Preparation of Photocatalytically Active Polyamine and Polyamide Containing Acridine Group in the Main Chain by Palladium-catalyzed Polycondensation

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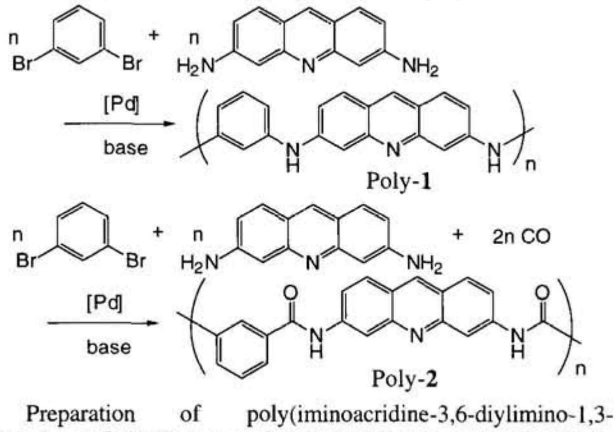
(Received April 8, 1998; CL-980260)

Palladium-catalyzed polycondensation and carbonylation polycondensation of 1,3-dibromobenzene and 3,6-diaminoacridine (proflavine) afforded new polyamine and polyamide with acridine units in the main chain. The polymers showed strong fluorescence and photosensitized reduction of methyl viologen.

Polymers containing photosensitizers have been investigated for potential use in electron and energy transfers.[1,2] Ruthenium-tris(bipyridyl) complexes are some of the most studied photosensitizers, and a variety of polymers containing the complex structure in the main chain as well as in pendant groups have been reported.[2] Meanwhile, 3,6-diaminoacridine (proflavine) has also been extensively studied as a photosensitizer for photoinduced hydrogen evolution from water.[3] However, there have been few reports on preparation of polymers containing the proflavine structure[4] and photoactivities of the polymers.[4c] Molecular design and preparation of polymers with well-defined structures would be crucial for the study of the new photoactive polymers.

On the other hand, numerous reports have been published on palladium complex catalyzed polycondensation to give various poly(arylene)s, aromatic polyesters, polyamides, and polyamines.[5] On these bases, we have prepared new polyamine and polyamide containing acridine units in the main chain by the Pd-catalyzed polycondensation of proflavine with 1,3-dibromobenzene and the Pd-catalyzed carbonylation polycondensation of proflavine and 1,3-dibromobenzene with carbon monoxide, respectively. We here report the results of preparation and preliminary photosensitizing properties of the polymers.



Preparation of poly(iminoacridine-3,6-diylimino-1,3-phenylene) (Poly-**1**) was carried out by stirring a mixture of 1,3-dibromobenzene (237 mg, 1 mmol), proflavine (210 mg, 1 mmol), NaO-*t*-Bu (289 mg, 3 mmol), tris(dibenzylideneacetone)-dipalladium (23 mg, 0.025 mmol), and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (47 mg, 0.075 mmol) in dioxane (15 cm^3) at 100 °C for 16 h under nitrogen.[5d] After cooling, the mixture was poured into methanol, and a reddish powder of Poly-**1** was washed thoroughly with aqueous ammonia and methanol (268 mg, 95% yield). Anal. Found: C, 79.8; H, 5.0; N, 13.3; Br, 1.5%. Calcd for $(C_{19}H_{13}N_3)_n$: C, 80.5; H, 4.6; N, 14.8%.

