J. Org. Chem. 1980, 45, 2903–2907

Poly(p-(trifluorovinyl)benzophenone) and Poly(p-(trifluorovinyl)acetophenone). Photostable Polymeric Triplet Energy Transfer Donors

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Received December 26, 1980

The synthesis of UV-stable photosensitizers poly(p-(trifluorovinyl)benzophenone) and poly(p-(trifluorovinyl)acetophenone) and their use as a homogeneous and heterogeneous triplet-state energy-transfer donor are herein described. The photosensitizers are advantageous both because of the separation advantages provided by the macromolecule and the nearly diffusion-controlled energy-transfer rate of a sensitizer in solution. Poly(p-(trifluorovinyl)acetophenone) is insoluble in certain solvents, thus providing the separation advantages of a heterogeneous energy-transfer donor.

Introduction

Benzophenone and acetophenone have been used widely as triplet photosensitizers since the concept of triplet-energy transfer in fluid solution was confirmed by Backstrom and Sandros.[1] Triplet sensitizers are catalysts of sorts, and the importance of these in photoprocesses is that triplet products can often differ from singlet products. Separation of sensitizers from reaction products may be difficult in synthetic processes, and there are many potential applications for heterogeneous photocatalysts.

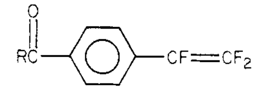
We have been studying polymer-based triplet photosensitizers which facilitate separation and can be used repetitively.[2] The studies herein were preceeded by the development of [P]-rose bengal,[3] and [P$_{Si}$]-rose bengal,[4] useful heterogeneous photosensitizers for singlet-oxygen formation, [P]-benzoyl,[5] an aromatic carbonyl derivative based on poly(styrene), and poly(divinylbenzophenone).[6]

In synthetic applications, [P]-benzoyl,[5] particularly, suffers from free-radical degradation reactions which compete with energy transfer. Photodecarboxylation of the styryl benzoate ester gives benzophenone as an observed product while hydrogen abstraction from the poly(styrene) by the triplet aromatic carbonyl group leads to direct cross-linking of the polymer backbone to the carbonyl group. These degradation reactions decrease energy-transfer efficiency significantly. Poly(p,p'-divinylbenzophenone), which has a more rigid structure, degrades by hydrogen atom abstraction from the polymer backbone but more slowly.[6]

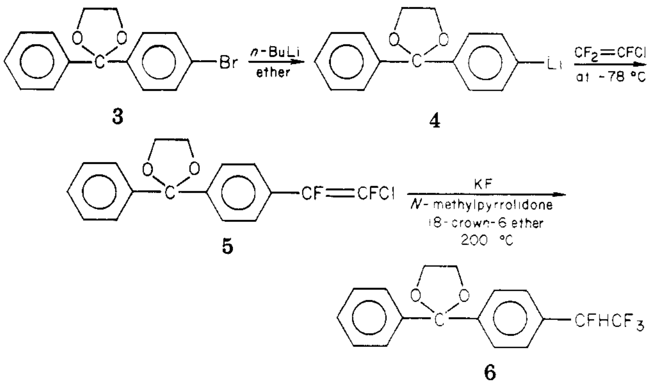
In this paper, we report the synthesis and use of the photostable triplet energy transfer donors poly(p-(trifluorovinyl)benzophenone), [TEF]-BP, and poly(p-(trifluorovinyl)acetophenone), [TEF]-AP. These fluorocarbon polymers, which are soluble in some solvents, may combine the useful separation characteristics of a high polymer with the energy-transfer efficiencies of a soluble photosensitizer. They are also among the first effective photostable aryl ketone photosensitizers to be used in a heterogeneous fashion.

Results and Discussion

Synthesis and Polymerization of Fluorovinyl Monomers. We encountered various difficulties while preparing the fluorovinyl monomers p-(trifluorovinyl)benzophenone (1) and p-(trifluorovinyl)acetophenone (2). n-BuLi with p-bromobenzophenone ketal or acetophenone ketal, for example, gave the lithium salts which, with tetrafluoroethylene under carefully controlled conditions, gave the monomers. But these anions with trifluorochloroethylene gave β-chloro-α,β-difluorovinylbenzophenone ethylene ketal in 83% yield,[7] in ether at −78 °C the *displacement of chloride being slower than displacement of fluoride.*



1, R = Ph
2, R = CH_3



With potassium fluoride in N-methylpyrrolidone, 5 in the presence of 18-crown-6 ether gave α-fluoro-β,β,β-trifluoroethylbenzophenone ethylene ketal 6 rather than p-(trifluorovinyl)benzophenone ethylene ketal (8). The initial product formed was likely the p-trifluorovinyl derivative which underwent further attack of F^- on the β site of the alkene to form a carbanion which abstracted a proton from solvent.

