

Preparation of network π -conjugated copolymers with Ullmann type polycondensation

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ABSTRACT

Ullmann type polycondensations in the presence of CuI and a base were carried out to afford network type π -conjugated copolymers. Infrared absorption spectroscopy measurements and surface observation using a scanning electron microscopy are carried out. Electron spin resonance spectroscopy measurements revealed that the cross-linked copolymers thus obtained contain small amount of copper. This polymerization conveniently allows production of network π -conjugated polymers. The polymer can be expected to have thermo-resistance.

Keywords: copolymer; cross-link; polyaniline; Ullmann reaction

1. INTRODUCTION

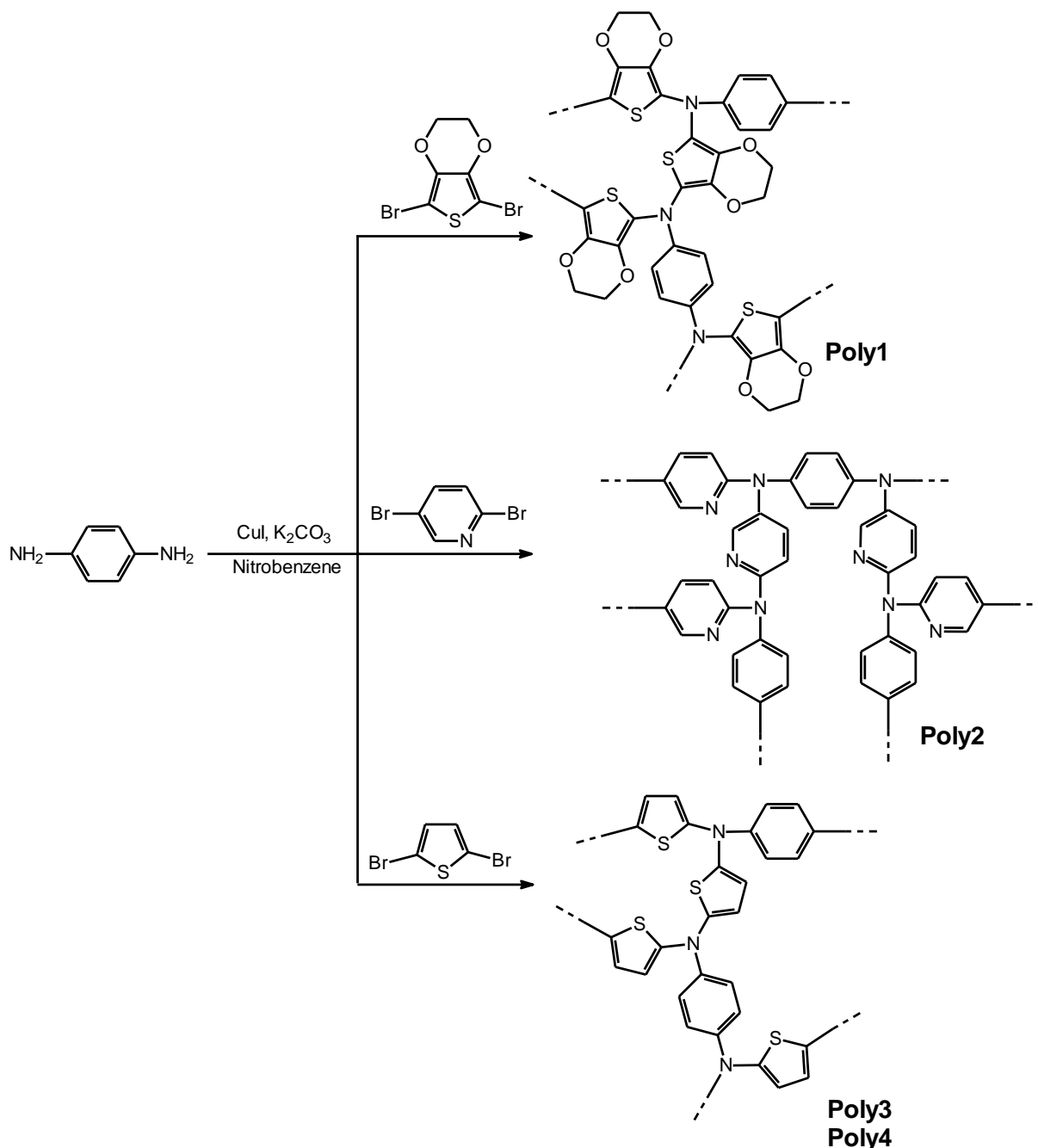
Polyaniline (PANI) [1] is one of the most promising conducting polymers because it has relatively high conductivity, and processability. PANI has been applied for sensors [2], anti-corrosion agent, and buffer layer for O-LED, electrochromics, and anti-static materials.