Poly(iminoisophthaloyliminoacridine-3,6-diyl) (Poly-**2**) was prepared according to a literature procedure.[5c] Tetrakis(triphenylphosphine)palladium (70 mg, 0.06 mmol) was added to a DMF (5 cm^3) solution of proflavine (210 mg, 1 mmol) and 1,3-dibromobenzene (237 mg, 1 mmol) in a Schlenk tube under nitrogen at room temperature. The tube was purged with carbon monoxide and warmed with stirring at 115 °C. To the mixture 1,8-diazabicyclo[5.4.0]-7-undecene (0.37 g, 2.4 mmol) was

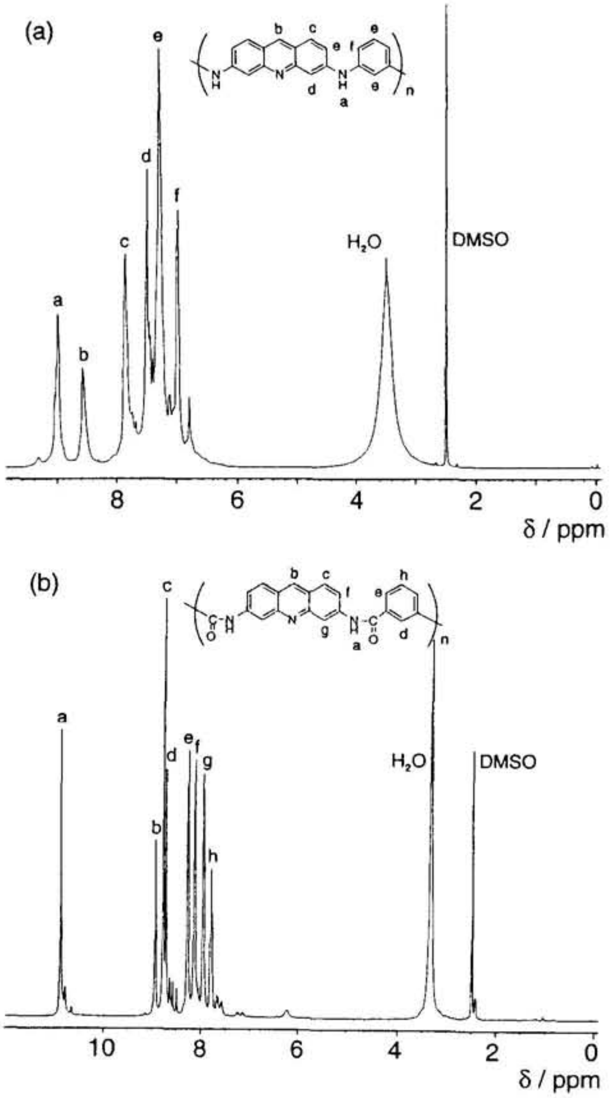


Figure 1. ^1H NMR spectra of (a) Poly-**1** and (b) Poly-**2** in DMSO-d_6.

added, and the reaction mixture was stirred at 115 °C for 3 h. After cooling, the mixture was poured into methanol. A yellow powder of Poly-**2** was washed thoroughly with methanol and $CHCl_3$ (336 mg, 99 % yield). Anal. Found: C,72.2; H, 4.9; N, 12.1; Br, 1.2%. Calcd for $(C_{21}H_{13}N_3O_2)_n$: C, 74.3; H, 3.9; N, 12.4%.

Poly-**1** and Poly-**2** are soluble in DMF, DMSO, NMP, and formic acid. Molecular weights calibrations of the polymers by GPC (eluent = LiCl/DMF (0.01 M); polystyrene standards) showed M_n = 11300, M_w = 29200 for Poly-**1** and M_n = 32600, M_w = 47800 for Poly-**2**, respectively.

Figure 1 shows the ^1H NMR spectra of the polymers in DMSO-d_6. No peak assignable to the NH_2 group (δ5.8 ppm for proflavine) is observed, and the ratios of the peak area agree with the suggested assignment. The structure of the polymers was also confirmed by IR and ^{13}C NMR spectroscopy.[6]

A DMF solution of Poly-**1** shows strong fluorescence with a peak at 525 nm when irradiated by 440 nm light. Poly-**2** also shows strong fluorescence in DMF with a main peak at 512 nm and a subpeak at 460 nm when irradiated by 390 nm light. However, adding acidic solvents such as formic acid to the solutions of the polymers led to a quench of the fluorescence, presumably due to protonation of proflavine unit.[3c]