Dehydrofluorination of 6 was unsuccessful. Reaction with neat 1,5-diazabicyclo[5.4.0]undecane (DBU), DBU in

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(1) (a) H. L. Backstrom and K. Sandros, *Acta Chim. Scand.*, 14, 48 (1960); (b) H. L. Backstrom and K. Sandros, *ibid.*, 12, 823 (1958).

(2) D. C. Neckers, *CHEMTECH*, 8, 108 (1978).

(3) E. C. Blossey, D. C. Neckers, A. L. Thayer, and A. P. Schaap, *J. Am. Chem. Soc.*, 95, 5820 (1973).

(4) S. Tamagaki, C. E. Liesner, and D. C. Neckers, *J. Org. Chem.*, 45, 1573 (1980).

(5) E. C. Blossey and D. C. Neckers, *Tetrahedron Lett.*, 323 (1974).

(6) S. N. Gupta, L. Thijs, and D. C. Neckers, *Macromolecules*, in press.

(7) There are three possible isomers, namely, the cis and trans isomers of the p-(β-chloro-α,β-difluorovinyl) derivative and the p-(α-chloro-α,α-difluorovinyl) derivative. GC analysis showed at least two isomers. They are probably cis–trans isomers of (β-chloro-α,β-difluorovinyl)benzophenone.

(8) Two isomers are possible, the p-(α-fluoro-β,β,β-trifluoromethyl) derivative or the p-(α,α-difluoro-β,β-difluoroethyl) derivative. Structure 6, p-(α-fluoro-β,β,β-trifluoroethyl)benzophenone, seemed reasonable on the basis of the stability of the formed anion. This structure was confirmed by a combination of fluorine and proton NMR analysis. The α-ethyl proton at 5.69 δ (1 H) was an octet. The α-ethyl fluorine at (δ $CFCl_3$) 194 ppm (octet, 1 F) and the β-ethyl fluorine at (δ $CFCl_3$) 79.5 ppm (quartet, 3 F) confirmed this structural assignment.

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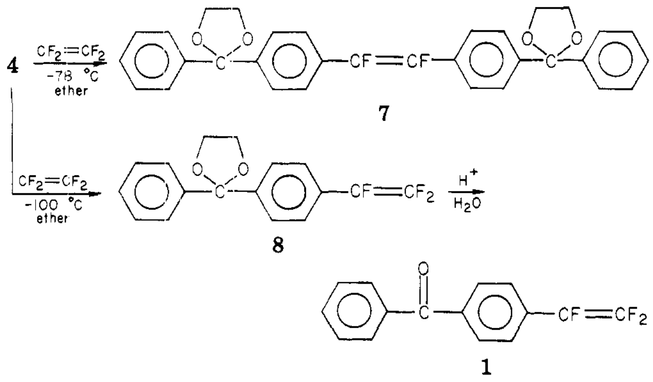
Table I. Photodegradation of [TEF]-BP[a]

time, min	0	290	1410	3810
% degraded[b]	0	0.2 ± 0.2	0.0 ± 0.2	0.8 ± 0.2

[a] In KBr, irradiated at 350 nm with Rayonet RUL 3500-Å lamps. [b] Followed by decrease in the 1670-cm^{-1} absorption band.

benzene, DBU in diethylene glycol, aqueous NaOH and KOH, methanolic NaOH or KOH, or molten NaOH or KOH produced no dehydrofluorination. The corresponding ketone of 6 also gave no 1 under any conditions.

The reaction of anion 4 with tetrafluoroethylene at −78 °C in ether gave the α,β-disubstituted product 7 but no 8 was observed. Reaction at −100 °C, however (liquid N_2/ether), gave the desired 8 and 48% of *p*-(trifluorovinyl)benzophenone was isolated after hydrolysis of the ketal. *p*-(Trifluorovinyl)acetophenone (2) was prepared in similar manner from *p*-bromoacetophenone ethylene ketal. The yield was 39% based on *p*-bromoacetophenone ethylene ketal.



Emulsion polymerization of 1 using potassium persulfate as the catalyst and *n*-dodecylamine hydrochloride as the emulsifying agent gave an 80% yield of poly(*p*-(trifluorovinyl)benzophenone), [TEF]-BP. In a similar manner, 2 gave a 59% yield of poly(*p*-(trifluorovinyl)acetophenone), [TEF]-AP.

[TEF]-BP and [TEF]-AP showed carbonyl stretching frequencies at 1670 and 1690 cm^{-1}, respectively. [TEF]-BP is soluble in benzene, $CHCl_3$, and CH_2Cl_2, while [TEF]-AP is also soluble in $CHCl_3$ and CH_2Cl_2 but not in benzene.

