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Photoinduced Electron-Transfer Reactions of Poly(4-trimethylsilylmethylstyrene) in the Presence of Polycyanobenzenes

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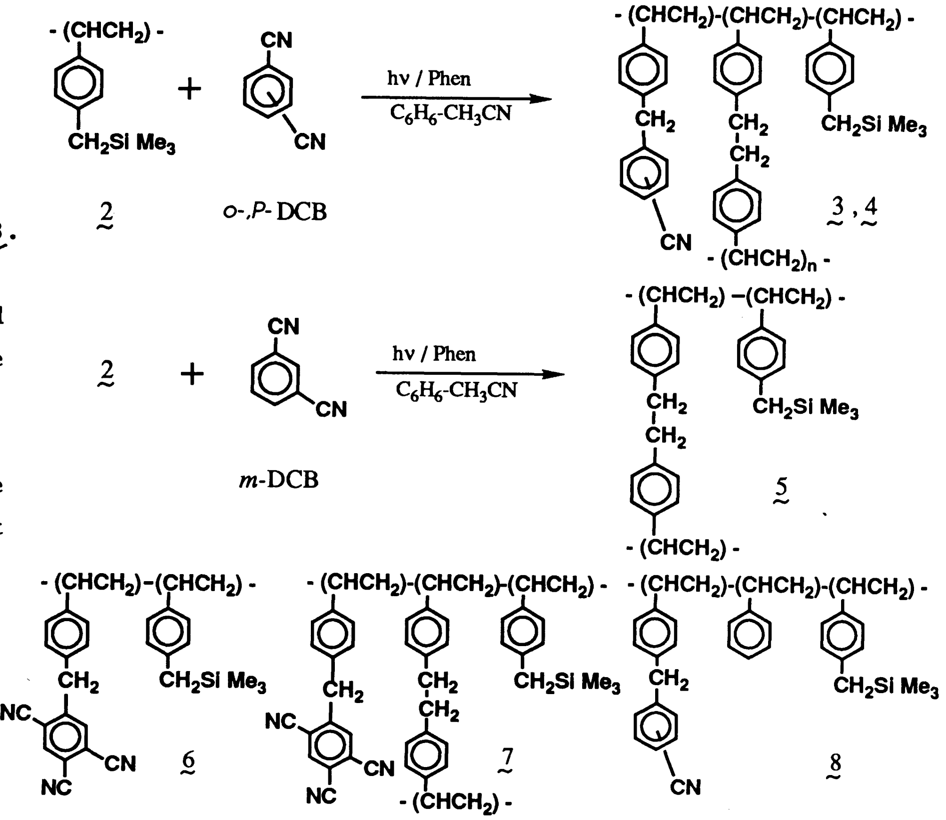
The photoreactions of poly(4-trimethylsilylmethylstyrene)(2) with o-, m-, and p-dicyanobenzenes in benzene-acetonitrile (3:2) afforded insoluble polymers in high yields. On the other hand, the photoreaction of 2 with 1,2,4,5-tetracyanobenzene gave a soluble polymer. In the latter photoreaction, the trimethylsilyl group of 2 was efficiently replaced by 2,4,5-tricyanophenyl group. The mechanistic features for the formation of insoluble polymers were also described.

Photochemical and photophysical properties of polymers bearing electron-donating and electron-accepting groups have been widely investigated in recent years.$^{1)}$ Formation of intramolecular excimers, exciplexes, and radical ion species has been observed upon irradiation of such polymers in solution. However, polymer-modifying photochemical reactions that proceed via these reactive species and lead to new functionalized polymers have not been much developed. We now report the photosubstitution and photo-cross-linking reactions of poly(4-trimethylsilylmethylstyrene) (2) in solution in the presence of polycyanobenzenes.

Polymer 2 was prepared by the radical polymerization of 4-trimethylsilylmethylstyrene (1)$^{2)}$ using azobisisobutyronitrile (AIBN) as an initiator, and it was purified by dissolving in a minimum quantity of benzene and reprecipitating with methanol for several times.

Irradiation of a benzene-acetonitrile (3:2) solution containing 2 (95 mg) and p-dicyanobenzene (p-DCB, 0.5 mmol) in the presence of phenanthrene (Phen, 0.2 mmol) as a photosensitizer under argon atmosphere with a high-pressure mercury lamp through a Pyrex filter gave an insoluble polymer 3 in organic solvents, which precipitated during the photoreaction in high yields. Similar irradiations of 2 in the presence of Phen and various amounts of p-DCB also afforded the insoluble polymer 3. The yields of the polymer 3 decreased with decreasing the added amounts of p-DCB.



In the absence of p-DCB, 3 was not formed and the starting materials, 2 and Phen, were recovered quantitatively. The photoreaction of 2 with p-DCB also occurred in THF-acetonitrile (3:2) to give 3. But, no photoreaction occurred in benzene, resulting in the completely recovery of the starting materials. Triphenylene was also served as sensitizer. However, anthracene and pyrene did not sensitize this photoreaction. In the absence of these aromatic hydrocarbons, the insoluble polymer was slowly produced.

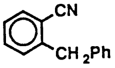
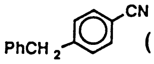
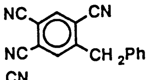
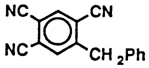
The structure of 3 was determined from its IR spectrum, electron probe micro analysis, and elemental analysis. Polymer 3 showed the absorption of cyano group at 2230 cm^{-1}. The intensity of this absorption increased with increasing the added amounts of p-DCB. The elemental analysis showed that the N content in 3 also increased with increasing the added amounts of p-DCB. The electron probe micro analysis showed that the Si content in 3 decreased compared with that in 2. From these results, we concluded that the trimethylsilyl group of 2 was partially replaced by 4-cyanophenyl group. The extent of the replacement of trimethylsilyl group was estimated from the elemental analysis of the polymers and the maximal yield was ca. 50%.

