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# Preparation of soluble and fluorescent poly(arylene)s by 1,3-dipolar polycycloaddition and properties of the polymers

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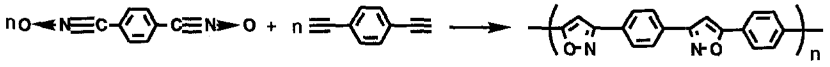
## Summary

1,3-Dipolar polycycloadditions of 2,3,5,6-tetramethylterephthalodinitrile oxide with 3,6-diethynyl-9-hexylcarbazole or 2,6-diethynylpyridine afford novel soluble poly(arylene)s. The polymers show strong fluorescence in solutions as well as in cast films with peaks at 340-490 nm.

## Introduction

Nitrile-N-oxide is an important class of 1,3-dipoles and used to form isoxazoline and isoxazole derivatives (1), and a number of polymers have been prepared by 1,3-dipolar polycycloadditions of dinitrile N-oxide compounds with olefins or diynes (2).


(1)

However, the solubility of the polymers so far prepared in common organic solvents has been low, and only a few reports on their detail characterization and optical properties in solutions as well as in cast films have been published.

On the other hand, potential usefulness of organic materials for making optoelectronic devices such as light-emitting diodes, solar cells, and waveguides is currently expanded, and a number of oxazole and oxadiazole derivatives have been synthesized and utilized as hole and/or electron transporting materials and emitting materials to make the devices (3). Recently, polymers containing oxadiazole unit in the main chain have been prepared, and applied researches of the polymers have also been carried out (4).

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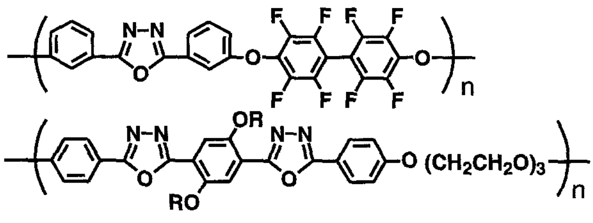

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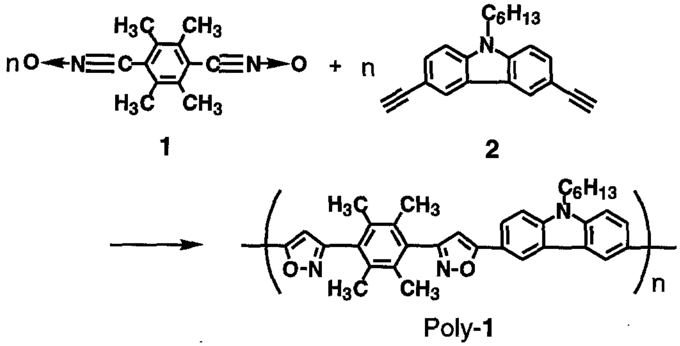
However, to our knowledge, applied studies of isoxazole derivatives, isomeric compounds of oxazole derivatives, for the optoelectronic materials have been limited (5); much less attention has been paid to polymers with isoxazole units.

These informations prompted us to design new soluble poly(arylene)s containing isoxazole units as well as optically active heteroaromatic units. We now report preparation of following poly(arylene)s by 1,3-dipolar polycycloadditions of 2,3,5,6-tetramethylterephthalodinitrile oxide **1** with 3,6-diethynyl-9-hexylcarbazole **2** and 2,6-diethynylpyridine **3** and their properties.



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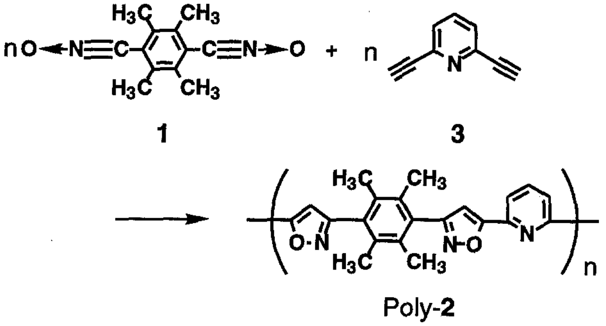


(3)

## Experimental

### *Materials*

**1** (2g), **2** (6), **3** (7), and 3-ethynyl-9-hexylcarbazole **4** (6) were prepared by modifying the reported methods.