Ullmann condensation reaction is widely known as a coupling reaction by using copper. Especially, this is quite useful for condensation reaction between amine and halogen to synthesize π -conjugated compounds. To obtain polyaniline (PANI), oxidative polycondensation with ammonium persulfate (APS) in the water has been employed. This method allows production of PANI in the form of doped state (emeraldine salt). Ullmann polycondensation [3] of *m*-chloro-aniline and *m*-dibromobenzene allows poly(*m*-aniline) [4]. Buchwald-Hartwig reaction with an aid of Pd catalyst allows reaction of aniline and halogen substituted aromatic group [5,6]. Palladium-catalyzed polycondensation of aryl dibromides with aryl primary diamines has been performed to afford linear polymers [7].

Classic Ullmann reaction has advantages for condensation reaction because low cost and the reaction can be conducted in the air, although high reaction temperature is required. The Ullmann polycondensation reaction can afford tertiary amines to give network polymers. Natural network polymers such as lignin have high strength. Phenol resin as a synthetic network polymers has been widely applied in industry. Therefore, network type π -conjugated

polymers can be expected for mechanical strength, durability, and electronic property derived from the π -electrons. In this research, we perform Ullmann type polycondensation to obtain network poly(arylene-*co*-polyaniline)s. Infrared absorption (IR) spectroscopy measurements, surface observation using a scanning electron (SEM) microscopy, electron spin resonance (ESR), and UV-VIS optical absorption spectroscopy measurements are carried out for the polymers thus obtained.

2. EXPERIMENT



Scheme 1. Synthesis of network polymers.

Poly1, quantity used: EDOTBr₂ (0.1 g, 0.335 mmol), *p*-phenylenediamine (0.36 g, 0.335 mmol), nitrobenzene (1 mL), CuI (6.5 mg, 3.4 × 10⁻⁵ mol), K₂CO₃ (46 mg, 3.3 × 10⁻⁴ mol). Y = 0.081 g.

Poly2, quantity used: 2,5-Dibromopyridine (0.5 g, 2.1 mmol), *p*-phenylenediamine (0.23 g, 2.1 mmol), nitrobenzene (5 mL), CuI (0.02 g, 1.05 × 10⁻⁴ mol), K₂CO₃ (0.3 g, 2.1 mmol). Y = 0.385 g.

Poly3, quantity used: 2,5-Dibromothiophene (3 g, 0.012 mol), *p*-phenylenediamine (1.34 g, 0.012 mol), nitrobenzene (20 mL), CuI (0.2 g, 1.05 × 10⁻³ mol), K₂CO₃ (1.66 g, 0.012 mmol). Y = 0.920 g.

Poly4, quantity used: 2,5-Dibromothiophene (3 g, 0.012 mol), *p*-phenylenediamine (1.34 g, 0.012 mol), nitrobenzene (20 mL), CuI (0.02 g, 1.05 × 10⁻⁴ mol), K₂CO₃ (1.66 g, 0.012 mmol). Y = 0.958 g.

Polymerization was conducted between dibromoarylene, such as dibromo-3,4-ethylenedioxythiophene (EDOTBr₂), 2,5-dibromothiophene, or 2,5-dibromopyridine), and *p*-phenylenediamine as shown in Scheme 1. A solution of the dibromoarylene, dibromobenzene, and K₂CO₃ in nitrobenzene was stirred for 24 h at 140 °C. Then, the reaction mixture was poured into a large volume of methanol. After filtration, the product was washed with a large volume of distilled water, and a large volume of methanol again. Filtration followed by drying in vacuum yielded network copolymers. The copolymers thus obtained are abbreviated as Poly1 (poly(EDOT-aniline), Poly2 (pyridine-aniline), Poly3 (thiophene-aniline). The copolymers are infusible because of formation of polymer network by cross-link.

3. RESULTS AND DISCUSSION

3. 1. IR

IR absorption spectroscopy measurements were carried out with the KBr method (Figure 1). Poly1 shows absorption bands at 1628 cm⁻¹ (C=C stretching, quinonoid) [8], 1518 cm⁻¹ (C=C stretching, benzenoid), and 1089 cm⁻¹ (C-O-C, stretching, benzenoid). An absorption bands at around 3300 cm⁻¹ due to N-H stretching was not observed. Wide range absorption from 4000-2000 cm⁻¹ indicates that the polymer is doped state. Poly4 shows the same absorption bands as Poly3.

