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Design and Synthesis of New Thermally Reversible Photoresponsive Polymers

James F. Cameron and Jean M. J. Fréchet*

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

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ABSTRACT: A novel photoresponsive polymer system involving the photocyclization of pendant 2,4,6-triisopropylbenzophenone groups into the corresponding benzocyclobutenols was investigated as a potential imaging material. Two monomers containing the photoactive 2,4,6-triisopropylbenzophenone moiety were prepared and their polymerizabilities investigated: A vinyl ether type monomer did not polymerize well either cationically or radically, though a copolymer with maleic anhydride could be obtained. A styrenic monomer containing 2,4,6-triisopropylbenzophenone pendant groups was also successfully copolymerized with styrene. In this way, new photoresponsive polymers that function both in solution and in the solid state were synthesized. Interestingly, the photoproducts, benzocyclobutenol-functionalized polymers, were found to be thermally sensitive such that the Norrish type II photocyclization was reversed on heating the styrene copolymers. The combination of photocyclization and thermal ring opening was found to constitute a reproducible process for polymer interconversion.

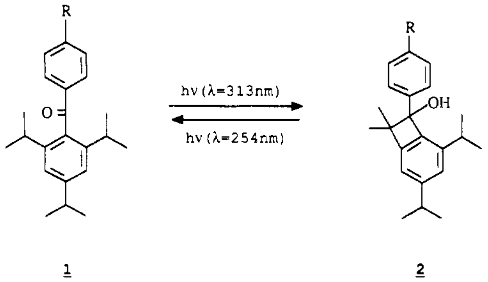
Introduction

The use of devices that function by way of photoresponsive polymers is becoming increasingly common. For instance, the microelectronic industry makes use of photoresists to image the required circuit pattern. These polymers function by the action of light, which causes a fundamental change in the structure either of the polymer or of an additive blended with it. This process allows imagewise development by selective differentiation[1] of the exposed and unexposed areas. Similarly, polymers that undergo a reversible photochemical reaction leading to a color change may be used as photochromic devices.[2] In such systems, the radiation causes a structural modification that manifests itself as a change in optical density; areas within the polymer that were originally opaque now become optical holes and vice versa.[3] Such photoresponsive polymer systems have significant potential as media for optical data storage.

Reactions that involve a photopromoted ring closure or ring opening are particularly attractive to create a suitable change in optical density or refractive index. However, for such reactions to be of any utility in imaging science, they must be capable of occurring in the solid state. This latter requirement can be easily fulfilled thanks to the pioneering work of Schmidt in developing the concept of solid-state topochemistry.[4] By using this concept, several photochemical reactions that are known to proceed efficiently in solution have been predicted, and subsequently proven, to proceed just as efficiently (or even more so) in the solid state.[4,5] For instance, some photochemical reactions that proceed by way of proton abstraction, such as the Norrish type II process, have been found to proceed in the solid state.[6] One such favorable case is the photocyclization (Scheme I) of some *p*-methyl- or *p*-methoxy-substituted 2,4,6-triisopropylbenzophenones **1** into the corresponding benzocyclobutenols **2**. It must be noted, however, that numerous other types of photochemical reactions are less effective in the solid state than they are in solution.

The photocyclization of **1** has been studied extensively in solution by Ito et al.,[7] but the solid-state photoreactivity was uncovered only recently.[8] Of particular note are the comparable quantum yields (Φ_{cb}) obtained[8] for the formation of some benzocyclobutenols **2** from **1** (R = OCH_3 or CH_3) both in the solid state and in solution (Table I). This observation led us to investigate polymers containing pendant photoactive 2,4,6-triisopropylbenzophenone moieties as potentially reversible photoresponsive polymeric information storage media.

Scheme I



Synthesis and Characterization

In order to create an efficient photoresponsive system based on the chemistry of 2,4,6-triisopropylbenzophenones **1**, it seemed appropriate to utilize a polymerizable ether function as a replacement for the methoxy group of **1a**, which offers the highest quantum yield of all models studied.[8] Therefore, the novel vinyl ether **3** was prepared in good yield via the facile three-step procedure outlined in Scheme II. In the first step, Friedel–Crafts reaction of 1,3,5-triisopropylbenzene with anisoyl chloride provided access to the necessary photoactive 2,4,6-triisopropylbenzophenone moiety. In the next step, removal of the 4′-methoxy substituent by reaction with hydriodic acid in acetic acid released the phenolic function. Finally, the substituted phenol[9] was transformed in one step and 84% was yielded into the desired vinyl ether **3** by treatment with divinylmercury[10] in toluene.

With this novel monomer **3** in hand, an investigation of its polymerizability was undertaken; aryl vinyl ethers are routinely polymerized cationically;[11,12] hence, it seemed appropriate to polymerize **3** in this manner. However, standard inert-atmosphere conditions employing dichloromethane as solvent and boron trifluoride etherate as Lewis acid at −20 to −78 °C failed to produce any high polymer from **3**. This repeated lack of success on attempted cationic polymerization of **3** is not overly

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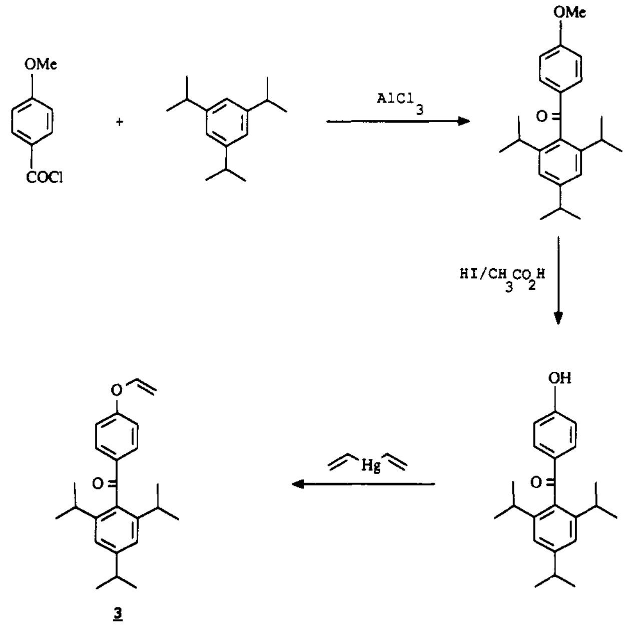
Table I
Quantum Yields[a] for the Formation of Benzocyclobutenols 2 from Benzophenones 1