The intrinsic viscosity [η] of [TEF]-BP in benzene solution was 0.276, using a concentration range of 0.3–1.0 g of polymer per 100 mL. This corresponds to an $[\bar{M}_n]$ = 30 400.[9] [TEF]-AP has [η] = 1.06 in $CHCl_3$ solution (concentration range 0.3–1.0 g/100 mL). This corresponds to $[\bar{M}_n]$ = 287 000. The softening points of [TEF]-BP and [TEF]-AP were 245–260 and 270–290 °C, respectively.[10]

Photochemistry of [TEF]-BP and [TEF]-AP. [TEF]-BP and [TEF]-AP have λ_{max} = 340 nm (ε 156) and λ_{max} = 325 (ε 71) in $CHCl_3$, respectively. When irradiated in a KBr disk for up to 60 h with Rayonet 350-nm lamps, both polymers were photostable. The data for [TEF]-BP are given in Table I. No substantial decrease in the carbonyl stretching frequency of the polymer was observed although both polymers turned slightly yellow during this period.

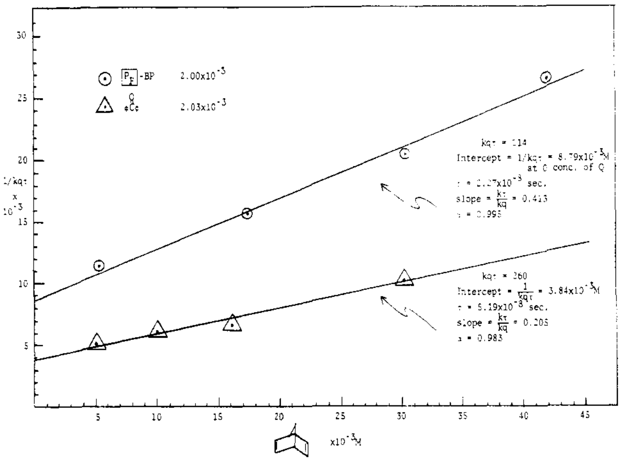


Figure 1. Plot of $1/k_q\tau$ of the photosensitized isomerization of norbornadiene to quadricyclene with PFVBP and with benzophenone vs. concentration of norbornadiene in presence of cyclohexadiene as a quencher.

The phosphorescence spectrum of [TEF]-BP was similar to that of benzophenone, though the 0–0 band was red shifted (413 nm, E_t = 65.7 kcal/mol at 77 °K) in poly(methylmethacrylate). The 0–0 band of the corresponding monomer was also slightly lower than that of benzophenone (407 nm, E_t = 68.6 kcal/mol at 77 K) in an EPA glass. However, this was not unexpected and is the pattern for benzophenones substituted with fluoroalkyl substituents.[11] No phosphorescence spectrum of [TEF]-AP could be obtained because it was not appropriately soluble. Indirect evidence suggests that this polymer probably has a higher triplet energy than [TEF]-BP and the corresponding monomer showed a 0–0 band at 403 nm (E_t = 71.0 kcal/mol) at 77 K in an EPA glass.

The lifetime of a triplet photosensitizer can be expressed by the following equations,

$$\tau = \frac{1}{k_d + k_t[S]}$$

or

$$\frac{1}{k_q\tau} = \frac{k_d}{k_q} + \frac{k_t}{k_q}[S]$$

where [S] = substrate concentration, k_t = energy-transfer rate constant, k_d = decay rate constant, and k_q = quenching rate constant. Using cyclohexadiene to quench the sensitized isomerization of norbornadiene to quadricyclene (Figure 1) gave $k_q\tau$ = 114 M^{-1} for [TEF]-BP, while for benzophenone under identical conditions, $k_q\tau$ = 260 M^{-1}. The triplet lifetime of [TEF]-BP is therefore either about half as long as that of benzophenone under these conditions or the quenching of polymer triplets is slower than diffusion controlled because of the restricted mobility of the macromolecule. Triplet–triplet absorption studies undertaken to determine the actual spectroscopic triplet lifetime of [TEF]-BP gave a value of 10^{-5} s[12] in benzene, an almost identical value with that of benzophenone. This implies that the restricted mobility of [TEF]-BP may be responsible for its lower $k_q\tau$ under the rather specific conditions described (Figure 1). The triplet lifetime of [TEF]-AP was, like that of acetophenone itself, too short to measure by triplet–triplet absorption techniques in fluid solution.

[TEF]-BP and [TEF]-AP were used for several triplet-sensitized reactions. These were the dimerization of indene,[13] the (2 + 2) cycloaddition of benzo[*b*]thiophene

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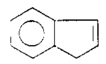
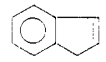
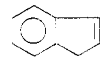
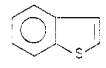
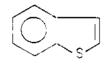
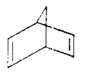
(9) D. H. Johnson and A. V. Tobolsky, *J. Am. Chem. Soc.*, 74, 938 (1952).