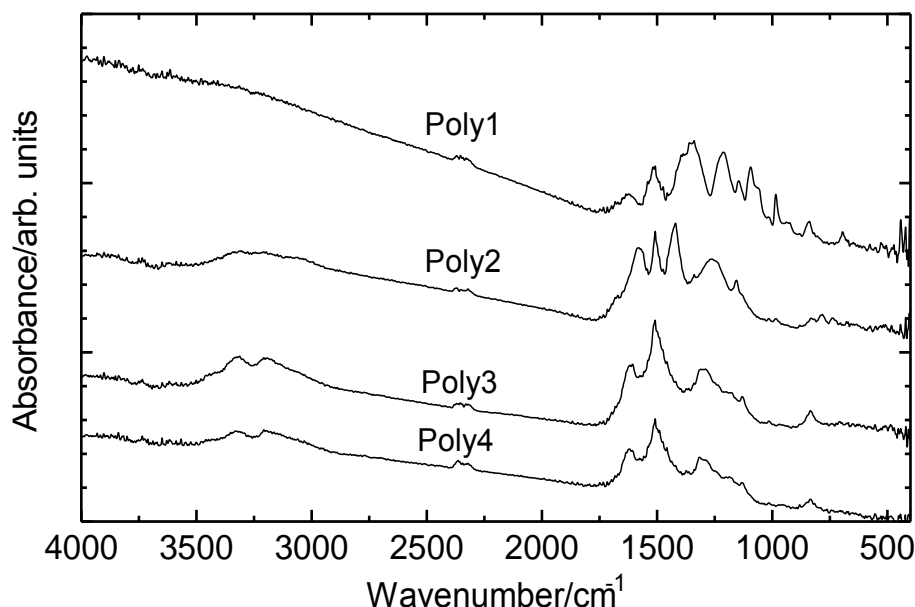


Figure 1. Infrared absorption spectra of the polymers.

HBr yielded during the reaction functioned to be a dopant to the resultant polymer (K_2CO_3 in the reaction may not neutralize it).

Poly1 shows electrical conductivity of 9.0×10^{-3} S/cm. Poly2 and Poly3 display absorption bands at long wavenumber due to N-H stretching, absorption at 3233, 3319, 3184. Poly2 (IR, cm^{-1}): 3233 (N-H stretching), 1579 (C=C stretching, quinonoid), 1505 (C=C stretching, benzenoid), 1420, 1260 (aromatic ring stretching).

Poly3 (IR, cm^{-1}): 3319 and 3184 (N-H stretching), 1616, 1505, 1303 cm^{-1} (aromatic ring stretching).

3. 2. SEM

Figures 2,3 show surface structure of the polymers. These polymers exhibit pebbles like structure [9,10]. Poly3 partly displays bubble-like structure.

3. 3. ESR

Electron spin resonance (ESR) measurements were carried out for the powder of the polymers [11]. Polymers show the ESR signals at around $g = 2.08$. Spin numbers of the polymers are to be in the range of $7-9 \times 10^{-6}$ spins/g. However, an ESR signal due to paramagnetic copper was overlapped on the polymers signal. This result indicates that removal of the trace amount of copper as a catalyst from the resultant polymer seems to be difficult.

