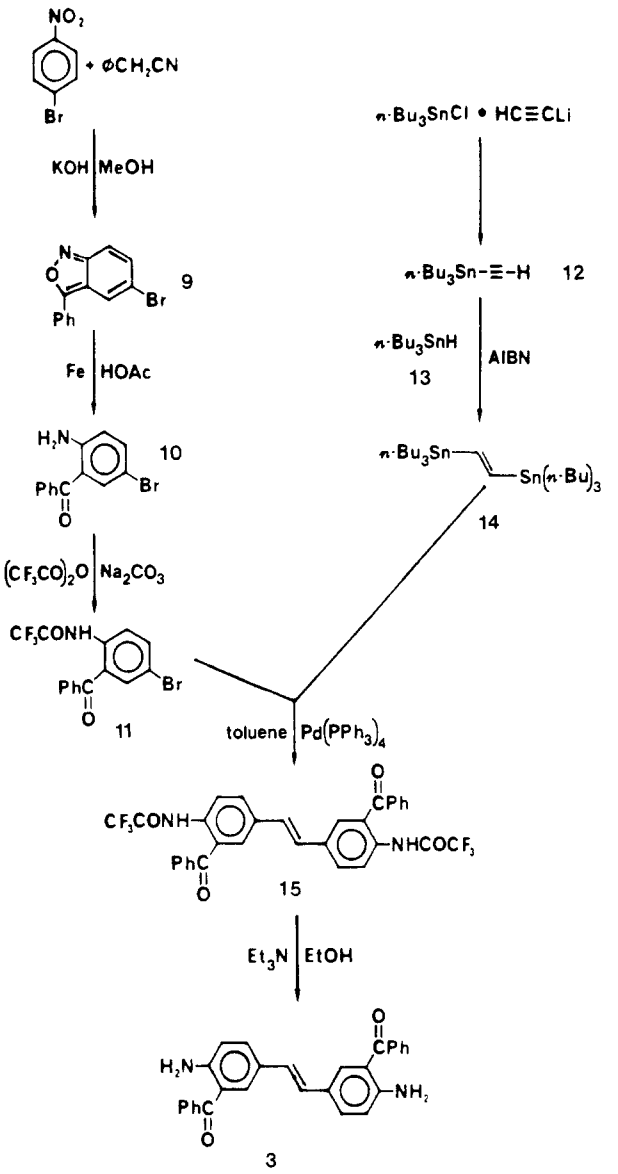
The two stilbene monomers, 4,4′-diacetylstilbene (**2**) and 4,4′-diamino-3,3′-dibenzoylstilbene (**3**), were then prepared. The diacetyl compound **2** had been synthesized by the direct Friedel–Crafts acylation of stilbene.[16] Unfortunately, the yield of this reaction was very low, only 5%, and as a result, an indirect synthetic route was used (Scheme I). Bibenzyl was acylated via a Friedel–Crafts reaction to yield 4,4′-diacetylbibenzyl (**4**). Protection of the carbonyl groups followed by free radical bromination gave bromoethane **5**. Dehydrohalogenation of **5** with alcoholic base and subsequent deprotection produced **2** in an overall yield after recrystallization of about 25%. Monomer **2** existed completely in the *E* form, as indicated by NMR.

To allow the maximum incorporation of stilbene units into the polymer, the other stilbene monomer, 4,4′-diamino-3,3′-dibenzoylstilbene (**3**), was prepared. With both stilbene monomers, the polyquinoline would contain two diphenylethylene groups per repeat unit.

The initial attempt to prepare **3** (Scheme II) relied on the 2,1-benzisoxazole to mask the *o*-aminoketo functionality, while a Wittig reaction was conducted on the aldehyde. The formyl functionality on *p*-nitrobenzaldehyde was protected as the ethylene ketal, and this material condensed with benzyl cyanide to yield the protected benzisoxazole. Deprotection gave 5-formyl-3-phenyl-2,1-benzisoxazole (**6**), which was then split into two portions. One portion was converted via a three-step sequence to the 5-phosphonium salt, which was coupled with the other portion to yield 5,5′-(1,2-ethenediyl)bis(3-phenyl-2,1-benzisoxazole) (**8**). To this point, all of the steps proceeded fairly cleanly and in good yield. However, this route to **3** failed because the final step, the reductive ring opening of the benzisoxazole, was unsuccessful. The usual methods for the reduction of benzisoxazoles,[17] such as iron/acetic acid or hydrazine hydrate, gave complex mixtures of products, possibly because of partial reduction of the olefin.

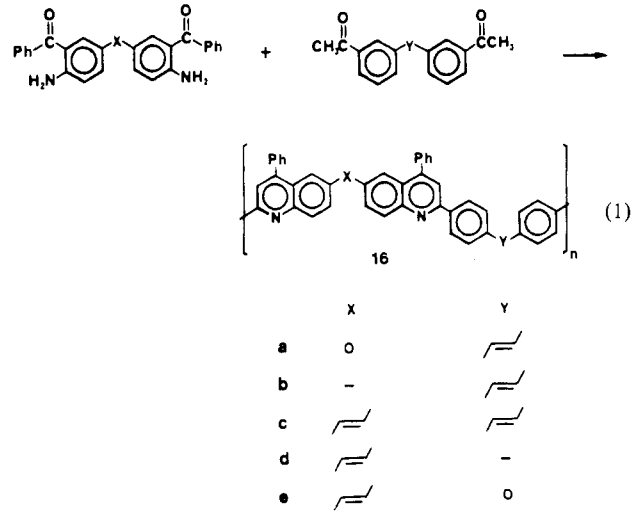
Because of the difficulty encountered in the last step of the previous sequence, an alternate route to **3** was sought.