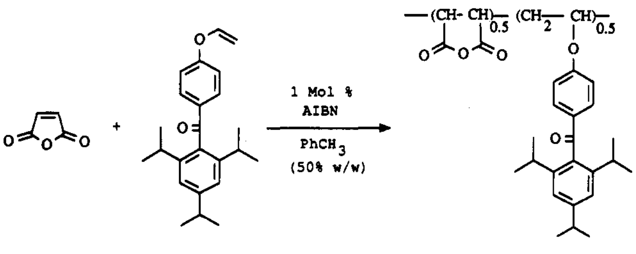
R	Φ_{cb}(solid)	Φ_{cb}(solution)
(a) OMe	0.56	0.48
(b) Me	0.48	0.42
(c) ᵗBu	0.20	0.38
(d) H	0.13	0.52
(e) Cl	0.072	0.51
(f) CF_3	0.011	0.30
(g) CO_2Me	0.001	0.13

[a] All quantum yields are taken from Ito et al.[8]

Scheme II



Scheme III



surprising as the para electron-withdrawing keto group can destabilize the intermediate vinyl ether cation to such an extent that cationic polymerization is disfavored. As was expected, attempted homopolymerization of **3** by radical means failed to give any recoverable polymer. In order to overcome this problem, it seemed possible to make use of the well-known alternating mode of radical copolymerization between an electron-rich and an electron-poor monomer.[13,14] Therefore, maleic anhydride was selected as the reactant of choice as it is reported[13] to form alternating copolymers with assorted electron-rich monomers. Free-radical initiation of a mixture of vinyl ether **3** with maleic anhydride afforded alternating copolymers **4** (Scheme III). The experimental data on two of these novel compounds **4a** and **4b**, which differ only in their GPC characteristics, are presented in Table II. As expected, **4a** and **4b** are 1:1 copolymers, in accordance with the reactivity ratios for such systems.[12] The degree of incorporation of the photoactive unit in the polymer is somewhat high at 50%, but this is unfortunately dictated by the mode of polymerization and variations from this 1:1 composition are not readily obtained. A consequence of such a high degree of functionalization is that irradiation may lead to the occurrence of intermolecular photoreactions or produces a cross-linked product rather than the preferred intramolecular process that affords a rearranged material.

In order to circumvent this problem and obtain materials of controlled composition, the preparation of 4′-(ethenylphenyl)-2,4,6-triisopropylbenzophenone (**5**) was investigated. Though this was expected to result in a lowering of the photoefficiency of the photocyclization due to substituent electronic effects (Table I),[8] it was anticipated that the ease of synthesis and of subsequent polymerization of the conventional styrene type monomer **5** would far outweigh this disadvantage. Indeed, the desired styrenic monomer **5** was easily obtained in fair yield by reaction of *p*-vinylbenzoyl chloride with the hindered 2,4,6-triisopropylphenylmagnesium bromide in dry THF (Scheme IV). Interestingly, the Grignard coupling reaction used to prepare **5** also furnished the novel 2,2,4-trisubstituted oxetane **6**. Vinyl monomer **5** was readily copolymerized with styrene to give copolymers **7** (Scheme V). Experimental data on these copolymerization reactions to give **7a** and **7b** containing, respectively, 5 and 2 mol % of monomer **5** are presented in Table III. The low concentration of photoactive unit incorporated in the copolymers is desirable to minimize the possibility of cross-linking via intermolecular photoreaction. Such a low incorporation of photoactive groups is currently impossible using the vinyl ether monomer **3**. Furthermore, the copolymerization of **5** with styrene gave copolymers in which the photocyclization could be monitored readily by infrared spectroscopy, while the polymers also possess suitable characteristics for spin coating. The molecular weights of the polymers were kept relatively low to allow for ease of spin coating in subsequent solid-state applications.

Photochemistry

General Procedures. The 2,4,6-triisopropylbenzophenone chromophore absorbs strongly at 260 nm and weakly at 345 nm. Therefore, irradiation with a mercury lamp should be sufficient to effect the desired transformation in solution. In the solid state, a Pyrex filter was deemed necessary to avoid the retroreaction that is reported to proceed on irradiation at 254 nm.[15]

(a) In Solution. Irradiation of a benzene solution of copolymer **7a** with a 450-W medium-pressure mercury lamp for 24 h resulted in quantitative photocyclization to give the benzocyclobutenol-functionalized polymer **8a** (Scheme VI).

The structural changes caused by this Norrish type II process was confirmed spectroscopically: ^1H NMR spectroscopy shows the disruption of the symmetry of the 2,4,6-triisopropylbenzene ring as photocyclization results in the loss of the 1:2 ratio of the isopropyl methine resonances at δ 2.54 and 2.91, respectively (Figure 1). ^{13}C NMR spectroscopy confirms that the ring closure has occurred by the obvious loss of the carbonyl resonance at δ 201.70 with concomitant appearance of aliphatic cyclobutenol resonances at δ 86.10 and 54.38 after photolysis (Figure 2). Infrared spectroscopy shows the loss of the carbonyl stretch at 1667 cm^{-1} after photolysis, thus providing further support for the occurrence of photocyclization (Figure 3).

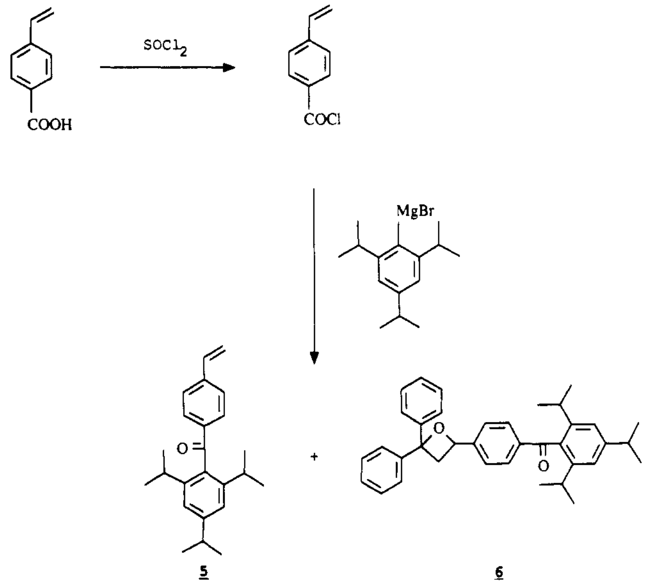
The photocyclized polymers **8a** and **8b** derived from **7a** and **7b**, respectively, remain highly soluble in standard organic solvents. This finding suggests that the photoreduction proceeds largely intramolecularly rather than intermolecularly and is in agreement with the Norrish type