### *Polymerization*

Reaction of **1** (108 mg, 0.5 mmol) and **2** (150 mg, 0.5 mmol) in 10 $cm^3$ of N,N-dimethylformamide DMF at reflux temperature (153 °C) for 24 h with stirring under nitrogen gave a pale-yellow DMF solution of Poly-**1**. The solution was cooled to room temperature and poured into acetone to precipitate the polymer. The precipitate was separated and washed thoroughly with methanol and acetone. Pale-yellow powder of Poly-**1** was purified by reprecipitation from $CHCl_3$/acetone (255 mg, 99% yield). Anal. Found: C, 78.3%, H, 6.5%, N, 8.0%. Calcd for $(C_{34}H_{33}N_3O_2)_n$: C, 79.2%, H, 6.5%, N, 8.2%. IR (KBr, $cm^{-1}$): 2924, 1604, 1476, 1428, 1407, 1150, 949, 881, 790. $^1H$ NMR ($CDCl_3$, ppm): 0.9 (3H), 1.2-1.5 (6H), 1.9 (2H), 2.2 (12H), 4.3-4.5 (2H), 6.6 (2H), 7.5 (2H), 8.0 (2H), 8.7 (2H). $^{13}C$ NMR ($CDCl_3$, ppm): 13.9, 17.6, 22.5, 26.9, 28.9, 31.5, 43.5, 99.9, 109.6, 118.6, 119.5, 123.1, 124.5, 130.7, 133.6, 141.9, 164.0, 170.9.

Preparation of Poly-**2** was carried out analogously. Poly-**2**: 37% yield. Anal. Found: C, 72.3%, H, 5.2%, N, 11.6%. Calcd for $(C_{21}H_{17}N_3O_2)_n$: C, 73.5%, H, 5.0%, N, 12.2%. IR (KBr, cm$^{-1}$): 2923, 1561, 1427, 1401, 1357, 1281, 990, 949, 892, 805, 765, 649. $^1$H NMR 2.1 (12H), 6.9-7.0 (3H), 8.1 (2H). ($CDCl_3$, ppm): . $^{13}$C NMR ($CDCl_3$, ppm): 17.6, 104.7, 121.5, 130.3, 133.7, 138.5, 147.0, 164.2, 168.8.

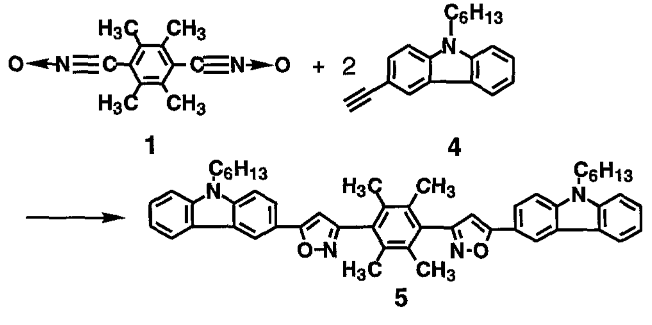
Model compound of Poly-**1**, **5** (see Eq. (4)), was also prepared analogously by using **1** (108 mg, 0.5 mmol) and **4** (275 mg, 1.0 mmol). Purification of **5** was carried out by column chromatography (262 mg, 73% yield). Anal. Found: C, 81.0%, H, 7.0%, N, 7.1%. Calcd for $(C_{52}H_{54}N_4O_2)$: C, 81.1%, H, 7.1%, N, 7.3%. IR (KBr, cm$^{-1}$): 2929, 1602, 1493, 1471, 1412, 1311, 1245, 1157, 948, 880, 794 ,745, 730. $^1$H NMR ($CDCl_3$, ppm): 0.9 (t, 6H), 1.2-1.4 (m, 12H), 1.9 (quint, 4H), 2.2 (s, 12H), 4.3 (t, 4H), 6.5 (s, 2H), 7.3 (quint, 2H), 7.4-7.6 (m, 6H), 8.0 (dd, 2H), 8.2 (d, 2H), 8.6 (d, 2H). $^{13}$C NMR ($CDCl_3$, ppm): 14.0, 17.6, 22.5, 26.9, 28.9, 31.5, 43.3, 99.5, 109.5, 118.4, 118.5, 119.6, 120.7, 122.8, 123.2, 123.7, 126.4, 130.7, 133.6, 141.0, 141.4, 164.0, 171.3.