Scheme III



The convergent sequence shown in Scheme III led successfully to **3**. Both the aryl bromide **10**[18] and the bis(tri-*n*-butylstannyl)ethylene **14**[19] were prepared according to literature procedures. The palladium-catalyzed direct coupling of the protected aryl bromide **11** with the vinyl tin **14** proceeded cleanly, in good yield, and rapidly at 100–110 °C. Because coupling of the amine **10** and **14** led to a complex mixture of products, protection of the amine as a trifluoroacetamide was necessary. The amine may have been coordinating to the palladium or forming a complex with the tin, both of which are precedented.[20,21] The workup of the coupled product **15** was very simple, since it crystallized from the reaction mixture as it was formed. Deprotection of **15** with triethylamine/ethanol yielded the desired monomer **3** in an overall yield of about 40% from *p*-bromonitrobenzene. Continuous extraction with triethylamine/ethanol slowly dissolved the protected material **15**, which then recrystallized in the pot as pure **3**.

Polymers. Synthesis. Stilbene-like monomers **2** and **3**, 4,4′-diacetyldiphenyl ether,[22] 4,4′-diamino-3,3′-dibenzoyldiphenyl ether,[23] 4,4′-diacetylbiphenyl,[24] and 3,3′-dibenzoylbenzidine[18] were used to prepare polymers with a range of flexibilities according to the published procedure (eq 1).[18] With the vinyl groups in their *E*



geometries, polymers **16b–d** should be rigid rods, while **16a** and **16e** should be semirigid. Polyquinoline **16c** has the maximum number of isomerizable stilbene-like groups, two per repeat unit. The polymers incorporating diacetylstilbene **2** contain a stilbene unit in the backbone, while those made with **3** contain a bis(quinolinyl)ethylene unit. On the basis of their different substitution patterns, these two units would be expected to behave differently.

Physical Properties. Dilute Solution. The intrinsic viscosities of both the original polymer solution, which had not been previously irradiated, and the irradiated solution were determined for each polymer (Table I). Polymer solutions were irradiated, and their intrinsic viscosities monitored until a viscosity decrease was no longer observed. Upon removal of the irradiation source, the viscosities slowly recovered to their original values.

The amino ketone and ketomethylene monomers were pure, as shown by HPLC. If the monomers were stoichiometrically balanced in each of the step-growth polymerizations, the molecular weights of the resulting polymers should have been approximately equal, since this reaction has been shown to yield high molecular weight materials.[15] The viscosities then should reflect differences in other properties such as chain flexibility. The intrinsic viscosity is proportional to the cube of the end-to-end distance of the chain, where Φ is a constant, M is molecular weight, and $(\bar{r}^2)^{3/2}$ is the root-mean-square end-to-end distance of the chain (eq 2).[25] Because of their extend-

$$[\eta] = \frac{\Phi(\bar{r}^2)^{3/2}}{M} \qquad (2)$$

ed-chain conformations then, rigid rods are more viscous than flexible polymers of the same molecular weight. As expected, the values for the viscosities of **16a** and **16e** were smaller, respectively, than those for the correspondingly more rigid **16b** and **16d**.

On the other hand, comparison of the values for the viscosities of **16a** and **16b** with those of **16c–e** indicates marked differences between the polymers incorporating diacetylstilbene **2** and those incorporating amino ketone **3**. The most obvious explanation is that the molecular weights of polymers **16c–e** are lower than those of **16a** and **16b**. Although the comonomers were pure and stoichiometrically balanced in each polymerization, monomer **3** may have been less reactive than other monomers toward the Friedlander synthesis, thus leading to lower molecular weight polymers. This seems unlikely though, since other monomers have given high molecular weight polymers, regardless of the functionality contained between the aromatic rings.[15] Alternatively, the lower molecular weight polymers may have been caused by slight decomposition of **3** under the polymerization conditions.

Table I
Viscosities and the Photoviscosity Effect[a]

polymer	$[\eta]_0$, dL/g	$[\eta]_{photo}$, dL/g	% change
16a	13.8	12.6	8.7
16b	14.7	11.4	23.8
16c	5.2	4.7	10.5
16d	5.2 (5.4)[b]	5.1 (5.5)[b]	1.9
16e	3.3	2.9	12.1

[a] Solvent: 0.1 mol % di-*m*-cresyl phosphate/*m*-cresol. Inherent error = ● 0.5 dL/g. [b] Duplicate measurement in parentheses.

Table II
Thermal Properties of Polyquinoline–Stilbenes

		DSC	
polymer	X, Y	T_g, °C	T_m, °C
16a		260	*a*
16b		355	545
16c		305	465
16d		295	405
16e		250	395
16f	O, O	266	448
16g	O, —	308	480
16h	—, O	305	*a*
16i	—, —	340	500

[a] No T_m detected.