Table II
Copolymers of Maleic Anhydride and 3 before and after Irradiation

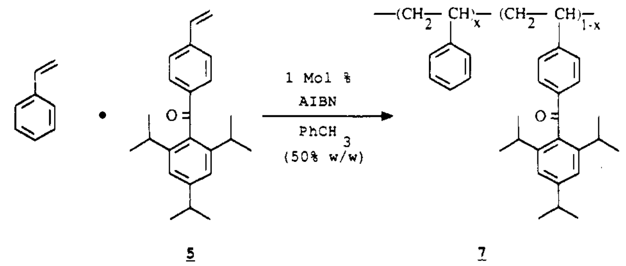
	monomer feed, g (mmol)		polymer				GPC data		
					% convn				
copolymer[a]	MA	3	wt, g	ratio[b] MA/3	MA	3	M_w	M_n	M_w/M_n
4a	0.25 (2.54)	0.89 (2.54)	0.690	52/48	64	60	20 000	9600	2.08
4b	0.13 (1.28)	0.45 (1.28)	0.349	52/48	65	60	12 000	6400	1.95
9				50/50			143 200	31800	4.50

[a] Polymers **4a** and **4b** were obtained by copolymerization of **3** with maleic anhydride (Scheme III). Polymer **9** is obtained by photolysis of **4a**. [b] Polymer composition was determined by using ^{1}H NMR integration.

Scheme IV



Scheme V



II pathway proposed for this photocyclization. This was also confirmed by gel permeation chromatography (GPC) data (Table III), through which no evidence for significant branching or cross-linking was found. The observed changes in the GPC data may reflect the changes in hydrodynamic volume on going from polymers of structure 7 to rearranged products having structure 8.

On the other hand, similar photolysis of copolymer **4a** resulted in quantitative isolation of a polymer that has greatly reduced solubility and shows unexpected spectral properties. Infrared spectroscopy shows the benzophenone type carbonyl stretch at 1667 cm^{-1} to be missing from this material. This is consistent with the photocyclization to structure **9** (Scheme VII) having taken place, but the presence of a new carbonyl absorption at 1740 cm^{-1} was unexpected. This new absorption is accompanied by a weakening of the characteristic asymmetric and symmetric carbonyl stretching bands at 1862 and 1785 cm^{-1}, respectively, for the pseudo succinic anhydride moiety (Figure 4), suggesting that the anhydride groups may be modified. As was the case in the conversion of copolymers 7 to 8 (Scheme VI), ^{1}H NMR spectroscopic analysis of both polymer **4a** and its solution photolysate product shows the characteristic disruption of the symmetry of the 2,4,6-triisopropylbenzophenone ring due to photocyclization, which results in the loss of the 1:2 ratio of the isopropyl methine resonances. Furthermore, ^{13}C NMR spectroscopy revealed the loss of the benzophenone carbonyl resonance at δ 199.94.

On the basis of this evidence, it seems that photocyclization of the triisopropylbenzophenone units of **4a** has occurred but that the photoproduct **9** undergoes some further reaction. A possible explanation for this is cross-esterification of the newly formed benzocyclobutenol with the pseudo succinic anhydride moieties to give a product containing ester branches. This is consistent with the observed infrared spectroscopic data and is further supported by the GPC data, which show very large molecular weight values and also a very high polydispersity index, suggesting that some branching had occurred (Table II). This is also in agreement with the observation that the isolated polymer had greatly reduced solubility in comparison to the starting polymer.

(b) In the Solid State. Thin films of copolymers 7 were cast onto sodium chloride disks and exposed to UV light through Pyrex glass in air until the carbonyl stretch at 1667 cm^{-1} disappeared as monitored by infrared spectroscopy. As shown in Figure 5, the conversion of **7a** into **8a** required about 15 min of exposure with a power output of 3.73 mW/cm^2.

The vinyl ether–maleic anhydride copolymer **4a** was similarly exposed in the solid state and was found to undergo clean photocyclization to **9** as witnessed by the disappearance of the carbonyl stretch at 1667 cm^{-1} over a period of 20 min of irradiation (Figure 6). In this instance, no additional carbonyl absorption due to side reactions during photolysis was observed.

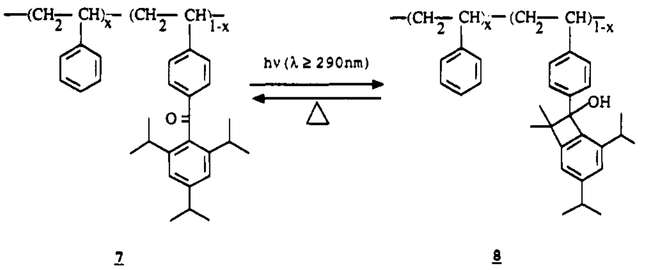
Having proven that the forward cyclization reaction utilizing light of wavelength >290 nm works well for both systems in the solid state, the reported photoreversal of the reaction using 254-nm light was investigated.[15] Exposure of thin films of the benzocyclobutenol polymer **8a** to UV light obtained by using a 254-nm narrow-band-pass filter for 30 min at a power output of 0.27 mW/cm^2 failed to ring open **8a** as confirmed by infrared spectroscopy. A possible explanation for this apparent anomaly is that the strong UV absorption due to the large styrene content in **8a** masks the UV absorption of the benzocyclobutenol chromophore. If this were the case, then the photocyclized vinyl ether–maleic anhydride copolymer **9** should undergo facile photoreversal to **4a** as the benzocyclobutenol chromophore is unmasked by other absorptions. However, subsequent photolysis of thin films of copolymer **9** at 254 nm failed to regenerate the original benzophenone moiety but rather caused the appearance of the same carbonyl absorption at 1740 cm^{-1} as witnessed in the solution photolysis of copolymer **4a**. Thus it seems that copolymer system 4 is unstable to deep UV irradiation in both the solid state and in solution as it undergoes facile photobranching perhaps through esterification of the benzo-

Table III
Data on Copolymers of Styrene and 5 before and after Irradiation

	monomer feed, g (mmol)		polymer				GPC data			
					% convn					
copolymer[a]	Sty	5	wt, g	ratio[b] Sty/5	Sty	5	M_w	M_n	M_w/M_n	T_g, °C
7a	4.69 (45)	0.50 (1.5)	2.89	95/5	53	84	33 000	20 200	1.68	106
7b	14.06 (135)	0.50 (1.5)	7.92	98/2	53	98	24 600	14 600	1.68	102
8a				95/5			43 800	25 100	1.74	112
8b				98/2			20 300	10 400	1.95	103

[a] Polymers **7a** and **7b** are obtained by copolymerization of **5** with styrene (Scheme V). Polymers **8a** and **8b** are obtained by photolysis of **7a** and **7b**, respectively. [b] Polymer composition was determined by using ^{1}H NMR integration.