### *Measurements*

IR spectra, NMR spectra, UV-visible spectra, and fluorescence spectra were recorded on a JASCO FT/IR-230 spectrometer, JEOL JNM-FX90Q or JNM-A400 NMR spectrometer, Shimadzu UV-265FS spectrometer, and Hitachi 650-10S spectrometer, respectively. Elemental analyses were carried out with a Yanaco CHN Corder MT-5. GPC analyses were performed with a JASCO 880 system using a Shodex K-804L column using $CHCl_3$ as a eluent (polystyrene standards). TGA curves were recorded on a Rigaku Thermal Analysis Station TAS 100.

## Results and Discussion

Table 1 summarizes the results of the preparation of Poly-**1** and Poly-**2**. As shown in Table 1, thermal polycycloaddition of **1** with **2** gives Poly-**1** in good yields in DMF over 100 °C. Use of toluene as a solvent also affords Poly-**1** in a good yield, however, in this case, the reaction proceeds in heterogeneous system at its initial period. The reaction in 1,1,2,2,-tetrachloroethane affords Poly-**1** with low molecular weight. The polycycloaddition of **1** with **3** in DMF affords Poly-**2**, however, the yield is low. This is because lower molecular weight fraction of Poly-**2** is presumably lost in the reprecipitation from methanol and acetone. Model reaction of **1** with **4** gives **5** under the same condition. Elemental analysis data of Poly-**1**, Poly-**2**, and **5** are reasonable for the corresponding compounds, respectively.



(4)

Table 1 Results of the Preparation of Poly-**1** and Poly-**2**[a)]

| Polymer | Solvent | Temp. / °C | Yield / % | $M_n \times 10^{-3}$ [b)] | $M_w \times 10^{-3}$ [b)] | $M_w/M_n$[b)] |
|---|---|---|---|---|---|---|
| Poly-**1** | DMF | Reflux | 99 | 10.5 | 14.2 | 1.36 |
| Poly-**1** | DMF | 100 | 74 | 8.9 | 11.2 | 1.27 |
| Poly-**1** | toluene | 100 | 76 | 13.4 | 26.7 | 1.99 |
| Poly-**1** | TCE[c)] | 100 | 83 | 5.0 | 6.1 | 1.21 |
| Poly-**2** | DMF | Reflux | 37 | 9.2 | 11.9 | 1.30 |
| Poly-**2** | DMF | 100 | 27 | 6.8 | 8.4 | 1.25 |

a) Stirred for 24 h under nitrogen.
b) Determined by GPC with polystyrene standards.
c) 1,1,2,2,-tetrachloroethane.

In contrast to low solubility of the reported poly(arylene)s prepared by the 1,3-dipolar polycycloaddition in common organic solvents except for conc. $H_2SO_4$, Poly-**1** and Poly-**2** are soluble in organic solvents such as $CHCl_3$, $CH_2Cl_2$, warm DMF, warm DMSO, and warm NMP. Their molecular weights have been estimated by GPC.