The magnitude of the photoviscosity effect (Table I) ranged from 2 to 23%. During these experiments, no attempt was made to study the rate of isomerization, beyond ensuring that the *E–Z* equilibrium, which achieved the maximum photoviscosity effect, had been attained. The polymers were irradiated in solution until no further viscosity change was observed. Considering the error inherent in the measurements, polymer **16b** was the only polymer to demonstrate a significant effect. The photovisocisity effect of the polyquinoline–stilbenes is smaller than those of previously reported systems, which have exhibited changes of up to 60%.[3]

Concentrated Solution. A 10% (w/w) solution of **16b** in a 20 mol % solution of di-*m*-cresyl phosphate/*m*-cresol displayed anisotropic behavior. Observed with a polarizing microscope, the anisotropic solution exhibited birefringence,[26] indicating that the rigid chains were aligned. The solution exhibited anisotropy upon gradual cooling from 140 °C and by shearing a thin film of the solution between two glass plates. Both of these techniques allowed the chains sufficient mobility to align themselves. With visible light, the anisotropic areas of the solution were gold and opaque, while the isotropic regions were orange and transparent. Ultraviolet irradiation of a thin film of the anisotropic solution produced no change in its anisotropy. Theoretically, irradiation would be expected to destroy the solution's anisotropy by converting some of the linear *E* isomers to the *Z* form. A 14% (w/w) solution of **16c** in the same solvent was not anisotropic.

Solid-State Thermal Properties. For comparison with other polyquinolines, the thermal properties of the polyquinoline–stilbenes were measured (Table II). Both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere. Comparison of the thermal properties of **16a–e** with those of **16f–i** again highlights the anomalous behavior of the polymers containing the bis(quinolinyl)-ethylene unit (**16c–e**). Nil/vinyl **16b** is the only polymer prepared that had thermal transitions similar to those of the corresponding polyquinoline, rigid rod **16i**. In fact, the

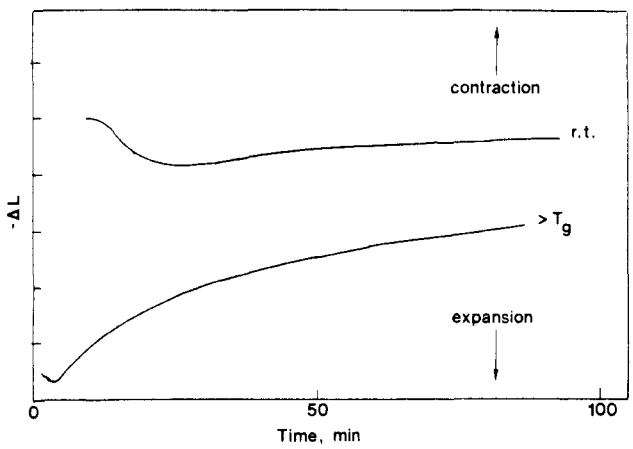


Figure 2. Contraction of **16b** film on irradiation.

Table III
Photomechanical Effect of Polyquinoline–Stilbenes

polymer	contraction at ≃70 °C, $-\Delta L/L \times 100$, %	contraction above T_g, $-\Delta L/L \times 100$, % (T, °C)
16a	1.17	1.17 (314)
16b	0.56	2.67 (385)
16c	0.82	3.38 (352)
16d	1.07	4.84 (344)
16e	0.80	2.41 (337)
16i	0.00	0.00 (405)

glass transition temperature (T_g) and the crystalline transition temperature (T_m) of **16b** were slightly higher than those of **16i**.

Solid-State Photochemical Properties. The photomechanical effect exhibited by the polyquinolines containing stilbene units was a contraction of a film sample, caused by the *E* to *Z* photoisomerization. The effect was investigated both at room temperature and above T_g. With increased chain mobility above T_g, isomerization could be expected to be more facile, therefore producing a larger effect.

The experiment was conducted by irradiating a sample at room temperature and observing the contraction of the film (Figure 2). The initial expansion (negative slope of curve) of the film probably resulted from the tension placed on the sample and from the heat generated by the UV lamp. Upon completion of the contraction, the lamp was turned off and the sample was heated to about 50 °C above T_g, during which *Z* to *E* isomerization took place. During this heating, the film usually lengthened about 0.254–0.508 mm, although this was not routinely recorded. After the temperature stabilized, the lamp was turned back on and the contraction was recorded.

In each of the experiments, the curves produced did not level off, but instead ended with a very slight positive slope (Figure 2).

Because of variations in the sizes of the film samples, the results are reported as fractional changes in the length of the film (Table III). The effect at room temperature varied from 0.5 to 1.2% contraction, while above T_g, it ranged from 1.2 to 4.8%. The effect shown here is much larger than that of a previous study, which reported a photomechanical effect of only 0.15–0.25%.[6]

Conclusion. Despite the behavior of **16c–e**, which had viscosities and thermal properties lower than anticipated, the polyquinoline–stilbenes were indeed photoresponsive, exhibiting both a photoviscosity effect and a photomechanical effect. The expected decrease in solution viscosity on irradiation was paralleled by a photomechanical contraction in the solid state. However, it remains to be determined whether the properties of photoresponsive rigid rod polyquinoline–stilbenes will simplify their processing.