Scheme VI



cyclobutenol moieties with the anhydride units of the copolymer.

Thermochemistry

A differential scanning calorimetry (DSC) study of the photocyclized polymer **8a** revealed that the photochemical cyclization is thermally reversible. This agrees with the literature reports[7] on low molecular weight benzocyclobutenols **2**. The starting polymer **7a** has a glass transition temperature (T_g) of 106 °C and exhibits no other thermochemical events until decomposition (about 350 °C). On the other hand, the photocyclized polymer **8a** has a T_g of 112 °C but also exhibits an exotherm at 150–250 °C before decomposition (350 °C). Heating samples of polymer **8a** beyond this exotherm causes reversal of the photocyclization; DSC shows the reversion of the polymer T_g back to that of the ring-opened polymer **7a** (T_g = 106 °C) while infrared spectroscopy shows the return of the carbonyl stretch at 1667 cm^{-1}, which is indicative of the retroreaction having taken place. Due to the low concentration of the photoactive moiety in copolymer **7b**, no significant change in the T_g was observed during studies on this copolymer but the thermal ring-opening reaction could be successfully followed by infrared spectroscopy.

A similar DSC study of the vinyl ether–maleic anhydride copolymer system revealed no such thermal reversion of the photocyclized material was available, but instead both starting polymer **4a** and photocyclized material **9** were rather unstable to successive heating and cooling DSC cycles. This was confirmed by infrared spectroscopy, which showed a new carbonyl stretching frequency at 1740 cm^{-1} arose on heating. Presumably, this is indicative of some degradative ring-opening reaction of the pseudo succinic anhydride groups.

Interconversion: Reproducibility and Repeatability

The processing sequences of photocyclization and thermal ring opening was studied in the solid state for the interconversion of copolymers **7a** and **8a**. A thin film of copolymer **7a** was sandwiched between two KBr disks and irradiated in air through Pyrex with a full UV lamp output of 3.73 mW/cm^2 until the carbonyl stretch at 1667 cm^{-1} disappeared. Once the photocyclization was complete, as indicated by infrared spectroscopy, the sample was heated in air on a hot stage at 180 °C to effect ring opening. The thermal reaction was followed by infrared spectroscopy until no further increase in the carbonyl stretch intensity at 1667 cm^{-1} was observed. This cycle was successfully performed for a total of three runs, during which the efficiency of each process slowly decreased, resulting in longer irradiation and heating times for completion of each run. Further runs resulted in deterioration of the polymer film such that distinguishing between the photocyclized and ring-opened polymer was no longer possible. At this stage the polymer film had acquired a yellow coloration

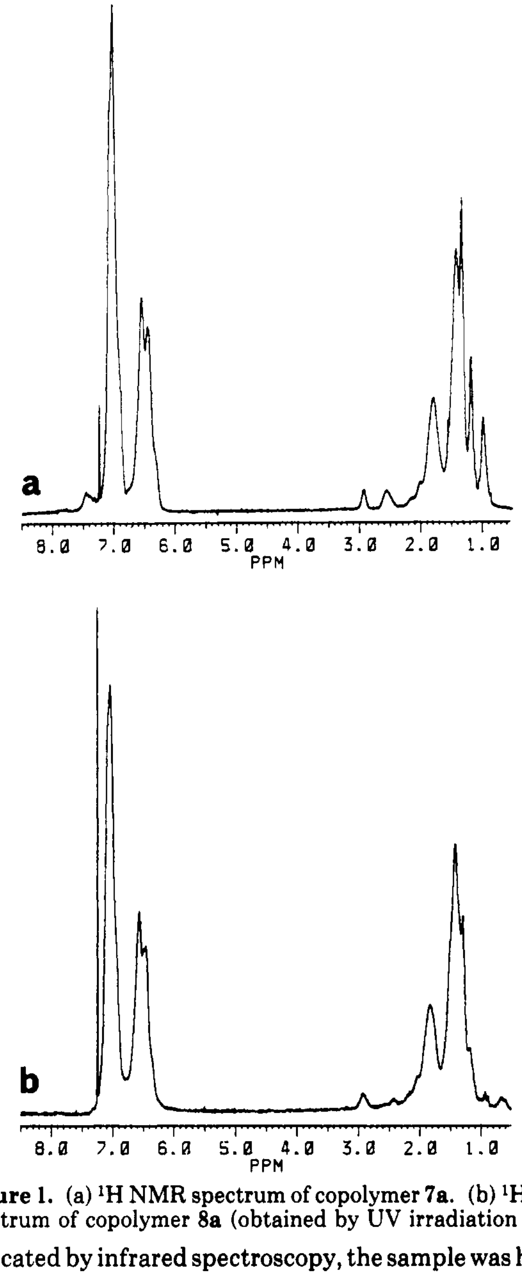


Figure 1. (a) ^{1}H NMR spectrum of copolymer **7a**. (b) ^{1}H NMR spectrum of copolymer **8a** (obtained by UV irradiation of **7a**).

