Radiation Induced One-Step One-pod Polymerization of Functional Conjugated Molecules

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1. Introduction

Metal-mediated cross-coupling reactions for the formation of aryl-aryl σ bonds such as Stille coupling have been extensively developed since 1960's.[1] These syntheses need severe experimental conditions, such as an inert atmosphere, strictly anhydrous solvents, and an use of a base or a high temperature. Many scientists have searched the simpler methods for forming the aryl-aryl σ bond.[2] Carbon radicals are important reactive intermediates in organic chemistry and are usually generated by the homolytic cleavage of the C-X bond: X= H, halogen, heteroatom, etc. The radical-mediated carbon-carbon bond formation based on the one-electron reduction of carbocations using dissociative electron attachment (DEA) has been extensively studied to date.[3] The dissociative process occurs when the bond dissociation energy is smaller than the electron affinity of the leaving group, and typically observed for C-Halogen bonds giving a set of a carbon centered radical and a haloanion.[4] The saturated tertiary amines such as triethylamine (TEA) and pyridine, are good electron donors and do not attach electrons significantly in their ground electronic states.[5] (Pyridine has a lone pair on the nitrogen atom and the transition states of pyridiniumyl radical cations, pyridine excited molecules and pyridyl radicals are stabilized at the carbon adjacent to the nitrogen atom.[6])

In this study, the metal-free one-step cross coupling reaction to form C-C σ bond between fluorene groups was investigated through DEA, and the reaction mechanisms were also demonstrated.

2. Experimental

2,7-dibromo-9,9'-di-*n*-hexylfluorene (DHF-Br₂) was used as received from Aldrich. Other solvents and chemicals were purchased from Wako Chemical Co. DHF-Br₂ was dissolved in various solvents: tetrahydrofuran (THF), cyclohexane, TEA/ benzene, TEA/ toluene, pyridine/ benzene, or pyridine at 10 - 20 wt% conc. at room temperature. The solutions were bubbled with dry Ar for 5 min or sealed under vacuum, and irradiated with the ⁶⁰Co γ -ray source at 27 - 430 kGy at ISIR, Osaka university.[7] The absorption spectra after the irradiation were measured with the corresponding solution diluted by benzene at 4.70×10^{-5} mol dm⁻³ conc. by using Shimadzu UV-3100PC spectrometer. Fluorescence measurement was performed using Perkin-Elmer LS-50B spectrophotometer. Mass spectra were obtained by PerSeptive Biosystems Voyager Linear DE-H MALDI-TOF MS. Molecular weight was measured using Shimadzu LC-10AT gel-permeation chromatography system.

Scheme 1

3. Results and discussion

The chemical structures of the oligomers ($n = 1 - 3$) were shown in scheme 1. UV-Vis absorption spectra after γ -irradiation are shown in fig. 1, and the differential absorption spectra of the solutions before / after the irradiations are shown

in fig.2. The dimer (DHF2-Br₂) and trimer (DHF3-Br₂) absorption peaks are overlapped at around 320-350 nm.[1] The UV-Vis absorption bands of DHF-Br₂, DHF2-Br₂, and DHF3-Br₂ were centered at 314 nm ($E_A = 3.92$ eV), 320 - 329 nm (3.74 - 3.86 eV), and 340 - 360 nm (3.43 - 3.63 eV), respectively. It was previously reported that a neutral 1-D singlet exciton state resulted that these electronic transitions are attributed to $\pi-\pi^*$ excitation of the fluorene backbones.[1]

Fig. 1. Absorption spectra of DHF-Br₂ solutions in various solvents at 10 ~ 20 wt% conc. after γ -ray irradiation at 360 ~ 430 kGy (r.t.).

The fluorescence spectra and excitation spectra were also measured to confirm the formation of DHF2-Br₂ and DHF3-Br₂. The conversion ratios of DHF2-Br₂ and DHF3-Br₂ in various solvents are summarized in Table 1. The total polymerization yield of DHF-Br₂ in THF, cyclohexane, TEA/ benzene, and TEA/ toluene are considerably lower than those in benzene, pyridine/ benzene mixtures, and pyridine. In pyridine/ benzene mixtures, the conversion ratio is decreased with increase of the benzene ratio. This suggests that pyridine is one of the best choices for polymerization than other solvents used in the present study. Based on our previous research[6], the primary reactions induced by radiations in pyridine (C₅H₅N) are suggested as follows:

Initially, pyridiniumyl radical cations (C₅H₅N^{•+}) and excess electrons are formed via ionization by irradiation. The electron reacts with DHF-Br₂ which has the high electron affinity. DHF-Br₂

Fig. 2. Differential absorption spectra of the solutions before / after the irradiation.