(10) J. Brandrup and E. H. Immergut, Eds., "Polymer Handbook", Interscience, New York, 1966.

(11) D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry", Plenum Press, New York, 1976.

(12) This experiment was kindly carried out for us by Dr. W. H. Herkstroeter, Eastman Kodak Co.

Table II. Sensitized Reactions Using [TEF]-BP and [TEF]-AP

reaction[a]	sensitizer (mol %)[g]	time, h	$\frac{[\phi] \text{ polymer}}{[\phi] \text{ B}^c}$	conversion, %	isolated[b] yield, %	loss of C=O, %
 (0.10 M in PhH)	1 (10)	17	0.92	70	82	
	1 (3) (run 1)	17	0.73	72	64	90
	1 (3) (run 2)[d]	17	0.36	35	27	95
	1 (3) (run 3)[e]	17	0.14	14	13	95
 (0.10 M in 1:1 CH_2Cl_2-PhH)	2 (3) (run 1)	17	0.78	76	70	14
	2 (3) (run 2)[d]	17	0.69	68	65	34 ± 2
	2 (3) (run 3)[e]	17	0.63	62	58	49 ± 2
 (0.15 M in PhH)	2 (3) heterogeneous	17	0.18	17	13	3 ± 2
	2 (10) heterogeneous in PhH	17	0.47	46	39	7 ± 2
 (0.50 M in CHCl=CHCl)	1 (14)	6	0.44	17		
	1 (14)	19	0.55	38		0.4 ± 2
	PhC(O)Ph	19	1.00	70		16
	2 (14)	6	0.44	17	16	1.2 ± 2
	2 (14)	19	0.56	39	38	0 ± 2
 (0.27 M in PhH + DMAD)	1 (14)	20	0.77	23	20	0 ± 2
	2 (14)	20	0.60	18	13	0 ± 2
 (0.20 M in PhH)	1 (10)	15	0.94			
	1 (10)	38	1.26			100[f]

[a] Rayonet reactor, 350-nm lamps. [b] Products in each experiment are as reported.[14-16] [c] Quantum yields of starting material disappearance. Benzophenone as a sensitizer used under identical conditions of solvent, irradiation time, and effective sensitizer concentration. [d] Recovered [TEF]-BP (3%) from run 1 or [TEF]-AP (3%) from run 1. [e] Recovered [TEF]-BP (3%) from run 2 or [TEF]-AP (3%) from run 2. [f] After 38 h under similar conditions with benzophenone, all benzophenone was converted to oxetane. Oxetane formation with [TEF]-BP occurred approximately 50% as rapidly as with benzophenone itself. [g] Molar concentration of aryl ketone function relative to acceptor concentration. [TEF]-BP = 1. [TEF]-AP = 2.

to dichloroethylene[14] and to dimethyl acetylenedicarboxylate (DMAD),[15] and the isomerization of norbornadiene.[16] Both polymer sensitizers were removed easily from a sample in which they were used by filtration after the addition of methanol to the mixture. Relative quantum yields of polymer-sensitized reactions compared with benzophenone under similar conditions were usually between 0.5 and 0.8. Likely due to the bimolecular nature of these reactions, the effective encounter of the reactants with a sterically crowded sensitizer is limited by the restricted accessability of the macromolecular sensitizer.

In the case of the isomerization of norbornadiene to quadricyclene, the relative quantum yield with [TEF]-BP appeared higher than that for benzophenone. Benzophenone was completely consumed by an excess of norbornadiene after 15 h of irradiation, while the carbonyl IR absorption of [TEF]-BP, however, only completely disappeared after 38 h of irradiation. Since energy transfer and oxetane formation are competing reactions, the observed higher efficacy of [TEF]-BP may be due to the fact that the ratio of energy transfer to oxetane formation for [TEF]-BP is higher than that of the free benzophenone, the oxetane forming in both cases but more slowly in the case of the polymer.

The yield of product obtained in sensitized reactions depended on the concentration of [TEF]-BP used in the cycloaddition of benzo[*b*]thiophene to *cis*-dichloroethylene as well as in the dimerization of indene (Figure 2). The photocycloaddition of benzo[*b*]thiophene to *cis*-dichloroethylene required more sensitizer than did the dimerization of indene. This may be because the triplet energy of benzo[*b*]thiophene is higher than that of indene and the efficacy of the former transfer is comparably lower. Thus, a 0.10 M indene solution (benzene) containing 10 mol % of [TEF]-BP gave 82% dimer after 4 h of irradiation, while 3 mol % of [TEF]-BP gave a 72% yield of indene dimer after 17 h of irradiation (Figure 2). In the benzo[*b*]thiophene reaction, 14% sensitizer gave only 38% yield of adduct.