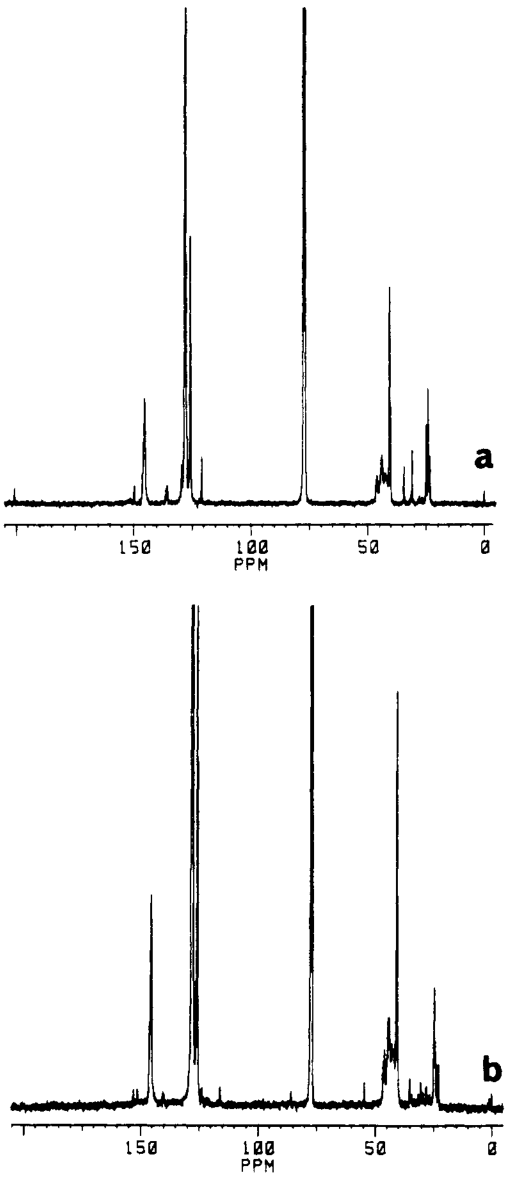


Figure 2. (a) ^{13}C NMR spectrum of copolymer **7a**. (b) ^{13}C NMR spectrum of copolymer **8a** (obtained by UV irradiation of **7a**).

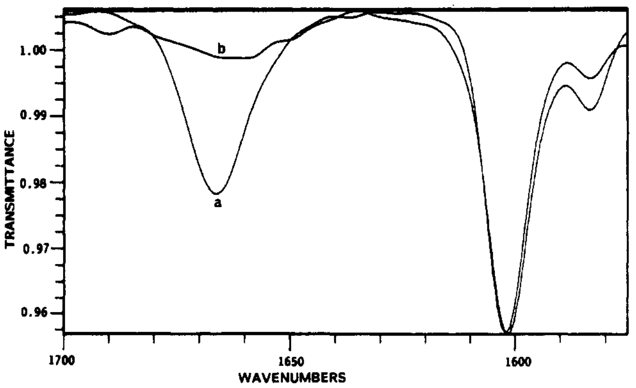


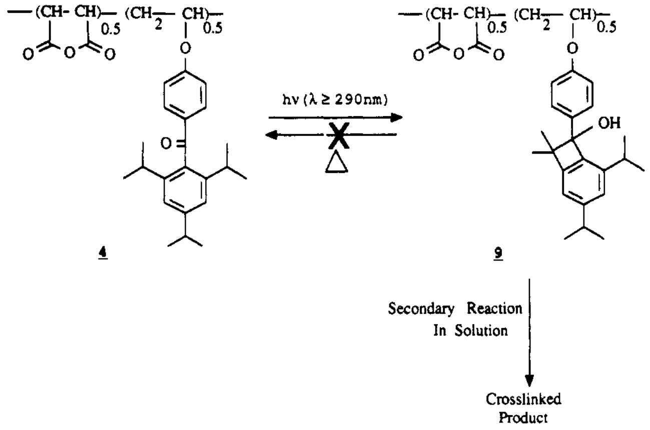
Figure 3. (a) IR spectrum of copolymer **7a**. (b) IR spectrum of copolymer **8a** (obtained by UV irradiation of **7a**).

presumably due to air oxidation or other photo or thermal processes during successive interconversions.

Conclusions

The Norrish type II photorearrangement of 2,4,6-triisopropylbenzophenones can be used to design novel photoresponsive polymeric media. In these systems, the photocyclization to polymers containing benzocyclobutenol side chains occurs quantitatively and may be reversed thermally but not photochemically. It may, however, be possible to design different systems[16] based on similar chemistry for which the photoreversal reaction may be possible. Though our work has focused on copolymers that only contain a low percentage of this triisopropylbenzophenone chromophore, it is possible to carry out the reaction with more concentrated materials. In the latter case intramolecular photocyclization is also accompanied by intermolecular processes, which result in cross-linking of the copolymers. We are currently designing novel materials incorporating similar but *photocatalyzed* processes for greater efficiency of new photoresponsive polymeric media.

Scheme VII



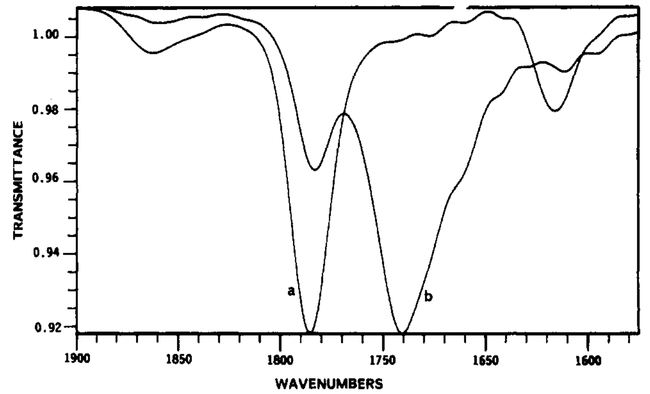


Figure 4. (a) IR spectrum of copolymer **4a** before irradiation. (b) IR spectrum of material obtained after solution photolysis of copolymer **4a**.

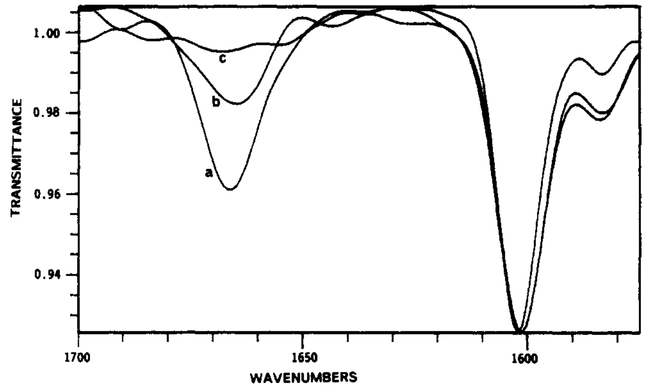


Figure 5. Change in the IR spectrum on conversion of copolymer **7a** to copolymer **8a** by UV irradiation. (a) Prior to irradiation. (b) After 8-min exposure. (c) After 15-min exposure.