Experimental Section

The *m*-cresol was distilled under nitrogen and stored under argon. Di-*m*-cresyl phosphate,[27] 5-bromo-3-phenyl-2,1-benzisoxazole,[18] 2-amino-5-bromobenzophenone,[18] tri-*n*-butyltin acetylide,[19] tri-*n*-butyltin hydride,[28] (*E*)-1,2-bis(tri-*n*-butylstannyl)ethylene,[19] 4,4′-diacetyldiphenyl ether,[22] 4,4′-diacetylbiphenyl,[24] 4,4′-diamino-3,3′-dibenzoyldiphenyl ether,[23] and 3,3′-dibenzoylbenzidine[18] were prepared according to literature methods. Starting materials were obtained from Aldrich Chemical Co. or Alfa Products, Morton Thiokol, Inc.

All melting points and boiling points are uncorrected. Radial chromatography was carried out with a Chromatotron (Harrison Research Co.). Flash chromatography was carried out according to the published procedure.[29] The ^1H NMR spectra were obtained on Varian EM-360 and IBM WP-270 spectrometers with tetramethylsilane or chloroform as the internal standard. The ^{13}C NMR spectra were obtained on a JEOL FX-100 or an IBM WP-270 spectrometer with chloroform-d_3 or dimethyl-d_6 sulfoxide as the internal standard. Infrared spectra were obtained on a Beckman 4240 spectrophotometer. The mass spectra were determined on a V.G. Micromass 16 mass spectrometer. The UV–visible spectra were recorded on a Varian Techtron UV–vis spectrophotometer 635. HPLC analyses were performed on Waters Associates 6000A and M-45 pumps with a 660 solvent programmer, a 440 absorbance detector, a U6K injector, and a 730 data module. A reverse μ-Bondapak C18 column was used for the HPLC analyses. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA, M–H–W Laboratories, Phoenix, AZ, or Micro-Tech Laboratories, Inc., Skokie IL.

The solution anisotropy was observed with a Carl Zeiss photomicroscope fitted with crossed polarization filters. The thermal characterization of the polymers was accomplished with a Du Pont Instruments 990 thermal analyzer connected to a cell base module II, a 951 thermogravimetric analyzer, or a 943 thermomechanical analyzer.

The photomechanical effect was studied with a modified 943 thermomechanical analyzer with a tension probe accessory kit. The TMA furnace was removed, and quartz glass–nichrome wire furnace with a gas inlet for a nitrogen purge was substituted. The glass furnace allowed the film sample to be irradiated while being heated. The film was irradiated with a Hanovia 654A medium-pressure mercury arc through a Corex filter (cut-off: 260 nm; useful range: >320 nm[30]). The temperature was measured by a chromel–alumel thermocouple connected to an Omega 2165A digital thermometer.

4,4′-Bis[2-(4-phenylquinolinyl)]stilbene (1). A mixture of 0.36 g (1.4 mmol) of 4,4′-diacetylstilbene (**2**), 0.54 g (2.7 mmol) of recrystallized 2-aminobenzophenone, 10 g (36 mmol) of di-*m*-cresyl phosphate, and 3.9 g (36 mmol) of *m*-cresol was stirred under argon for 20 min and then heated to 140 °C for 20 h. The solution was poured into a stirred solution of 200 mL of ethanol and 50 mL of triethylamine to precipitate the product. The product was isolated by suction filtration and dried in vacuo at 110 °C to give 0.71 g (88%) of **1**: mp 273.5–275.5 °C; UV max (CH_2Cl_2) 373 (7.4 × 10^4), 243 (5.8 × 10^4) nm; ^1H NMR ($CDCl_3$, 270 MHz) δ 8.25–7.55 (m, 28 H), 7.29 (s, 2 H). Anal. Calcd for $C_{44}H_{30}N_2$: C, 90.07; H, 5.15; N, 4.77. Found: C, 90.04; H, 5.16; N, 4.73.

4,4′-Diacetylbibenzyl (4). A slurry of 60 g (0.45 mol) of anhydrous aluminum chloride and 32 mL (0.45 mol) of freshly distilled acetyl chloride in 200 mL of methylene chloride was stirred for 30 min under argon. After cooling in an ice bath, a solution of 28 g (0.15 mol) of bibenzyl in 100 mL of methylene chloride was added dropwise over 1.5 h. The reaction mixture was then warmed to room temperature, stirred for 3.5 h, slowly poured into a mixture of 300 g of ice and 150 mL of concentrated hydrochloric acid, and stirred until completely quenched. The methylene chloride layer was then separated, and the aqueous layer was extracted with methylene chloride. The organic extracts were combined, washed with water, a saturated sodium bi-

carbonate solution, and water, and dried ($MgSO_4$). Removal of the solvent yielded 29.7 g (74%) of **4**: mp 167.5–168.5 °C (lit.[31] mp 166–168 °C). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.96; H, 6.83.

1,2-Bis[4-(2-methyl-1,3-dioxolan-2-yl)phenyl]bromoethane (5). A solution of 29.7 g (0.11 mol) of **4**, 1 g (0.005 mol) of *p*-toluenesulfonic acid monohydrate, and 30 mL (0.5 mol) of ethylene glycol in 250 mL of toluene was heated to reflux and the water removed azeotropically. Upon complete removal of the water, toluene was removed by rotary evaporation, and the residue was washed with ethanol, collected by suction filtration, and dried in vacuo.