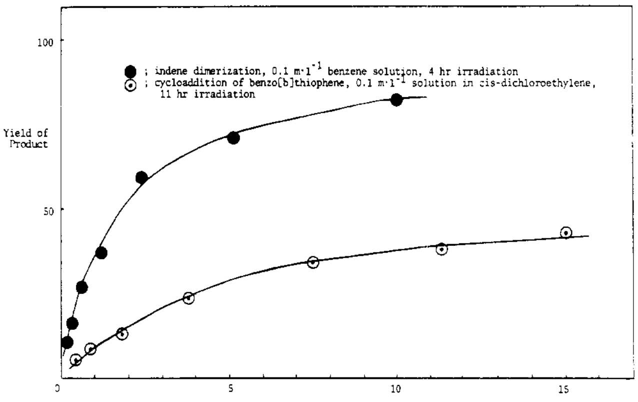


Figure 2. Dependence of yield on amount of PFVBP for dimerization of indene and cycloaddition of benzo[*b*]thiophene to *cis*-dichloroethylene.

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(13) S. Bowyer and D. N. Porter, *Aust. J. Chem.*, **19**, 1455 (1966).
(14) D. C. Neckers, J. H. Dopper, and H. Wynberg, *J. Org. Chem.*, **35**, 1582 (1970).
(15) D. C. Neckers and J. H. Dopper, *J. Org. Chem.*, **36**, 3755 (1971).
(16) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964).

Recovered [TEF]-BP from the indene dimerization retained only 10% of the carbonyl group infrared absorption. Elemental analysis of the recovered [TEF]-BP after a third use (Table II) was nearly in accordance with that expected for polymer oxetane. The ^{13}C NMR spectrum and the weight of recovered polymer also suggested polymer oxetane formation.

[TEF]-AP gave yields of products similar to those obtained by the use of [TEF]-BP in all example reactions but was easier to recycle in the dimerization of indene than was [TEF]-BP. It also showed less than 50% degradation after three successive 17-h uses due, we expect, to the higher triplet energy of [TEF]-AP than [TEF]-BP.

Heterogeneous conversion of indene to its dimer with [TEF]-AP using conditions similar to those of a solution in CH_2Cl_2/PhH gave 17% conversion to dimer. However, 46% conversion was observed when 10 mol % of [TEF]-AP was used and the concentration of indene was increased by 50% (0.15 M).

Thus, both [TEF]-BP and [TEF]-AP are useful sensitizers and have advantages over monomeric sensitizers which include the following: (1) Facile recovery from reaction mixtures facilitates synthetic reactions in which the polymeric sensitizers are used. (2) The fluorocarbon sensitizers are relatively photostable and, especially [TEF]-AP, can be used repeatedly. They can be used even for reactions in which oxetane formation competes with energy transfer. (3) [TEF]-AP, insoluble in benzene, is useful as a heterogeneous sensitizer.

The efficiency of energy transfer from the polymeric sensitizer may be somewhat lower than that of free benzophenone because quenching of the triplet state of the polymeric sensitizer is slower than the normal diffusion-controlled rate which is approximately 5×10^9 s^{-1} for benzophenone in fluid solution.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting-point apparatus and are not corrected. Infrared spectra were obtained with a Perkin-Elmer 337 infrared spectrophotometer. NMR spectra were recorded on a Varian CFT-20 spectrometer with deuteriochloroform as the solvent. Reference is to tetramethylsilane. Mass spectra were taken on a Varian MAT Model CH7 mass spectrometer. UV spectra were recorded on a Beckman Acta MIV spectrometer. Phosphorescence spectra were obtained with a Perkin-Elmer MPF-44A spectrophotometer. Quantitative GLC was carried out with a Hewlett-Packard 5710A. *p*-Bromobenzophenone ethylene ketal and *p*-bromoacetophenone ethylene ketal were prepared from the corresponding ketone by using ethylene glycol and a catalytic amount of *p*-toluenesulfonic acid according to the method for benzophenone described elsewhere.[17] Fluorine NMR spectra were taken on a Varian EM-360 in $CFCl_3$ which also served as the internal standard.

p-(β-Chloro-α,β-difluorovinyl)benzophenone Ethylene Ketal (5). *n*-BuLi (2.8 mL, 2.4 M in *n*-hexane, 0.007 mol) in 10 mL of ether was added dropwise to a solution of *p*-bromobenzophenone ethylene ketal (2 g, 0.007 mol) in 10 mL of ether under N_2 at 20 °C and the solution was stirred for 4 h. Pale yellow crystals appeared during this period. The mixture was cooled to −78 °C (dry ice-acetone), chlorotrifluoroethylene (0.007 mol) was introduced dropwise, and the reaction was stirred for 1 h at −78 °C under an N_2 atmosphere. Then the temperature was allowed to rise to room temperature. After being filtered and dried, the solvent was removed. The residue was chromatographed over a silica gel column with benzene–hexane (1:1) as an eluant to give 1.77 g (83%) of **5**: mp 53.5–54.5 °C (hexane); IR 1690 cm^{-1} (CF=CFCl); mass spectrum, *m/e* 322. Anal. Calcd for $C_{17}H_{13}O_2ClF_2$: C, 63.26; H, 4.07; Cl, 10.98; F, 11.77. Found: C, 63.32; H, 4.14; Cl, 11.04; F, 11.85.