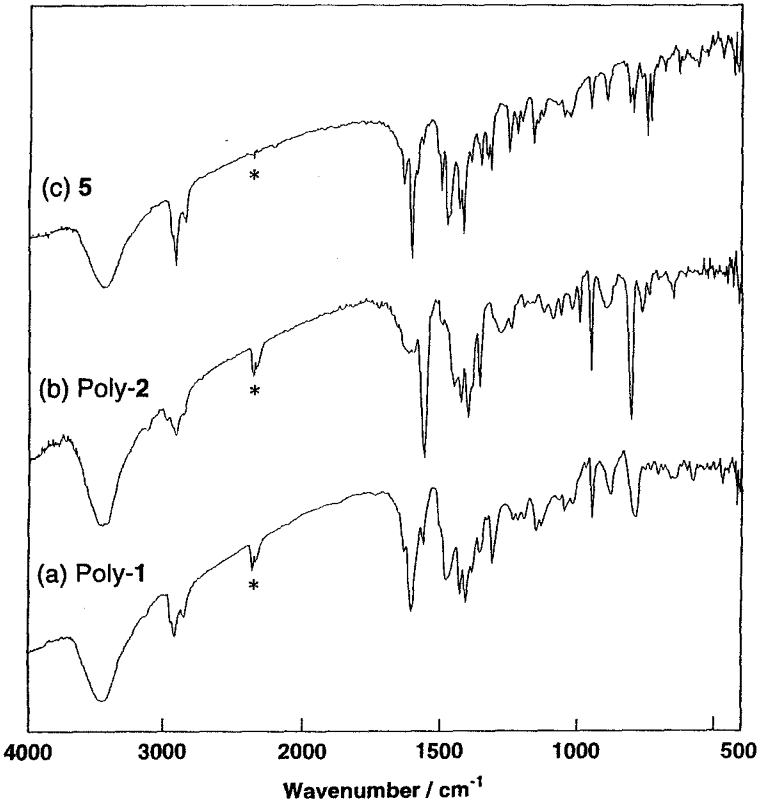
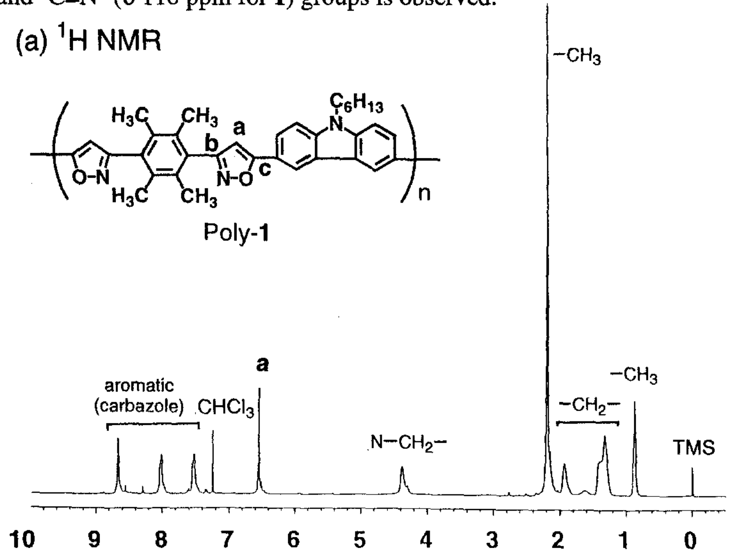


Figure 1. Infrared spectra of (a) Poly-**1**, (b) Poly-**2**, and (c) **5**. Peaks with * mark are due to $CO_2$ in air.