A solution of 33.9 g (95.8 mmol) of the above material, 18.8 g (105 mmol) of recrystallized[32] *N*-bromosuccinimide, and 0.24 g (1.0 mmol, 1 mol %) of benzoyl peroxide in 400 mL of carbon tetrachloride was heated to reflux under argon for 5 h. After cooling, the solvent was removed by rotary evaporation, yielding 41.5 g (87%) of **5**. The material was used immediately without further purification.

4,4′-Diacetylstilbene (2). A slurry of 41.5 g (95.8 mmol) of **5** and 18.2 g (325 mmol) of potassium hydroxide in 350 mL of absolute ethanol was heated to reflux for 5 h under argon, during which it turned light brown. After cooling, the slurry was poured into 500 mL of water and extracted with methylene chloride. The organic extracts were combined, washed with water, and dried ($MgSO_4$), and the solvent was removed.

A mixture of 29.0 g (82.3 mmol) of the above material, 125 mL of THF, 20 mL of concentrated hydrochloric acid, and 100 mL of water was heated to reflux for 18 h. After cooling, the reaction mixture was extracted with methylene chloride. The organic extracts were combined and dried ($MgSO_4$). The solvent was removed, and the crude product was recrystallized once from toluene and once from 55% ethanol/45% benzene. This gave 11.0 g (44% overall) of **2**, which was shown to be pure by HPLC (80% acetonitrile/20% water, 1.5 mL/min, t_r 3.00 min): mp 208.5–209.5 °C (lit.[16] mp 210–211 °C); UV max (CH_2Cl_2) 343 nm; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.98 (d, 4 H, J = 8.3 Hz), 7.62 (d, 4 H, J = 8.3 Hz), 7.26 (s, 2 H), 2.63 (s, 6 H). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 80.65; H, 6.00.

5-Formyl-3-phenyl-2,1-benzisoxazole (6). A mixture of 25.0 g (0.166 mol) of 4-nitrobenzaldehyde, 1 g (0.005 mol) of *p*-toluenesulfonic acid monohydrate, and 20 mL (0.4 mol) of ethylene glycol in 250 mL of toluene was heated to reflux and the water formed was removed azeotropically. Upon complete removal of the water, the toluene was removed by rotary evaporation, and the solid was washed with ethanol, collected by suction filtration, and dried in vacuo.

The benzisoxazole was prepared by a modification of a published procedure.[33] To a solution of 29.7 g (0.744 mol) of sodium hydroxide in 150 mL of methanol was added 17.4 g (0.149 mol) of benzyl cyanide. Then 29.0 g (0.149 mol) of the above material in 50 mL of methanol was added, and the reaction mixture was stirred for 16 h at room temperature. The precipitate was collected by suction filtration, washed with water followed by a small amount of cold methanol until the solid was a pale yellow, and then dried in vacuo.

A solution of 33.5 g (0.125 mol) of the above material and 1 g (0.005 mol) of *p*-toluenesulfonic acid monohydrate in 250 mL of benzene and 100 mL of water was heated to reflux for 16 h. After cooling, the benzene was removed by rotary evaporation and the product was collected by suction filtration. Recrystallization from methanol gave 15.0 g (44% overall) of **6**: mp 155.5–157.5 °C; ^1H NMR ($CDCl_3$, 270 MHz) δ 10.01 (s, 1 H), 8.41–7.63 (m, 8 H). Anal. Calcd for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.27. Found: C, 75.10; H, 4.11; N, 6.23.

5-(Hydroxymethyl)-3-phenyl-2,1-benzisoxazole. A solution of 7.0 g (31 mmol) of **6** in 400 mL of ethanol was added slowly to a solution of 0.38 g (10 mmol) of sodium borohydride and 0.5 g (10 mmol) of sodium hydroxide in 10 mL of ethanol. After stirring for 2 h at room temperature, the reaction was quenched by the dropwise addition of 10 mL (12 mmol) of 10% aqueous hydrochloric acid. The ethanol was removed, and the solid was dissolved in methylene chloride and extracted with water. The organic layer was dried ($MgSO_4$), and the solvent was removed, giving 6.3 g (90%) of the alcohol: mp 147.0–149.0 °C; ^1H NMR ($CDCl_3$, 270 MHz) δ 8.01–7.30 (m, 8 H), 4.75 (s, 2 H), 2.95 (br s, 1 H). Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.74; H, 4.99; N, 6.18.

5-(Chloromethyl)-3-phenyl-2,1-benzisoxazole (7). A solution of 6.0 g (27 mmol) of 5-(hydroxymethyl)-3-phenyl-2,1-benzisoxazole and 7.7 g (29 mmol) of recrystallized triphenylphosphine in 150 mL of freshly distilled carbon tetrachloride was stirred under argon at 65 °C for 48 h. The solvent was removed and the product was purified by flash chromatography (methylene chloride) to give 4.2 g (65%) of **7**: mp 124–126 °C; ^1H NMR ($CDCl_3$, 270 MHz) δ 8.01–7.36 (m, 8 H), 4.64 (s, 2 H). Anal. Calcd for $C_{14}H_{10}NOCl$: C, 69.00; H, 4.14; N, 5.75; Cl, 14.55. Found: C, 68.78; H, 4.17; N, 5.67; Cl, 14.62.