p-(α-Fluoro-β,β,β-trifluoroethyl)benzophenone Ethylene Ketal (6) and Corresponding Ketone. A mixture of **5** (1.9 g, 0.0059 mol), potassium fluoride (6.0 g 0.10 mol), and 18-crown-6 ether (0.3 g, 0.001 mol) in 15 mL of *N*-methylpyrrolidone was heated at 200 °C with stirring for 8 h. The reaction mixture was poured into water and extracted with ether, the organic layer was washed with water and dried ($MgSO_4$), and solvent was removed in vacuo. The residue was chromatographed (silica gel, benzene–hexane (1:1)). **6** (1.2 g, 62%) was obtained as a light yellow oil. Acid hydrolysis (10% H_2SO_4, 25% H_2O, 65% methanol) gave the corresponding ketone, p-(α-fluoro-β,β,β-trifluoroethyl)benzophenone: mp 57–58 °C (hexane); IR 1670 cm^{-1} (C=O); mass spectrum, *m/e* 282. Anal. Calcd for $C_{15}H_{10}OF_4$: C, 63.83; H, 3.58; F, 26.93. Found: C, 63.76; H, 3.53; F, 26.89.

p-(Trifluorovinyl)benzophenone (1). *n*-BuLi (5 mL of 2.4 M solution in *n*-hexane, 0.012 mol) in 40 mL of ether was added dropwise to a solution of *p*-bromobenzophenone ethylene ketal (3.66 g, 0.012 mol) in ether (40 mL) under N_2 at 20 °C, and the solution was stirred for 4 h. During this period pale yellow crystals appeared. Tetramethylenediamine (1.4 g, 0.012 mol) in ether (25 mL) was added slowly at 20 °C to make a homogeneous solution. Then the anionic solution was added slowly to a stirred solution of tetrafluoroethylene (20 mol excess) in 60 mL of ether over 40 min at −100 °C (liquid N_2/ether bath). Stirring was continued under a positive pressure of N_2 for 1 h at −100 °C. The reaction mixture was then filtered and solvent was removed in vacuo. To the residue was added 50 mL of acid (10% H_2SO_4, 25% H_2O, 65% methanol), and the mixture was stirred for 1 h at 50 °C. The mixture was poured into 100 mL of water and extracted three times with $CHCl_3$. The extracts were combined, extracted with 1 N H_2SO_4, aqueous $NaHCO_3$, and water, and then dried over $MgSO_4$. The solvent was then removed. To the residue was added 100 mL of hexane and the crystals which precipitated were collected and washed with benzene. A total of 320 mg (13%) of the 2:1 adduct **7** was obtained: mp 223–224 °C (benzene); IR 1650 cm^{-1} (C=O). Anal. Calcd for $C_{28}H_{18}O_2F_2$: C, 79.23; H, 4.28; F, 8.95. Found: C, 79.14; H, 4.21; F, 9.06. The solvent from the filtrate was removed in vacuo and the residue was chromatographed over a silica gel column with benzene–hexane (1:2) as an eluant. The first fraction was *p*-(trifluorovinyl)benzophenone (1 1.52 g, 48%): mp 44.5–45.4 °C (hexane); IR 1755 cm^{-1} (CF=CF$_2$), 1670 cm^{-1} (C=O); mass spectrum, *m/e* 262. Anal. Calcd for $C_{15}H_9OF_3$: C, 68.70; H, 3.47; F, 21.74. Found: C, 68.54; H, 3.62; F, 21.84.