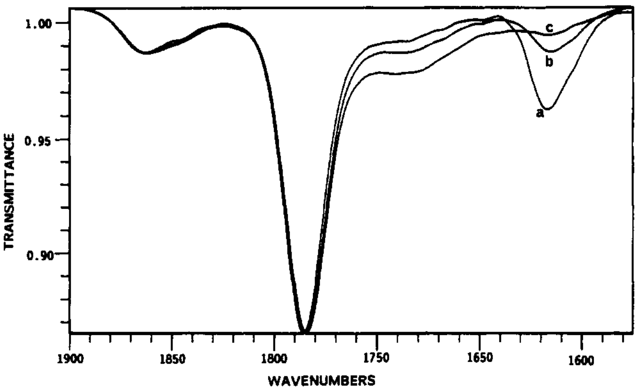


Figure 6. Change in the IR spectrum on conversion of copolymer **4a** to copolymer **9** by UV irradiation. (a) Prior to irradiation. (b) After 5-min exposure. (c) After 20-min exposure.

Experimental Section

General Procedures. Melting points were recorded on a Gallenkamp apparatus, and infrared spectra were obtained on a Nicolet FTIR/44 spectrometer. NMR spectra were recorded on a Bruker AF300 spectrometer using tetramethylsilane as internal standard. Mass spectra were obtained by using a Kratos MS980 high-resolution spectrometer. DSC was performed by using a Mettler DSC30 low-temperature cell. TGA was performed on a Mettler TG50 thermobalance. Both techniques used a heating rate of 10 °C/min. Molecular weights were determined by GPC on a Nicolet 9560 liquid chromatograph equipped with five Polymer Laboratories GPC columns using THF as the mobile phase and polystyrene calibration. Spin coating was performed by using a Headway Research spin-coater. Film thickness measurements were obtained on a Tencor α-step. Solid-state photolyses were performed by using an OAI exposure tool. Solution photolyses were performed in Ace Glass quartz glassware by using a Canrad-Hanovia 450-W mercury source. Solid-state thermochemistry was performed on a Bruker hot stage. Microanalyses were performed by MHW Laboratories, Phoenix, AZ.

Preparation of [4-(Ethenyloxy)phenyl][2,4,6-tris(1-methylethyl)phenyl]methanone (3). A solution of divinylmercury[10] (5.35 g, 21.73 mmol) in toluene (35 mL) containing 4′-hydroxy-2,4,6-triisopropylbenzophenone[9] (7.05 g, 21.73 mmol) was heated at reflux under nitrogen for 36 h. After cooling to room temperature, the solid mass was taken up in ether (100 mL) and filtered through a Celite pad to remove elemental mercury. The filtrate was then concentrated by removal of the solvent by distillation to give a solid residue (12.73 g), which was shown by thin-layer chromatography to be a two-component mixture. This mixture was separated by flash chromatography; the crude vinyl ether **3** was isolated as an off-white solid (6.15 g) by elution with 2.5% EtOAc/97.5% hexane. Recrystallization of this solid from hexane afforded the desired vinyl ether **3** as a white crystalline solid [4.96 g, 84% (based on unrecovered starting material)]; mp 92–94 °C.

IR (KBr): 1655 (s, C=O str), 1646 (s, C=C str), 1595 and 1582 (s, C–C str), 1248 and 1243 cm^{-1} (s, C–O str).

^1H NMR ($CDCl_3$): δ 1.07 [6 H, d (J = 7 Hz), $-CH(\mathit{CH}_3)_2$], 1.17 [6 H, d (J = 7 Hz), $-CH(\mathit{CH}_3)_2$], 1.28 [6 H, d (J = 7 Hz), $-CH(C\mathit{H}_3)_2$], 2.62 [2 H, septet (J = 7 Hz), 2 $C\mathit{H}Me_2$ ortho to COAr], 2.93 [1 H, septet (J = 7 Hz), $-C\mathit{H}Me_2$ para to COAr], 4.59 [1 H, dd (J_{cis} = 6 Hz, J_{gem} = 2 Hz), $ArOCH{=}CH\mathit{H}$], 4.92 [1 H, dd (J_{trans} = 14 Hz, J_{gem} = 2 Hz), $ArOCH{=}CH\mathit{H}$], 6.69 [1 H, dd (J_{trans} = 14 Hz, J_{cis} = 6 Hz), $ArO\mathit{CH}{=}CH_2$], 7.02 [2 H, d (J_0 = 8 Hz), 2 H ortho to $-OCH{=}CH_2$], 7.05 [2 H, s, 2 H ortho to $-CHMe_2$], 7.83 [2 H, d (J_0 = 8 Hz), 2 H meta to $-OCH{=}CH_2$].

^{13}C NMR ($CDCl_3$): δ 23.44 ($CH_3CH\mathit{CH}_3{}^b$ ortho to COAr), 24.02 ($CH(\mathit{CH}_3)_2$ para to COAr), 24.87 ($^a\mathit{CH}_3CHCH_3$ ortho to COAr), 30.99 ($C\mathit{H}Me_2$ ortho to COAr), 34.36 ($\mathit{CH}Me_2$ para to COAr), 97.76 ($ArOCH{=}\mathit{C}H_2$), 116.06 (C ortho to $OCH{=}CH_2$), 120.97 (C ortho to $CHMe_2$), 131.80 (C meta to $OCH{=}CH_2$), 133.29 (C para to $OCH{=}CH_2$), 135.04 (C ipso to COAr), 144.89 ($ArO\mathit{C}H{=}CH_2$), 146.38 (C ortho to COAr), 149.65 (C para to COAr), 160.81 (C ipso to $-OCH{=}CH_2$), 199.69 ($Ar\mathit{CO}Ar'$).

MS for $C_{24}H_{30}O_2$: calcd. M^+ = 350.505; found, M^+ = 350.226.