5,5′-(1,2-Ethenediyl)bis(3-phenyl-2,1-benzisoxazole) (8). A solution of 4.0 g (16 mmol) of **7** and 5.8 g (22 mmol) of recrystallized triphenylphosphine in 100 mL of xylene was heated to reflux for 16 h. After cooling, the precipitate was collected by suction filtration, washed with xylene, and dried in vacuo to give 6.6 g (79%) of the phosphonium chloride, which was used without further purification.

A 0.2 M ethanolic lithium ethoxide solution (0.102 g, 13.6 mmol of Li wire in 68 mL of absolute ethanol) was added dropwise to a slurry of 6.57 g (13.0 mmol) of the phosphonium chloride and 3.10 g (13.9 mmol) of **6** in 38 mL of absolute ethanol. After stirring for 1.5 h, 71 mL of water was added to quench the reaction and make a 60% aqueous ethanol solution, which triphenylphosphine oxide is soluble in. The precipitated product was collected by suction filtration, washed with 60% aqueous ethanol, and dried in vacuo to give 5.35 g (99%) of **8**: mp 184.0–186.0 °C; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.77–7.52 (m, 16 H), 6.74 (s, 2 H). Anal. Calcd for $C_{28}H_{18}N_2O_2$: C, 81.14; H, 4.38; N, 6.76. Found: C, 81.00; H, 4.43; N, 6.76.

Attempted Synthesis of 4,4′-Diamino-3,3′-dibenzoylstilbene. (a) Iron(0)/Acetic Acid Method.[34] To a mechanically stirred solution of 1.0 g (2.4 mmol) of **8** in 12.6 mL of glacial acetic acid at 95 °C was added 1.88 g (33.6 mmol) of iron(0) powder and 4 mL of water in four portions over 2.5 h. After cooling, the iron salts were removed by filtration and the filtrate was extracted with methylene chloride. The organic extracts were combined and neutralized with saturated sodium bicarbonate solution. The organic layer was separated and dried ($MgSO_4$). The solvent was removed and purification by radial spinning chromatography was attempted. However, none of the desired product was observed.

(b) Hydrazine Hydrate Method.[35] A solution of 0.25 g (0.60 mmol) of **8** and 0.12 mL (2.4 mmol) of hydrazine hydrate in 12 mL of 2-methoxyethanol was stirred under argon at 90 °C for 47 h. At this point, starting material was still evident by TLC (silica gel, 5% ethyl acetate/95% methylene chloride) so an additional 0.46 mL (9.6 mmol) of hydrazine hydrate was added. After 3 h, no starting material was left and only a complex mixture of products was evident.

5-Bromo-2-(trifluoroacetamido)benzophenone (11). To a solution of 10 g (0.036 mol) of 2-amino-5-bromobenzophenone[18] in 360 mL of freshly distilled (Na/benzophenone) diethyl ether was added 37.6 g (0.226 mol) of anhydrous sodium carbonate. The reaction mixture was cooled in an ice bath, and 25.6 mL (0.181 mol) of freshly distilled trifluoroacetic anhydride was added dropwise as rapidly as possible while maintaining a gentle reflux. Upon completion of the addition, the ice bath was removed and the reaction mixture stirred for 20 min. The reaction mixture was separated between 500 mL of methylene chloride and 500 mL of water. After removal of the aqueous layer, the organic layer was washed again with water and dried ($MgSO_4$). Removal of the solvent gave 12.8 g (95%) of **11**: mp 136–138 °C; IR (Nujol) 1725, 1640 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 8.53 (m, 1 H), 7.79–7.49 (m, 8 H); mass spectrum, m/z (relative intensity) 373.1 (14.3, $C_{15}H_9{}^{81}BrF_3NO_2$), 371.1 (14.5, $C_{15}H_9{}^{79}BrF_3NO_2$), 105.1 (61.9, C_6H_5CO). Anal. Calcd for $C_{15}H_9BrF_3NO_2$: C, 48.41; H, 2.44; N, 3.76. Found: C, 48.53; H, 2.61; N, 3.71.

4,4′-Bis(trifluoroacetamido)-3,3′-dibenzoylstilbene (15). A solution of 12.0 g (32.2 mmol) of **11** in 60 mL of freshly distilled (CaH_2) deoxygenated toluene was added to a solution of 0.74 g (0.64 mmol, 2 mol %) of tetrakis(triphenylphosphine)palladium(0)[36] in 50 mL of toluene under argon, and this mixture was heated to reflux. To this mixture was added dropwise over 1 h a solution of 9.8 g (16.1 mmol) of (*E*)-1,2-bis(tri-*n*-butylstannyl)ethylene[19] in 50 mL of toluene. After heating for an additional 4 h, the

reaction was cooled and the product isolated by suction filtration. After washing with hexane to remove most of the tri-*n*-butyltin bromide, the product was dried at 110 °C at 0.05 mmHg to give 7.66 g (78%) of **15**: mp 281–283 °C; IR (Nujol) 1725, 1630 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 8.64 (d, 2 H, J = 8.6 Hz), 7.82–7.51 (m, 16 H), 6.95 (s, 2 H); mass spectrum, m/z (relative intensity) 610.4 (29.3, M^+). Anal. Calcd for $C_{32}H_{20}F_6N_2O_4$: C, 62.96; H, 3.30; N, 4.59. Found: C, 63.09; H, 3.39; N, 4.40.