Figure 1 shows IR spectra of Poly-**1**, Poly-**2**, and **5**. The peaks due to skeletal ring vibrations ν(C=C, C=N) (1650-1600 cm$^{-1}$ for Poly-**1**) resemble those of **5**, and the bands due to ν(C≡N) (2297 cm$^{-1}$ for **1**), ν(C≡C) (2099 cm$^{-1}$ for **2**, 2105 cm$^{-1}$ for **3**, 2103 cm$^{-1}$ for **4**), and ν(≡C-H) (3267 cm$^{-1}$ for **2**, 3276 cm$^{-1}$ for **3**, 3305 cm$^{-1}$ for **4**) of the starting materials are not observable in the IR spectra of the products.

Figure 2 shows $^1$H and $^{13}$C NMR spectra of Poly-**1** in CDCl$_3$. The peaks are assigned by comparing the position of the peaks with those of monomers and **5**. In Fig. 2(a), a peak attributable to 4-H proton of the isoxazole ring is observed at δ 6.6 ppm, and no peak assignable to the ≡C-H (δ 3.1 ppm for **2**) group is observed. The ratios of the peak area assist the structure suggested for Poly-**1**. The $^{13}$C NMR spectrum of Poly-**1** shows 18 peaks, and three peaks at δ 100, 164, and 171 ppm are due to the carbons of isoxazole ring. As depicted in Fig. 2(b), no peak assigned to the -C≡C- (δ 76 and 82 ppm for **2**) and -C≡N- (δ 118 ppm for **1**) groups is observed.

(a) $^1$H NMR



(b) $^{13}$C NMR

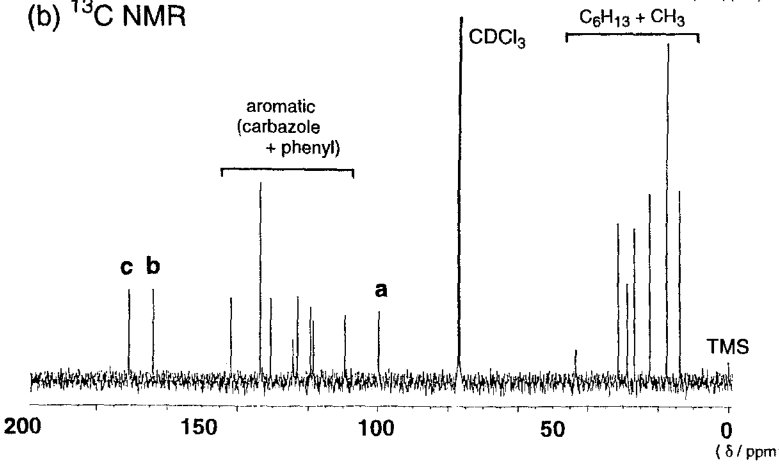


Figure 2. $^1$H (a) and $^{13}$C (b) NMR spectra of Poly-**1** in CDCl$_3$.

The structure of Poly-**2** is also confirmed by IR and NMR analyses. In $^1$H NMR spectrum of Poly-**2** in $CDCl_3$, a peak at δ 6.9 ppm assignable to 4-H proton of the isoxazole ring is observable. $^{13}$C NMR spectrum of Poly-**2** depicts three peaks at δ 105, 164, and 169 ppm assigned to the carbons of the isoxazole ring.

Thus, the elemental analyses, molecular weights, and IR and NMR data indicate the proposed structures of the polymers. Accordingly, the formation of a furoxan unit due to the dimerization of nitrile oxide group (1,8) is negligible in these polymers.

The UV-visible spectrum of Poly-**1** in $CHCl_3$ exhibits four absorption peaks at 261, 281, 308, and 334 nm presumably based on π-π* transition, while Poly-**2** shows two π-π* absorption peaks at 282 and 315 nm.