Proflavine is known to undergo photoinduced electron-transfer with electron acceptors such as methyl viologen (1,1'-dimethyl-4,4'-bipyridinium salt, MV^{2+}) in the presence of electron donors such as ethylenediaminetetraacetic acid.[3] The polymers have also been expected to act as a photosensitizer. Figure 2 shows the spectral changes observed on light irradiation of Poly-**1** in the presence of triethanolamine and MV^{2+} dichloride in a mixture of DMF-H_2O (9/1, v/v) under nitrogen.[7] Illumination with visible light (436 nm) led to the appearance of new peaks at 400 and 608 nm, while the absorption peak of Poly-**1** at 438 nm remained intact. The new peaks at 400 and 500-700 nm were characterized by viologen radical cation ($MV^{+\bullet}$).[3a,8] The absorption peak at 608 nm increased in proportion to light irradiation time, and the spectrum was restored by exposure to air. These results indicate Poly-**1** serves as the photosensitizer for photoinduced reduction of MV^{2+} to $MV^{+\bullet}$ similar to proflavine.[3]

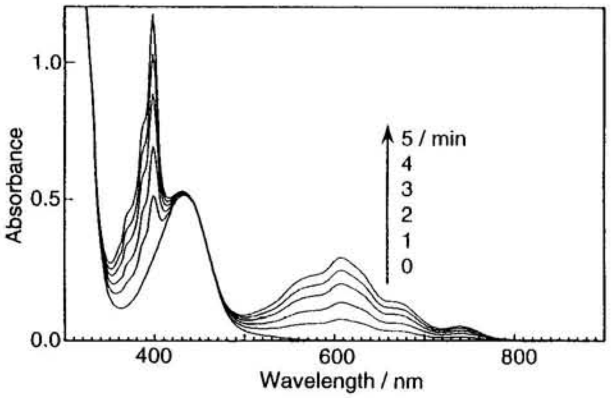


Figure 2. Changes in the absorption spectrum of a DMF/H_2O (9/1, v/v) solution containing Poly-**1** (2 x 10^{-5} M of monomer unit), MV^{2+} (1 x 10^{-3} M), and triethanolamine (5 x 10^{-3} M) during light irradiation (436 nm) under N_2.

Poly-**2** also showed photocatalytic activity for the reduction of MV^{2+} with triethanolamine in an aqueous DMF under an anaerobic condition and a similar changes in the absorption spectrum when irradiated at 405 nm light.[7]

As described above, new polyamine and polyamide containing acridine units in the main chain were prepared by the Pd-catalyzed polycondensation, and the polymers exhibited photoinduced electron-transfer reactivity. Although the optical properties of the polymers such as photoexcited lifetime and photosensitivity are not clear in the present study, the polymers could be expected to provide new photosensitizing films for solar energy conversion. Further studies are in progress, including preparation of polymer derivatives and applications of the polymers.

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6 Poly-**1**: IR (KBr, cm^{-1}): 3390, 3050, 1590, 1490, 1455, 1390, 1290, 773, 695; ^{13}C NMR (DMSO-d_6, ppm): δ 105.4, 108.9, 112.0, 119.5, 120.4, 129.5, 130.0, 134.5, 142.9, 145.3, 150.9. Poly-**2**: IR (KBr,cm^{-1}): 3280, 3065, 1655, 1617, 1573, 1535, 1490, 1338, 1298, 1250, 804, 717; ^{13}C NMR (DMSO-d_6, ppm): δ 115.7, 121.0, 122.9, 127.3, 128.8, 129.0, 131.1, 135.1, 135.2, 140.7, 149.6, 165.7.

7 Light irradiation was carried out with a 500 W ultra high-pressure mercury lamp. Wavelength was selected at 436 nm using Corning 7-59 and 3-73 cutoff filters, and at 405 nm using Corning 7-59 cutoff filter and an aqueous solution filter (0.25 M $NaNO_3$ / 0.1 M $NaNO_2$), respectively; F. G. Kari, S. Hilger, and S. Canonica, *Environ. Sci. Technol.*, **29**, 1008 (1995).

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