4,4′-Diamino-3,3′-dibenzoylstilbene (3). A mixture of 7.00 g (11.5 mmol) of **15** and 9.5 g (58 mmol) of anhydrous sodium carbonate in 180 mL of ethanol and 40 mL of water was heated to reflux for 6 days. After cooling, the solids were isolated by suction filtration and then stirred in 150 mL of water to dissolve any remaining sodium carbonate. After filtration and drying, the slightly impure product was continuously extracted for 6 days with 10% triethylamine/ethanol until all of the product had dissolved and recrystallized in the pot. Filtration and drying yielded 4.0 g (83%) of **3**, which was shown to be pure by HPLC (70% acetonitrile/30% water, 1.5 mL/min, t_r 7.00 min): mp 272–273 °C; IR (Nujol) 3480, 3350, 1630 cm^{-1}; UV max (CH_2Cl_2) 340 (2.3×10^4), 253 (2.3×10^4) nm; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.66 (m, 4 H), 7.48 (m, 12 H), 6.71 (d, 2 H, J = 8.4 Hz), 6.64 (s, 2 H), 6.12 (br s, 4 H); ^{13}C NMR (Me_2SO-d_6, 68 MHz) δ 197.56, 150.86, 139.72, 131.99, 130.90, 130.78, 128.52, 128.14, 124.16, 123.94, 117.36, 116.14; mass spectrum, m/z (relative intensity) 418.1 (100, M^+), 105.1 (75.4, C_6H_5CO). Anal. Calcd for $C_{28}H_{22}N_2O_2$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.61; H, 5.33; N, 6.77.

General Polymerization Procedure. A solution of 1.363 mmol of the bis(amino ketone) monomer and 1.363 mmol of the bis(ketomethylene) monomer in 3.9 g (36 mmol) of *m*-cresol and 10 g (36 mmol) of di-*m*-cresyl phosphate was placed in a resin kettle fitted with a mechanical stirrer and two gas inlets. With stirring, the reaction mixture was purged with argon for 20 min. The reaction mixture was heated to 140 °C for 48 h under a positive pressure of argon. If the polymerization dope became too viscous, it was diluted with *m*-cresol. After cooling, the polymerization dope was slowly poured into a stirred solution of 250 mL of ethanol and 25 mL of triethylamine. The precipitated polymer was then chopped up in a Waring blender and collected by suction filtration. The polymer was continously extracted for 24 h with a 10% triethylamine/ethanol solution and then dried in vacuo.

Fabrication of Films. Films were prepared from a solution of 20 mg of the appropriate polymer in 2 g of a di-*m*-cresyl phosphate/*m*-cresol solution. For **16** and **20**, the solvent was a 3.2% (w/w) solution of di-*m*-cresyl phosphate in *m*-cresol. The polymer solution was poured into a rectangular (2.5 cm × 7.5 cm) trough bordered by four microscope slides on a glass plate. Most of the *m*-cresol was evaporated by placing the glass plate on a hot plate warmed to about 50 °C for 18 h. The final traces of *m*-cresol were removed by placing the glass plate in a vacuum oven at 100 °C for 6 h. The glass plate was then placed in a 10% triethylamine/ethanol solution to remove most of the di-*m*-cresyl phosphate. The film was removed from the plate and continuously extracted for 24 h with 10% triethylamine/ethanol solution. The film was air-dried while clamped to a microscope slide to prevent curling.

Determination of UV–Vis Spectra. Spectra were taken of 1×10^{-5} M solutions in HPLC grade, spectral grade methylene chloride in 1-cm path length quartz UV cells. To accomplish the *E* to *Z* isomerization of **1**, the UV cell containing the sample solution was placed in a Rayonet photochemical reactor and irradiated with 300- and 350-nm wavelength lamps for 1 h.

Dilute Polymer Solution Properties. The viscosity measurements were made with a Cannon-Ubbelohde semimicro type viscometer, No. 200, at 25 ± 0.1 °C. The solvent was a 0.1 mol % di-*m*-cresyl phosphate/*m*-cresol solution, and the solution concentration ranged from 0.100 to 0.050 g/dL. The intrinsic viscosity was determined by the intersection of the plots of $[\eta]_{inh}$ and $[\eta]_{red}$ vs. concentration.

The photoviscosity measurements were obtained as described above. To irradiate the solution, the viscometer containing the polymer solution was placed in a Rayonet photochemical reactor containing 300- and 350-nm lamps, initially for 45 min and after each subsequent dilution for 15 min. These time intervals were more than that necessary to reach a steady viscosity.

Solution Anisotropy. To 1.0 g of a 20 mol % solution of di-*m*-cresyl phosphate in *m*-cresol was added 0.10 g of **17**, and this mixture was heated to 140 °C for 24 h to dissolve the polymer. A small amount of solution was placed on a microscope slide and then spread into a thin film with a cover glass.