Fig. 3. Dependence of exposure dose on conversion ratios of DHF2-Br₂ and DHF3-Br₂, which was collected from the absorption at 324 and 345 nm in pyridine for DHF2-Br₂ and DHF3-Br₂, respectively.

radical anion ([DHF-Br₂]^{•-}) leads to DHF-Br radical ([DHF-Br][•]) and bromine anion (Br⁻) by DEA. DHF-Br[•] reacts with each other, giving rise to 2,7-dibromo-9,9'-di-*n*-hexylfluorene dimer (DHF2-Br₂). The trimerization also occurs through the similar processes. Based on the yield of DHF2-Br₂, the G value (number of reactions per 100 eV absorbed) of aryl-aryl bond formation was estimated as 0.36 molecules/ 100 eV. The free ion yield of pyridine was reported as 0.4 molecules/ 100 eV[6], which corresponds to the G value of the bond formation. C₅H₅N^{•+} can react with pyridine, leading to bipyridyl and (C₅H₅N)_n^{•+} through sequential polymerization steps.[6] Thus, it is plausible that Br⁻ is scavenged by (C₅H₅N)_n^{•+}, and stabilized by salting out. The free ion yield of benzene (0.05 molecules/ 100 eV) [8] is very lower than that in pyridine. This is the case giving the considerable drop in the conversion ratio of

Table 1. Conversion ratio of DHF2-Br₂ and DHF3-Br₂ in various solvents.

Entry	DHF-Br ₂ conc. (wt %)	Exposure dose (kGy)	DHF2-Br ₂ Conversion (%)	DHF3-Br ₂ Conversion (%)
Pyridine	10	360	10.0	0.43
Pyridine/Benzene: 8/1	10	360	9.7	0.50
Pyridine/Benzene: 5/1	10	360	9.3	0.48
Pyridine/Benzene: 2/1	10	360	9.5	0.40
Pyridine/Benzene: 1/1	10	360	9.4	0.42
Pyridine/Benzene: 1/2	10	360	9.6	0.46
Pyridine/Benzene: 1/5	10	360	7.6	0.11
Pyridine/Benzene: 1/8	10	360	7.8	0.12
Pyridine/Benzene: 1/10	10	360	7.7	0.11
Benzene	10	360	5.2	0.00
Cyclohexane	10	360	2.2	0.067
THF	20	430	1.4	0.33
TEA / Toluene: 1/10	10	430	2.7	0.40
TEA / Benzene: 1/10	10	430	3.2	0.00

oligomerization in benzene. The irradiation dose dependence on the conversion ratio of DHF2-Br₂ and DHF3-Br₂ in pyridine is displayed in fig. 3. The yield of the dimers shows rapid growth in doses of 0 – 50 kGy, followed by gradual increase with the higher irradiation dose. It may be due to the consumption of monomers and dimers via sequential steps of oligomerization and/or the inhibition effects of accumulated C₅H₅N⁺, H⁺, or C₅H₄N[•] for the oligomerization. The other possibility of the process of oligomerization is also assumed that [DHF-Br₂]^{•-} and C₅H₅N⁺ form the CT complex. Consequently, Br⁻ is eliminated from [DHF-Br₂]^{•-} by C₅H₅N⁺ to give [DHF-Br][•] and the salts of Br⁻ with C₅H₅N⁺.

In summary, the polymerization of DHF-Br₂ in the condensed phase was demonstrated by γ -irradiation through DEA. This method is very simple and easy metal-free one-step cross coupling reaction to form C-C σ bond between aryl groups. The formation of DHF2-Br₂ and DHF3-Br₂ in the various solvents was confirmed by optical and mass spectroscopy measurements. The conversion ratio of polymerization in pyridine is higher than that in the other solvents. It suggests that the formation yield of the C-C σ bond between aryl groups is increased with the formation of the salts of Br⁻ with (C₅H₅N)_n^{•+}.

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