Poly-**1** shows strong fluorescence in solutions as well as in cast films. Figure 3 shows fluorescence spectra of Poly-**1** in DMF and $CHCl_3$, and model compound **5** in $CHCl_3$. As shown in Fig. 3(a), the fluorescence spectrum of Poly-**1** in DMF exhibits a main peak at 390 nm and a subpeak at 372 nm, whereas Poly-**1** in $CHCl_3$ exhibits two fluorescence peaks at 392 nm and about 440 nm (Fig. 3(b)). The casted films from $CHCl_3$ and DMF solutions of Poly-**1** give similar fluorescence spectra to that of the $CHCl_3$ solution of Poly-**1**. The fluorescence spectra of **5** in $CHCl_3$ and DMF (Fig. 3(c)) are essentially similar to that of Poly-**1** in DMF. The shape of the fluorescence spectra is essentially unvaried over a relatively wide range of concentrations ($10^{-7}$ - $10^{-3}$ M of the repeating unit of Poly-**1**). A number of reports on emission properties of the poly-(vinylcarbazole) and its related polymers have been published (9), and partially overlapped second excimer fluorescence (at about 370 nm) and sandwich excimer fluorescence (at about 420 nm) between neighboring carbazole units in the polymer chain have been observed. These results suggest Poly-**1** forms partially overlapped

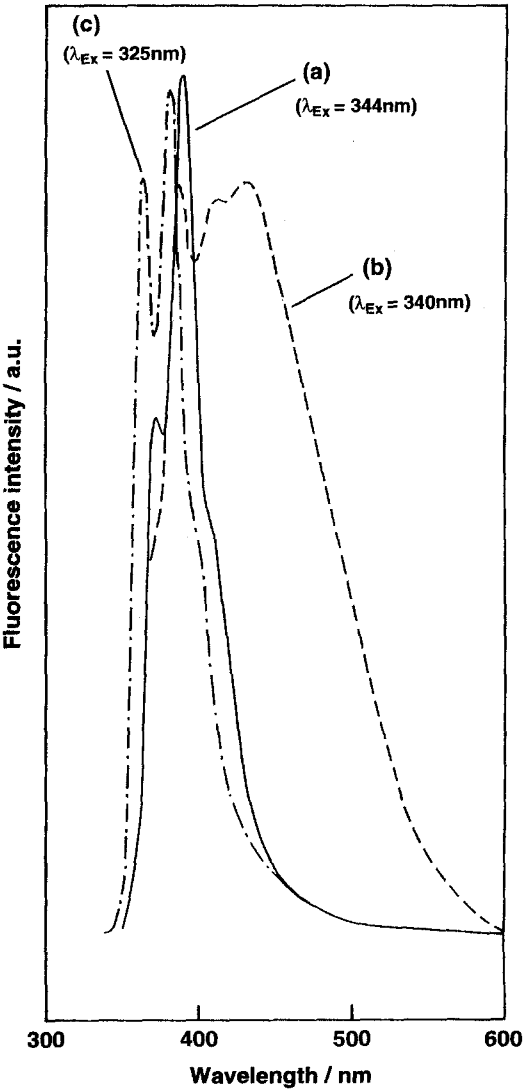


Figure 3. Fluorescence spectra of Poly-**1** in DMF (a) and in $CHCl_3$ (b), and **5** in $CHCl_3$ (c).

excimer and sandwich excimer between the intermolecular carbazole units in the polymer chain.

Poly-**2** also shows moderately strong fluorescence in DMF and $CHCl_3$ with a main peak at 350 nm and a subpeak at about 490 nm. The subpeak is tentatively assigned to an emission from an excimer formed between intermolecular pyridine units or an exciplex formed between pyridine units and adjacent isoxazole units in Poly-**2**.

The polymers are properly thermally stable as determined by TGA under nitrogen. No weight loss is observed below 300 °C, and the temperatures for 10% weight loss ($T_{d10}$) of Poly-**1** and Poly-**2** are 400 and 355 °C, respectively.

As described above, new soluble and fluorescent poly(arylene)s are easily obtained by 1,3-dipolar polycycloaddition. The present method could provide a variety of poly(arylene)s by changing the structure of dinitrile oxides and diynes, and the scope of the preparation and application of the poly(arylene)s will be expanded.

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