The photoreaction of 2 with o-dicyanobenzene (o-DCB) under similar conditions also afforded an insoluble polymer 4. In this polymer, the trimethylsilyl group was found to be partially replaced by 2-cyanophenyl group. Although the photoreaction of 2 with m-dicyanobenzene (m-DCB) in the presence of Phen gave an insoluble polymer 5, Phen and m-DCB were recovered quantitatively in this photoreaction. The polymer 5 did not contain 3-cyanophenyl group. However, the content of Si atom in 5 decreased compared with that in 2. These results strongly suggest that the photoreaction of 2 with m-DCB afforded a cross-linked polymer via the radical coupling of benzyl radical.

The photoreaction of 2 with 1,2,4,5-tetracyanobenzene (TCNB) in the presence of Phen afforded a soluble polymer 6. The IR spectrum of 6 showed that the trimethylsilyl group of 2 was replaced to a large extent by 2,4,5-tricyanophenyl group in this polymer. The addition of $Mg(ClO_4)_2$ afforded an insoluble polymer 7. When the co-polymer of styrene and 1 (19:1 ratio) was used in place of 2 as a substrate, a soluble polymer 8 was obtained. The ^1H NMR and ^{13}C NMR spectra of 6 and 8 showed that these polymers contain the cyanophenyl.

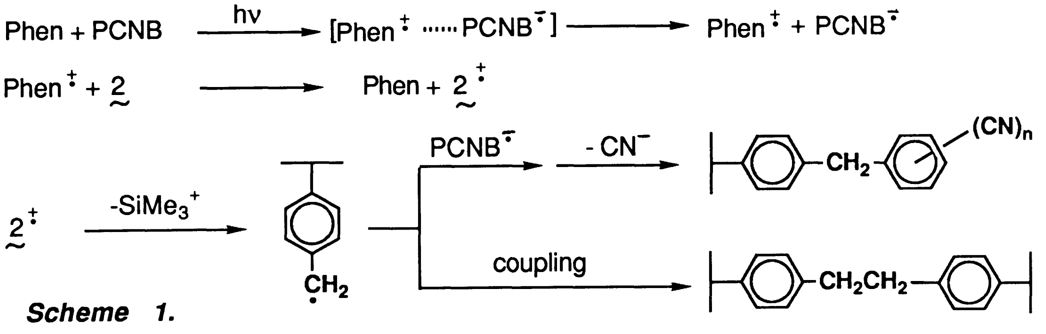
The above structural elucidation of the polymers suggests that the insoluble polymers are produced by the radical coupling of benzylic radical and the soluble polymers are produced by the photosubstitution of trimethylsilyl group in the polymers with cyanoaromatics. This is supported by the products analyses in the photoreactions of monomer models; that is the photoreactions of benzyltrimethylsilane with polycyanobenzenes (PCNB). The results are shown in Table 1. The yield of 1,2-diphenylethane (9) in these photoreactions depended on the nature of PCNB. In the cases of o-, p-DCB, both 9 and the substitution products were produced. In the case of m-DCB, only the coupling product 9 was produced. On the other hand, the substitution product was obtained in the case of TCNB. These results are consistent with the fact that insoluble polymers were formed in the photoreaction of 2 with o-, m-, and p-DCB.

Table 1. Photoreactions of Polycyanobenzenes with 2 and Benzyltrimethylsilane in the Presence of Phenanthrene

PCNB	Product(s) (Yield(s)/%)		
	2		$PhCH_2SiMe_3$[a)]
o-DCB	4 (94)	insoluble	9 (32) +  (17)
m-DCB	5 (≥95)	insoluble	9 (45)
p-DCB	3 (≥95)	insoluble	9 (18) +  (63)
TCNB[b)]	6 (85)	soluble	9 (trace) +  (90)
TCNB[c)]	7 (≥95)	insoluble	9 (15) +  (70)

a) The molar ratio; PCNB : $PhCH_2SiMe_3$: Phen = 1 : 1 : 0.4.
b) See Ref. 5. c) In the presence of $Mg(ClO_4)_2$ (0.1 mmol).

From these results, we propose the mechanism of Scheme 1 for the photoreaction of **2** with PCNB in solution involving photoinduced electron transfer. The carbon-silicon bond of **2**$^{+\cdot}$ is cleaved by assistance of nucleophile (probably acetonitrile), giving benzyl radical and trimethylsilyl cation species. When p-DCB and o-DCB are used as electron acceptor, the benzyl radical attacks DCB$^{-\cdot}$ to give the substitution products. This is the major pathway for these photoreactions. A minor pathway is the coupling of benzyl radical to give insoluble polymers. When m-DCB is used, the coupling reaction of the benzyl radical predominates to give insoluble cross-linked polymers. On the other hand, when TCNB is used, only the photosubstitution occurs to give **6**.



Scheme 1.

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References

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3) Tg 89.5 °C, Mn 3.38 x 10^4, Mw 7.66 x 10^4, Mw/Mn = 2.27, ^{1}H NMR ($CDCl_3$) δ -0.03 (br s, 9H), 1.35 (br s, 2H), 1.8 (br s, 1H), 1.95 (br s, 2H), 6.2-6.8 (m, 4H); ^{13}C NMR δ 26.4, 39.9, 45.0, 127.5, 136.8, 141.4.

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