Further elution of the column with 25% EtOAc/75% hexane allowed recovery of some starting phenol as an off-white solid (1.59 g, 23%). This material had spectral data consistent with that reported earlier for this compound.[9]

General Procedure for Copolymerization of [4-(Ethenyloxy)phenyl][2,4,6-tris(1-methylethyl)phenyl]methanone (3) with Maleic Anhydride. A mixture of the two monomers as a 50% w/w solution in dry toluene containing 1.0 mol % AIBN under nitrogen was stirred at room temperature for 2 h and then heated at 70 °C for 24 h. After cooling to room temperature, the viscous solution was diluted with tetrahydrofuran and the polymer precipitated into hexane. The solid was collected by filtration and reprecipitated from tetrahydrofuran into hexane. The polymer **4** was filtered off and dried in vacuo at 50 °C to give a white powder.

Copolymers **4** prepared in this way had spectral characteristics consistent with their proposed structure. For instance, copolymer **4a** had the following spectral data.

IR (thin film): 1862 (w, asymm anhydride C=O str), 1785 (s, symm anhydride C=O str), 1667 (m, benzophenone C=O str), 1233 cm^{-1} (s, C–O str).

^1H NMR ($CDCl_3$): δ 0.60–1.40 (CH_2 of backbone), 1.04 [$-CH(\mathit{CH}_3)_2$], 1.10 [$-CH(\mathit{CH}_3)_2$], 1.75–4.45 (CH of backbone), 2.49 [2 $\mathit{CH}(CH_3)_2$ ortho to keto group], 2.91 [$CH(\mathit{CH}_3)_2$ para to keto group], 7.02 [ArH meta to keto group], 7.73 [ArH ortho to keto group].

Preparation of (4-Ethenylphenyl)[2,4,6-tris(1-methylethyl)phenyl]methanone (5) and Oxetane 6. To a suspension of dry, clean magnesium turnings (0.481 g, 19.8 mmol) in anhydrous tetrahydrofuran (10 mL) at room temperature under nitrogen was added a few drops of a solution of 1-bromo-2,4,6-triisopropylbenzene (5.353 g, 18.9 mmol) in dry tetrahydrofuran (15 mL). A crystal of iodine was then added to initiate formation of the Grignard reagent; subsequently, the remaining bromide solution was added at such a rate as to maintain a gentle reflux of the reaction mixture. After a further 1 h at reflux, the reaction mixture was cooled to 0 °C and added dropwise over 1 h to a solution of p-vinylbenzoyl chloride (2.998 g, 18.0 mmol)[17] in dry tetrahydrofuran (75 mL) containing cuprous iodide (3.599 g, 18.9 mmol) at −78 °C. The resulting mixture was allowed to warm up to room temperature overnight and then was heated at reflux for 4 h. After cooling, the reaction mixture was concentrated in vacuo and the residue taken up in ether (75 mL) and washed with saturated ammonium chloride (2 × 25 mL), water (2 × 25 mL), saturated sodium bicarbonate (2 × 25 mL), water (1 × 25 mL), amd brine (1 × 25 mL). The organic phase was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a yellow solid (6.40 g). Trituration with ether gave a white solid (0.992 g, 15%), which was identified spectroscopically as the novel 2,2,4-trisubstituted oxetane **6**: mp 159–161 °C.

Anal. Calcd for $C_{48}H_{60}O_2$ (668.96): C, 86.18; H, 9.04. Found: C, 86.03; H, 8.90.

IR (KBr): 1674 (s, C=O str), 1620 (w, C=C str), 1605 cm^{-1} (s, C–C str).

^1H NMR ($CDCl_3$): δ 0.89–1.30 [36 H, series of doublets, $-CH(\mathit{CH}_3)_2$], 2.50 [2 H, septet, $-\mathit{CH}(CH_3)_2$ ortho to carbonyl function], 2.59 [3 H, septet, $-\mathit{CH}(CH_3)_2$ groups of other triisopropylbenzene ring], 2.90 [1 H, septet, $-\mathit{CH}(CH_3)_2$ para to carbonyl function], 3.33–3.53 [2 H, complex m, oxetane CH_2], 4.62–4.73 [1 H, complex m, oxetane CH], 5.36 [1 H, d (J_{cis} = 11 Hz), $ArCH{=}CH\mathit{H}$], 5.81 [1 H, d (J_{trans} = 18 Hz), $ArCH{=}CH\mathit{H}$], 6.68 [1 H, dd (J_{trans} = 18 Hz, J_{cis} = 11 Hz), $Ar\mathit{CH}{=}CH_2$], 6.87 [2 H, s, triisopropylbenzene ring protons meta to oxetane ring], 7.01 [2 H, s, triisopropylbenzene ring protons meta to carbonyl group], 7.13 [2 H, d (J_0 = 8 Hz), 2 H ortho to oxetane ring], 7.37 [2 H, d (J_0 = 8 Hz), 2 H meta to COAr], 7.66 [2 H, d (J_0 = 8 Hz), 2 H ortho to oxetane ring], 7.79 [2 H, d (J_0 = 8 Hz), 2 H ortho to COAr].

The mother liquor was concentrated in vacuo to give an orange oil (5.84 g), which on flash chromatography (2% EtOAc/98% hexane) afforded the requisite pure monomer **5** as an off-white solid [1.673 g, 33% (based on starting material unaccounted for)]: mp 70–73 °C.

Anal. Calcd for $C_{24}H_{30}O$ (334.48): C, 86.18; H, 9.04. Found: C, 85.98; H, 8.89.

IR (KBr): 1667 (s, C═O str), 1620 (m, C═C str), 1604 cm^{-1} (s, C–C str).

^{1}H NMR ($CDCl_3$): δ 1.05 [6 H, d (J = 7 Hz), $-CH(CH_3)_2$], 1.16 [6 H, d (J = 7 Hz), $-CH(CH_3)_2$], 1.28 [6 H, d (J = 7 Hz), $-CH(CH_3)_2$], 2.61 [2 H, septet (J = 7 Hz), 2 $CH(CH_3)_2$ ortho to COAr], 2.94 [1 H, septet (J = 7 Hz), $CH(CH_3)_2$ para to –COAr], 5.40 [1 H, d (J_{cis} = 10 Hz) $ArCH{=}CHH$], 5.88 [1 H, d (J_{trans} = 18 Hz), $ArHC{=}CHH$], 6.76 [1 H, dd (J_{cis} = 10 Hz, J_{trans} = 18 Hz), $ArCH{=}CH_2$], 7.06 [2 H, s, 2 H meta to COAr], 7.47 [2 H, d (J_0 = 8 Hz), 2 H ortho to vinyl group], 7.80 [2 H, d (J_0 = 8 Hz), 2 H ortho to COAr].

