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Synthesis and Properties of Polymer-Supported Cyanoaromatic Compounds

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The photoreaction of a styrene/4-tributylstannylmethylstyrene (4:1) copolymer with di- and tetra-cyanoaromatic compounds in benzene-acetonitrile (1:1) gave polymers having cyanoaromatic functions in the side chain. These polymers were soluble in benzene and served as effective and recoverable sensitizers for three different types of photoinduced electron-transfer mediated organic photoreactions.

Cyanoaromatic compounds have been widely used as sensitizers for various types of photoinduced electron transfer reactions.1) However, they are sometimes not much stable under the reaction conditions and react with substrate molecules present in the reaction system.2) In addition, it is often difficult to separate them from the reaction mixture. Most of these disadvantages concerning photosensitizers of this class may be overcome by use of polymer-supported cyanoaromatics, and these polymers are expected to become a new class of practical photosensitizing materials.3,4) Previously, we reported that the cyano group in polycyanobenzenes can be replaced by benzylic groups through the photoreaction with benzylic silanes.5) We also found that the photoreaction of poly(4-trimethylsilylmethylstyrene) with dicyanoaromatic compounds in the side chain.6) However, this photoreaction was usually accompanied by a cross-linking reaction of the polymer, producing a large amount of an insoluble polymer in organic solvents.

We now report an effective method for the synthesis of polymer-supported cyanoaromatic compounds by utilizing the photosubstitution reaction of a styrene/4-tributylstannylmethylstyrene copolymer with di- and tetra-cyanoaromatic compounds. In this photoreaction, the photosubstitution predominated substantially over the photocross-linking. In this paper, the photochemical properties of the newly synthesized polymers are described.

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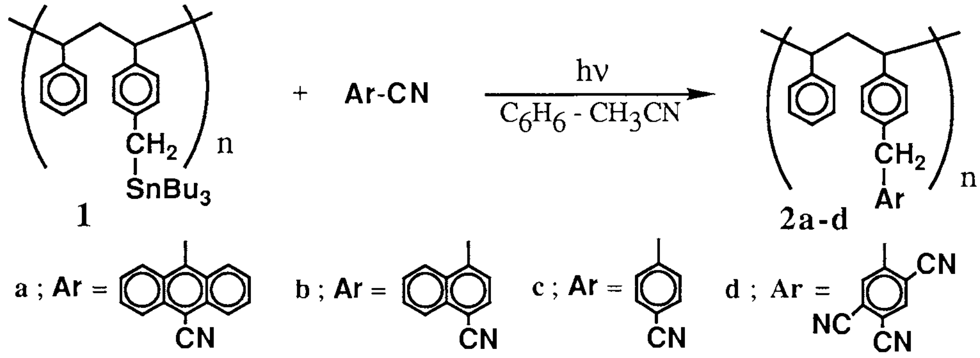
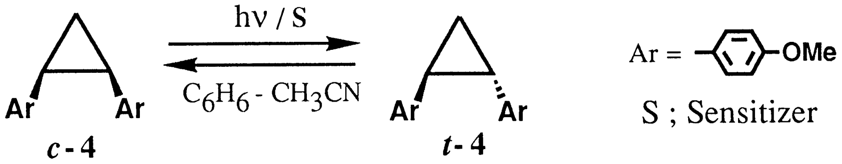
The copolymer **1** was prepared by a radical polymerization of a 4:1 mixture of styrene and 4-tributylstannylmethylstyrene[7)] in benzene using azobisisobutyronitrile (AIBN) as initiator and purified by repeated reprecipitation from saturated benzene solutions of the copolymer with methanol. The elemental analysis indicated that the copolymer contained the styrene and 4-tributylstannylmethylstyrene components in a 4:1 ratio.

Irradiation of a benzene-acetonitrile (1:1) solution containing **1** and five fold excess of 9,10-dicyanoanthracene (DCA) with a 300 W high pressure mercury lamp through an aqueous NH_3-$CuSO_4$ filter (>400 nm light) gave the new polymer **2a**, in which all the tributylstannyl group of **1** had been replaced by the 10-cyanoanthryl function.[8)] The polymer **2a** was soluble in benzene. The photoreactions of **1** with



1,4-dicyanonaphthalene (DCN), 1,4-dicyanobenzene (DCB), and 1,2,4,5-tetracyanobenzene (TCNB) in a similar manner afforded the polymers **2b-d** that were also soluble in benzene. These polymers were purified by repeated reprecipitation from saturated benzene solutions with methanol. The structures of **2a-d** were assigned from their spectral properties (^1H and ^{13}C NMR, UV, IR, and fluorescence spectra) and elemental analyses. The ^1H NMR spectra revealed that there were no tributylstannyl group in the synthesized polymers. The UV and fluorescence spectra of **2a** were similar in shapes to those of 9-cyano-10-methylanthracene. It is likely that **2a-d** are formed via photoinduced electron transfer from **1** to the excited singlet states of cyanoaromatic compounds.[9)] This was supported by the fact that the fluorescence of DCA was efficiently quenched by **1** in benzene-acetonitrile.