p-(Trifluorovinyl)acetophenone (2). *n*-BuLi (8 mL of 2.4 M solution in *n*-hexane, 0.019 mol) in ether (50 mL) was added dropwise to a solution of *p*-bromoacetophenone ethylene ketal (4.66 g, 0.019 mol) in 50 mL of ether under a N_2 atmosphere at room temperature and stirred for 4 h. The anionic solution was added slowly to a stirred solution of tetrafluoroethylene (10 molar excess) in ether (80 mL) over 40 min at −100 °C. The solution was stirred for an additional 1 h under a N_2 atmosphere at −100 °C. The solution was filtered and the solvent was removed in vacuo. To the residue was added 80 mL of acid solution (10% H_2SO_4, 25% H_2O, 65% methanol) and the solution was stirred for 1 h at 50 °C. The solution was poured into 150 mL of water and the hydrolyzed product was extracted with $CHCl_3$ three times. The extracts were combined, washed with aqueous $NaHCO_3$ and water, and dried ($MgSO_4$), and the solvent was removed at reduced pressure. To the residue was added 150 mL of hexane and crystals separated which were washed with hexane to give 347 mg (12%) of 2:1 adduct: mp 217.5–218.5 (benzene); IR 1675 (C=O) cm^{-1}; mass spectrum, *m/e* 300. Anal. Calcd for $C_{18}H_{14}O_2F_2$: C, 71.98; H, 4.71; F, 12.65. Found: C, 72.05; H, 4.73; F, 12.76. The solvent from the filtrate was removed in vacuo. The residue was chromatographed over a silica gel column with benzene–hexane (1:2) as eluant to give 1.50 g (39%) of *p*-(trifluorovinyl)acetophenone: mp 32–33 °C (hexane); IR 1760, (CF=CF$_2$), 1690 (C=O) cm^{-1}; NMR δ 2.61 (3 H, CH_3), 8.01 and 7.56 (A_2B_2, 4 H, Ph, J_{AB} = 8.6 Hz); mass spectrum, *m/e* 200, 185 (CH_3), 157 ($COCH_3$).

Polymerization of p-(Trifluorovinyl)benzophenone (1). Emulsion polymerization was carried out. **1** (35 mg, 1.34 mmol), potassium persulfate (3 mg, 0.011 mol), *N*-dodecylamine hydrochloride emulsifier (60 mg, 0.27 mmol), and 4 mL of H_2O were introduced to a Pyrex glass tube, which was degassed by four

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[17] R. B. Wagner and M. D. Zook, "Synthetic Organic Chemistry", Wiley, New York, 1953.

freeze-pump-thaw cycles and sealed. The sealed tube was shaken for 48 h (52 °C) after which the polymer was precipitated with methanol, washed with methanol and then water, and dried in vacuo. The polymer was dissolved in a minimum of $CHCl_3$, filtered, precipitated with methanol, washed, and dried to insure that unreacted monomer had been removed. Repetition of this procedure (2x) gave 280 mg (80%) of white fibrous poly(*p*-(trifluorovinyl)benzophenone): softening point 245–260 °C; IR 1690 cm^{-1} (C=O). Anal. Calcd for $C_{15}H_9OF_3$ (monomer): C, 68.70; H, 3.47; C, 21.74. Found: C, 68.29; H, 3.52; F, 21.38.

Polymerization of *p*-(Trifluorovinyl)acetophenone. Polymerization was carried out in the same manner as that described for *p*-(trifluorovinyl)benzophenone: yield 59%; softening point 270–290 °C. Anal. Calcd for $C_{10}H_7OF_3$ (monomer): C, 60.00; H, 3.53; F, 28.48. Found: C, 59.59; H, 3.35; F, 28.21.

Determination of Intrinsic Viscosity. The intrinsic viscosity of the two polymers was determined by a Thomas D10 viscometer using concentration ranges of 0.3–1.0 g of polymer per 100 mL. The intrinsic viscosity of poly(*p*-(trifluorovinyl)benzophenone), [TEF]-BP, in benzene solution at 30 °C was 0.276. That of poly(*p*-(trifluorovinyl)acetophenone), [TEF]-AP, in $CHCl_3$ solution at 30 °C was 1.06. These values probably correspond to $[M_n]$ of 30600 and 287000 for [TEF]-BP and [TEF]-AP, respectively.

Determination of Photoisomerization Rate of Norbornadiene. A solution for a typical kinetic run was prepared by pipetting a desired amount of norbornadiene, cyclohexadiene, and a benzene solution of [TEF]-BP (or benzophenone) into a 2-mL volumetric flask. The solution, 1.5 mL, was pipetted into Pyrex glass tubes (12 mm) which were degassed by three freeze-thaw cycles and sealed. The tubes were placed in a merry-go-round and irradiated (Rayonet 3500-Å lamps) for the desired time (15 min for [TEF]-BP solution; 10 min for benzophenone solution). The estimation of product, quadricyclene, was done by quantitative VPC analysis using a 10% SE-30 12-ft column at 85 °C.