^{13}C NMR ($CDCl_3$): δ 23.31 ($CH_3CHCH_3{}^b$ ortho to COAr), 23.92 [$-CH(CH_3)_2$ para to COAr], 24.78 ($^aCH_3CHCH_3$ ortho to COAr), 30.94 [$-CH(CH_3)_2$ ortho to COAr], 34.29 [$-CH(CH_3)_2$ para to COAr], 116.72 ($-CH{=}CH_2$), 120.88 [C ortho to $-CH(CH_3)_2$], 126.25 (C ortho to $-CH{=}CH_2$), 129.80 (C meta to $-CH{=}CH_2$), 135.09 ($-CH{=}CH_2$), 135.98 (C ipso to COAr), 137.47 (C para to $-CH{=}CH_2$), 142.32 (C ipso to $-CH{=}CH_2$), 144.93 (C ortho to COAr), 149.62 (C para to COAr), 200.40 (ArCOAr′).

General Procedure for Copolymerization of (4-Ethenylphenyl)[2,4,6-tris(1-methylethyl)phenyl]methanone (5) with Styrene. A mixture of two monomers as a 50% w/w solution in dry toluene containing 1.0 mol % AIBN under nitrogen was stirred at room temperature for 2 h and then heated at 70 °C for 8 h. After cooling to room temperature, the viscous solution was diluted with toluene and the polymer precipitated into methanol. The solid was collected by filtration and reprecipitated from dichloromethane into methanol. The polymer **7** was filtered off and dried in vacuo at 50 °C to give a white powder.

Copolymers **7** prepared in this way had spectral characteristics consistent with their proposed structure. For example, copolymer **7a** had the following spectral data.

IR (thin film): 1667 cm^{-1} (C═O str).

^{1}H NMR ($CDCl_3$): δ 0.97 [$-CH(CH_3)_2$], 1.18 [$-CH(CH_3)_2$], 1.31 [$-CH(CH_3)_2$], 1.39 (CH_2 of backbone), 1.78 (CH of backbone), 2.55 [2 $CH(CH_3)_2$ ortho to COAr], 2.91 [$CH(CH_3)_2$ para to COAr], 6.49 [ArH of styryl ring ortho to backbone], 6.99 [ArH of styryl ring meta and para to backbone and ArH of benzophenone system meta to keto function], 7.45 [ArH of benzophenone system ortho to keto group].

^{13}C NMR: see Figure 2a.

Other analytical data on these polymers are presented in Table III.

Solution Photolysis. (a) Solution Photocyclization of Copolymers 7. A solution of copolymer **7a** (0.578 g, 0.25 mmol keto moieties) in dry, degassed benzene (250 mL) was irradiated with a 450-W medium-pressure mercury lamp for 24 h. The photolysate was concentrated to a 10 mL volume and precipitated into methanol. The solid was collected and reprecipitated from dichloromethane into methanol. The resulting polymer **8a** was filtered off and dried in vacuo at 50 °C to give a slightly yellow powder (0.540 g, 93%).

IR (thin film): 3550–3300 cm^{-1} (vw, O–H str).

^{1}H NMR ($CDCl_3$): δ 0.60–2.20 [benzocyclobutenyl 2 CH_3 and OH and ortho $CH(CH_3)_2$], 1.25 [$CH(CH_3)_2$], 1.35 [$CH(CH_3)_2$], 1.45 (CH_2 of backbone), 1.85 (CH of backbone), 2.94 [para $-CH(CH_3)_2$], 6.50 (ArH of styryl ring ortho to backbone), 7.00 (ArH of styryl ring meta and para to backbone and ArH of benzocyclobutenol system).

^{13}C NMR: see Figure 2b.

Similar treatment of polymer **7b** gave the benzocyclobutenol functionalized polymer **8b** in 96% yield. GPC and T_g data on this polymer are presented in Table III.

(b) Solution Photocyclization of Copolymer 4a. A solution of copolymer **4a** (0.224 g, 1.00 mmol keto moieties) in dry degassed benzene (250 mL) was irradiated with a 450-W medium-pressure mercury lamp for 24 h. The photolysate was concentrated in vacuo; the residue was taken up in dichloromethane and precipitated into methanol. The resulting solid was collected and dried in vacuo for 48 h to give a yellow powder (0.205 g, 92%).

IR (thin film): 3600–3300 (w, O–H str), 1862 (w, asymm anhydride C═O str), 1785 (m, symm anhydride C═O str), 1740 (s, C═O str), 1233 cm^{-1} (s, C–O str).

^{1}H NMR ($CDCl_3$): δ 0.50–2.00 [CH_2 of backbone, CH_3 groups, ortho $-CH(CH_3)_2$ and OH], 2.20–4.55 (CH of backbone), 2.90 [para $-CH(CH_3)_2$], 6.25–7.45 (ArH).

Solid-State Photolysis. (a) Solid-State Photocyclization of Copolymer 7a. A 22% w/w solution of copolymer **7a** in diglyme was filtered via a 0.5-μm filter and was subsequently used to cast 1-μm polymer films onto standard sodium chloride, quartz, and silicon wafers. The films were dried at 80 °C for 10 min prior to UV exposure. UV exposure through Pyrex was performed in air with a lamp output of 3.73 mW/cm^2, and the changes in the IR spectra were monitored over a 15-min period. During this period, the carbonyl stretch at 1667 cm^{-1} was observed to disappear as the photocylization to form polymer **8a** proceeded (Figure 3).

A similar change in the IR spectrum of thin films of copolymer **7b** was also observed on UV exposure through Pyrex.

(b) Solid-State Photocyclization of Copolymer 4a. A 10% w/w solution of copolymer **4a** was filtered via a 0.5-μm filter and was subsequently used to cast 0.5-μm polymer films onto standard sodium chloride, quartz, and silicon wafers. The films were dried at 50 °C for 5 min prior to exposure as described above. During a 20-min period, infrared spectroscopy showed the disappearance of the carbonyl stretch at 1667 cm^{-1} as the photocyclization to give copolymer **9** proceeded.

Interconversion of Copolymers 7a and 8a. Solid-state photocyclization of **7a** was performed as above while thermal ring opening of **8a** was effected by heating 1-μm-thick polymer films between two sodium chloride disks at 180 °C in air using a hot stage. For each process, the time required to effect complete reaction, as monitored by infrared spectroscopy, was found to increase with each cycle until polymer degradation set in.

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