The polymers **2a** and **2d** served as sensitizers for some photoinduced electron transfer reactions. Irradiation of *cis*-1,2-bis(4-methoxyphenyl)cyclopropane (*c*-**4**, 0.05 mol/dm^3) in benzene-acetonitrile (1 : 1) in the presence of a small amount (20 mg) of **2a** under argon atmosphere with >400 nm light gave the *trans* isomer of the cyclopropane, *t*-**4**.[2a)] Continual irradiation resulted in the formation of a photostationary mixture containing *c*-**4** and *t*-**4** in a 5 : 95 ratio. The photoreaction of *t*-**4** under the same conditions gave the same photostationary mixture. This photoisomerization was appreciably accelerated by adding $Mg(ClO_4)_2$ (0.025 mol/dm^3). The results shown in Fig. 1 indicate that **2a** serves as a sensitizer of the photoisomerizatrion of *c*-**4**. The photooxygenation of *c*-**4** and *t*-**4** was also



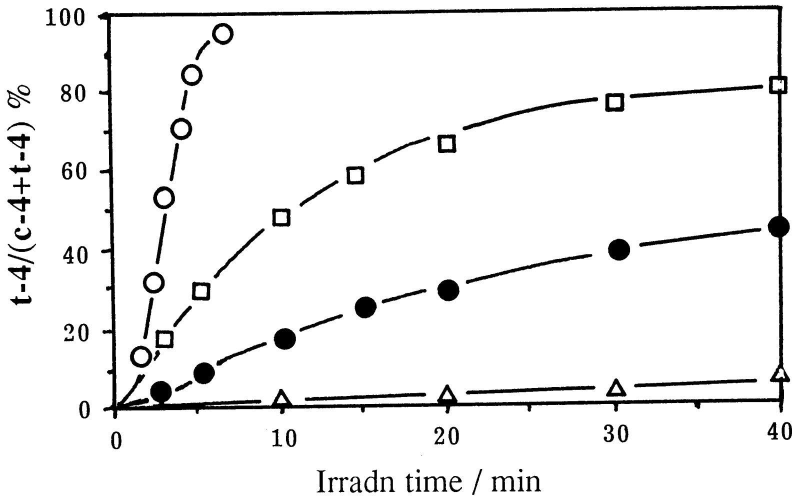
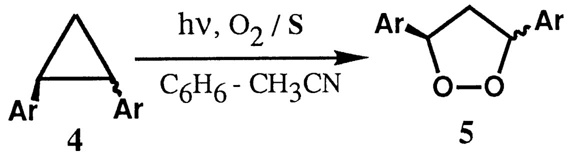


Fig. 1. Effect of sensitizers on the photoisomerization of **4** in benzene-acetonitrile. Plots of **t-4** /(**c-4** + **t-4**) % vs. the irradiation time (min): —○—; 2a / Mg(ClO$_4$)$_2$, —□—; DCA, —●—; 2a, —△—; None.



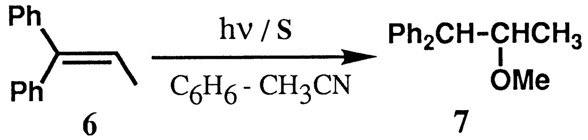


Table 1. Effect of Sensitizers on the Photooxygeneation of **4**[a)]

Sensitizer	Φ_{rel}[b)]
DCA	1.0
2a	0.13
None	0

a) Irradn time : 20 min. b) Relative quantum yields for the formation of **5**.

Table 2. Effect of Sensitizers on the Photoaddition of Methanol to **6**[a)]

Sensitizer	Φ_{rel}[b)]
DCA	1.0
2a	0.023
2d	0.026
None	0

a) Irradn time : 30 min. b) Relative quantum yiels for the formation of **7**.

sensitized by **2a**. Irradiation of a 5 : 95 mixture of *c*-**4** and *t*-**4** in benzene-acetonitrile (1 : 1) in the presence of **2a** (20 mg) under oxygen atmosphere with >400 nm light gave a 2 : 1 mixture of *cis*- and *trans*-3,5-bis(4-methoxyphenyl)-1,2-dioxolanes (*c*-**5** and *t*-**5**).10) This photooxygenation was also accelerated by adding Mg(ClO$_4$)$_2$. The effect of sensitizers on the photoreaction is shown in Table 1.

The third photoreaction that was sensitized by **2a** was the photoaddition of methanol to 1,1-diphenyl-1-propene (**6**).[11] Irradiation of a benzene-acetonitrile (1:1) solution containing **6** (0.02 mol/dm^3), methanol (1 mol/dm^3), and **2a** (20 mg) under nitrogen atmosphere with > 400 nm light gave 2-methoxy-1,1-diphenylpropane (**7**). This photoreaction was also sensitized by **2d**. The effect of sensitizers on this photoreaction are given in Table 2.

The fluorescence of **2a** in benzene-acetonitrile (1:1) was efficiently quenched by ***c*-4**, ***t*-4** and **6**. All the above results verify that the polymer-supported cyanoaromatic compounds can be used as electron-transfer sensitizers for photoinduced electron transfer reactions, although their sensitizing capability is smaller than that of DCA. However, as an advantage of the polymer sensitizer we found that the sensitizers could be recovered easily by adding hexane into the reaction mixtures and the recovered sensitizers exhibited essentially the same sensitizing ability as that of the freshly prepared ones.

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8) Spectral properties of **2a**: ^{1}H NMR (270 MHz, CDCl3) δ 1.41(br s), 1.54(br s), 1.84(br s), 5.26(br s), 6.27-7.56(m); ^{13}C NMR δ 29.6, 40.5, 44.2, 119.3, 125.7, 178.2; IR (KBr) 663, 756, 1454, 1493, 1603, 2360, 2926 cm^{-1}; Anal. Found C, 89.96; H, 7.38; N, 0.51%.
9) Any indication of CT interaction was not obtained between **1** and DCA in the UV-visible region of spectra in benzene and acetonitrile.
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