Photosensitized Cycloaddition of Benzo[*b*]thiophene to Dimethyl Acetylenedicarboxylate with Polymer Sensitizer and Benzophenone. Benzo[*b*]thiophene (143 mg, 1.1 mmol), dimethyl acetylenedicarboxylate (184 mg, 1.3 mmol), and [TEF]-BP (40 mg, 0.15 mmol) were dissolved in 4 mL of benzene. The tube was irradiated for 20 h at 350 nm. Solvent was removed in vacuo ([TEF]-BP was soluble in the residue) and 50 mL of methanol was added slowly. The precipitated polymer was recovered quantitatively (40 mg) and unchanged. The solvent was removed from the filtrate in vacuo. To the residue was added toluene (58 mg) as an internal standard for quantitative analysis by NMR which showed 23% conversion to the cycloadduct.[14] The product solutions were combined and the solvent was removed in vacuo. The residue was chromatographed (silica gel TLC) with benzene as eluant to give 58 mg (20%) of adduct.

Photosensitized cycloadditions with [TEF]-AP and free benzophenone were carried out in an identical manner. Benzene–CH_2Cl_2 (1:1) was used for the [TEF]-AP sensitized reaction. Workup of the sensitized reaction was in the manner previously reported.[14]

Photosensitized Cycloaddition of Benzo[*b*]thiophene to *cis*-Dichloroethylene with the Polymer Sensitizer and with Free Benzophenone. Benzo[*b*]thiophene (407 mg, 3.0 mmol) and [TEF]-AP (83 mg, 0.42 mol, 14 mol % relative to benzo[*b*]thiophene) were dissolved in 6 mL of *cis*-dichloroethylene and irradiated for 19 h at 350 nm. The solvent was removed in vacuo, 50 mL of methanol was added slowly to precipitate [TEF]-AP, and the mixture was filtered. The polymer was recovered quantitatively. Solvent was removed from the filtrate in vacuo and 172 mg of toluene was added for quantitative NMR analysis. NMR analysis showed 39% conversion to cycloadduct.[13] The product solutions were combined and the solvent was removed in vacuo. The residue was chromatographed on silica gel TLC with benzene as eluant to give 268 mg (38%) of cycloadduct. The photosensitized cycloadditions with [TEF]-BP and free benzophenone were done under identical conditions as those for [TEF]-AP. Workup of the free benzophenone sensitized reaction was carried out in the manner previously reported.[13]

Photosensitized Dimerization of Indene with the Polymer Sensitizer and with Free Benzophenone. Indene (476 mg, 4.1 mmol) and [TEF]-AP (25 mg, 0.125 mol % relative to indene) were dissolved in 40 mL of benzene–CH_2Cl_2 (1:1) and irradiated for 17 h at 350 nm. The solvent was removed in vacuo and 50 mL of methanol added slowly. The [TEF]-AP which precipitated was collected (25 mg). The solvent was removed in vacuo and 330 mg of toluene was added as an internal standard for quantitative NMR analysis. Conversion to the dimer was 76%. The product solutions were combined and the solvent was removed. Preparative silica gel TLC of the residue with hexane as eluant gave 334 mg (70%) of dimer, mp 109.5–110.5 °C (methanol) (lit.[12] 107.5–111 °C). [TEF]-BP and free benzophenone sensitized dimerizations were carried out in an identical manner as that described above. However, benzene was used as a solvent for [TEF]-BP sensitized reaction.

Heterogeneous Photosensitization with [TEF]-AP for the Dimerization of Indene. Indene (313 mg, 2.7 mmol) and powdered [TEF]-AP (54 mg, 0.2 mmol, 10 mol % related to indene) in 18 mL of benzene were irradiated for 17 h with vigorous stirring. The solution was filtered and worked up in the same manner as that described above. [TEF]-AP (54 mg) was recovered. NMR analysis showed 46% conversion to dimer and 121 mg (39%) of the dimer was isolated.

Photosensitized Isomerization of Norbornadiene to Quadricyclene with [TEF]-BP and Free Benzophenone. Norbornadiene (91 mg, 1.0 mmol) and [TEF]-BP (27 mg, 0.10 mmol) were dissolved in 5 mL of benzene and irradiated for 15 and 38 h at 350 nm. The estimation of quadricyclene was carried out by quantitative VPC analysis using a 10% SE-30 12-ft column.

Acknowledgment. Support of this work by the National Science Foundation (DMR78-08493) is gratefully acknowledged.

Registry No. 1, 73558-50-6; 2, 73558-52-8; 3, 59793-76-9; 5, 73557-70-7; 6, 73557-71-8; 7, 73574-36-4; chlorotrifluoroethylene, 79-38-9; *p*-(α-fluoro-β,β,β-trifluoroethyl)benzophenone, 73557-72-9; tetrafluoroethylene, 116-14-3; [TEF]-BP, 73558-51-7; [TEF]-AP, 73558-53-9; norbornadiene, 121-46-0; quadricyclene, 278-06-8; benzo[*b*]thiophene, 95-15-8; dimethyl acetylenedicarboxylate, 762-42-5; *cis*-dichloroethylene, 156-59-2; indene, 95-13-6; indene dimer, 26085-07-4.