Bulk Polymer Properties. The T_g and T_m of the polymers were determined by differential scanning calorimetry on a pressed powder sample. The thermogravimetric analysis of polymer **18** was also determined on a pressed powder sample. The pressed powder samples were prepared by compressing 65 mg of polymer in a KBr press.

The photomechanical effect was determined by using film samples which were fabricated as described above. The film, which was about 4 mm × 2.5 mm × 0.015 mm, was held by clamps, which were hung on the hooks of the tension probe. After the clamps were attached, the film exposed between the clamps was measured precisely with a micrometer and calipers. The film was placed under tension by placing an 8-g mass on the weight tray of the TMA apparatus. After the furnace was positioned around the sample and the instrument was adjusted, the sample was irradiated at room temperature. The heat generated by the UV lamp usually caused the sample to heat to about 75 °C. After the contraction of the film ceased, the lamp was turned off, and the sample was heated to about 50 °C above T_g. The lamp was turned back on after the temperature had stabilized to record the contraction in the rubbery state. The contraction of the film was plotted by the recorder in mils ($^1/_{1000}$ in).

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Polymerization Properties of Amphiphilic Diacetylene Pyridinium and Bipyridinium Salts in the Crystalline State, in Multilayers, and in Aqueous Dispersions

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ABSTRACT: Surface-active *N*-alkylpyridinium salts and *N,N'*-dialkyl-4,4'-bipyridinium salts were synthesized carrying long aliphatic chains with a diacetylene unit in the midchain position. All compounds polymerized in the solid state, when exposed to UV and γ-irradiation. In the case of the *N*-alkylpyridinium salts a complete conversion to polymer was obtained. X-ray structure studies revealed a head–head–tail–tail arrangement of the amphiphiles. During polymerization the structure was completely retained. Some of the *N*-alkylpyridinium salts formed polymers, which were soluble in a 1:1 mixture of chloroform and methanol. Monomeric crystals of the bipyridinium salts showed solid-to-solid and solid-to-liquid crystalline phase transitions, which disappeared upon the polymerization process. Monolayers of the amphiphiles at the air–water interface were of low stability and could be transferred onto substrates only in mixtures with cadmium arachidate. UV irradiation of the mixed multilayers caused a solid-state polymerization of the diacetylene amphiphiles on the substrate. Aqueous suspensions of the monomeric *N*-alkylpyridinium salts turned into clear, micellar solutions at temperatures above 46.5 °C. Sonication of aqueous dispersions resulted in the formation of translucent, slightly opaque solutions in which the amphiphiles formed spherical aggregates of diameters between 100 and 250 nm. Micellar solutions as well as dispersions of the spherical aggregates were completely photoinactive in UV light. However, the spherical aggregates rapidly rearranged into thin particles of oval or polygonal shape of more than 1 μm in diameter (multilamellar layers), which were highly photoreactive. The polymerized amphiphile dispersions neither disintegrated into micelles at elevated temperature nor precipitated within several weeks.

Introduction

In recent years it has been demonstrated that the UV-initiated solid-state polymerization of diacetylene derivatives[1,2] can also be applied to lipid bilayer-type structures. Amphiphilic molecules with diyne units in the aliphatic chains are photoreactive in monomolecular layers, Langmuir–Blodgett (LB) type multilayers, and liposomes,[3-8] provided that the molecules form a condensed phase with a crystal-like arrangement in small domains. Average domain sizes are in the range 10^{-2}–10^{2} μm in diameter.[5,9,10]

Previous studies mainly dealt with the photopolymerization of long-chain fatty acids,[9,11] their cadmium salts,[3-5,9,10] phospholipids,[6-8] and lipid analogues.[12] Polymerization properties of cationic amphiphiles, however, have been studied much less in detail.

Cationic amphiphiles with pyridine and bipyridine units as polar headgroups, for example, are of interest because of their ability to form a variety of salts and metal complexes, acting as carriers able to incorporate photochemically and photophysically active moieties in lipid bilayer-type structures. Corresponding amphiphiles with 4,4'-bipyridine units as polar headgroups are excellently suited as mediators in the photochemically induced generation of hydrogen from water, acting as functional electron relays.[13,14]

Further, *N*-alkylpyridinium salts easily form micellar aggregates in aqueous solution[15] and are adsorbed by inorganic materials.[16] Polymerization of thin layers or bilayer type aggregates of these compounds should stabilize the corresponding structures. A novel type of ultrathin stable devices with potential biophysical applications would thus become accessible.

In a previous study, the polymerization properties of pyridine amphiphiles carrying the hydrophobic tail at the 4-position, e.g., 4-(((*n*-pentacosa-10,12-diynyl)oxy)-carbonyl)pyridine, and some of its salt and metal complex derivatives, have been reported.[17] This study describes the polymerization properties of *N*-alkylpyridinium salts and analogous *N,N'*-dialkyl-4,4'-bipyridinium salts, so-called viologenes, both containing diyne units in their aliphatic chains. Besides the polymerization in the crystalline state, attempts to polymerize these compounds in less ordered systems such as Langmuir–Blodgett multilayers, vesicles, or micelles will be reported.

The amphiphile structures are shown together with abbreviations.

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