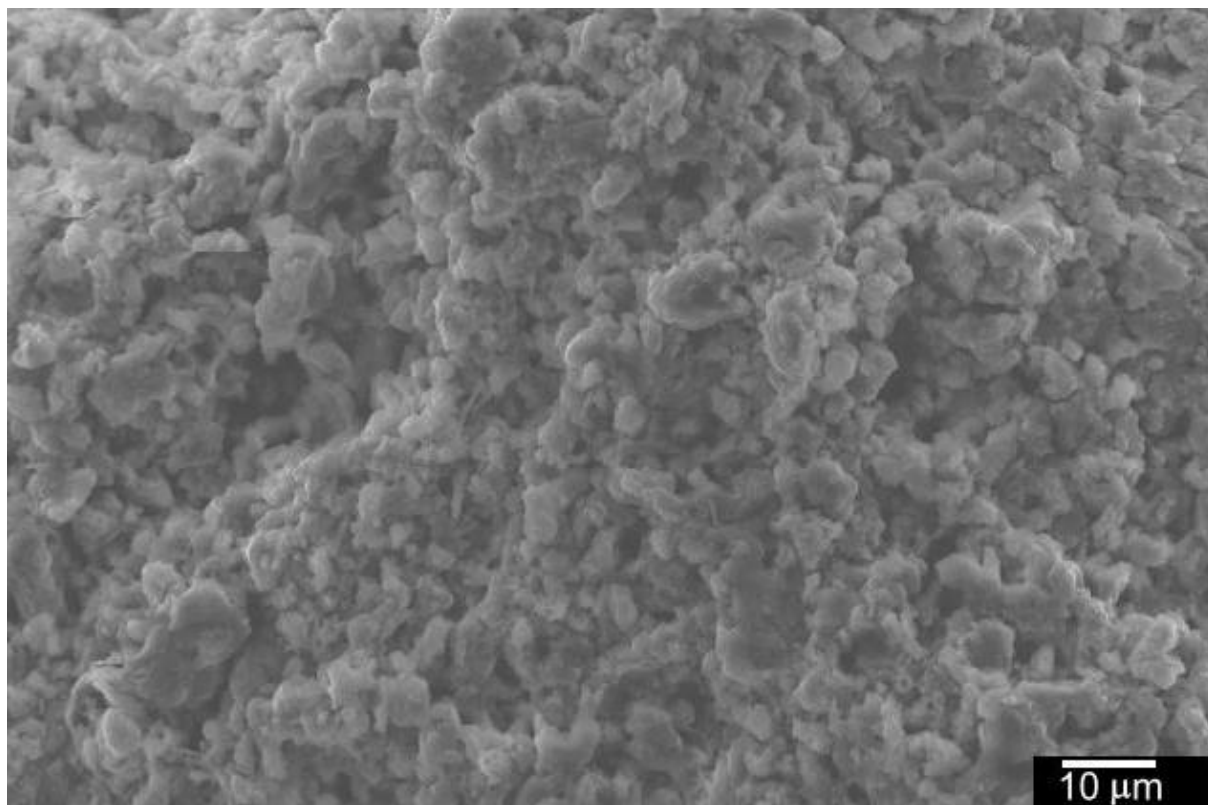


Figure 2. Scanning electron microscopy (SEM) images of Poly2 (1,000 \times).

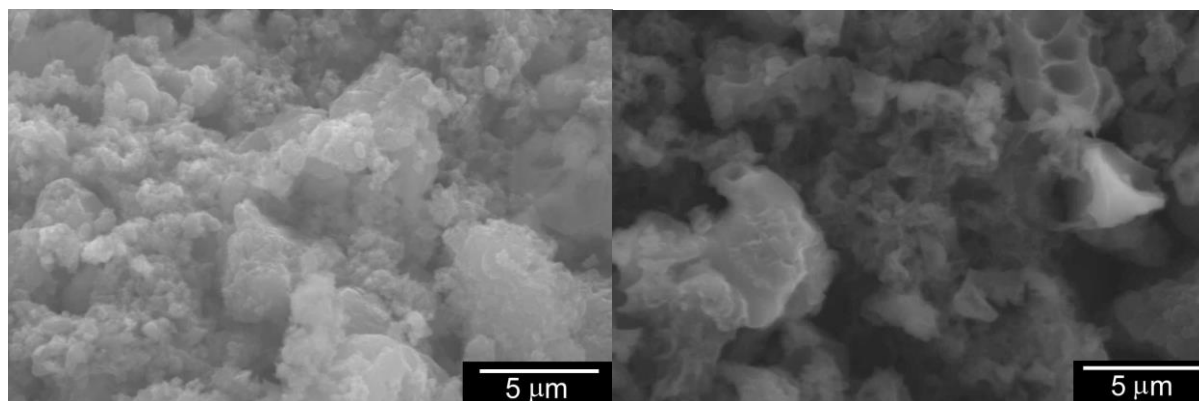


Figure 3. SEM images of Poly1 (left, 5,000×) and Poly3 (right, 5,000×).

3. 4. UV-VIS

The polymers are slightly soluble in *N*-methyl pyrrolidone (NMP). The UV-VIS optical absorption spectra of the polymers are shown in Figure 4. These polymers display an absorption band at 540 nm except Poly2 (sh, 698 nm) due to π - π^* transition of the main skeleton [12]. This result demonstrates that the network polymers are consisting of π -conjugate system.

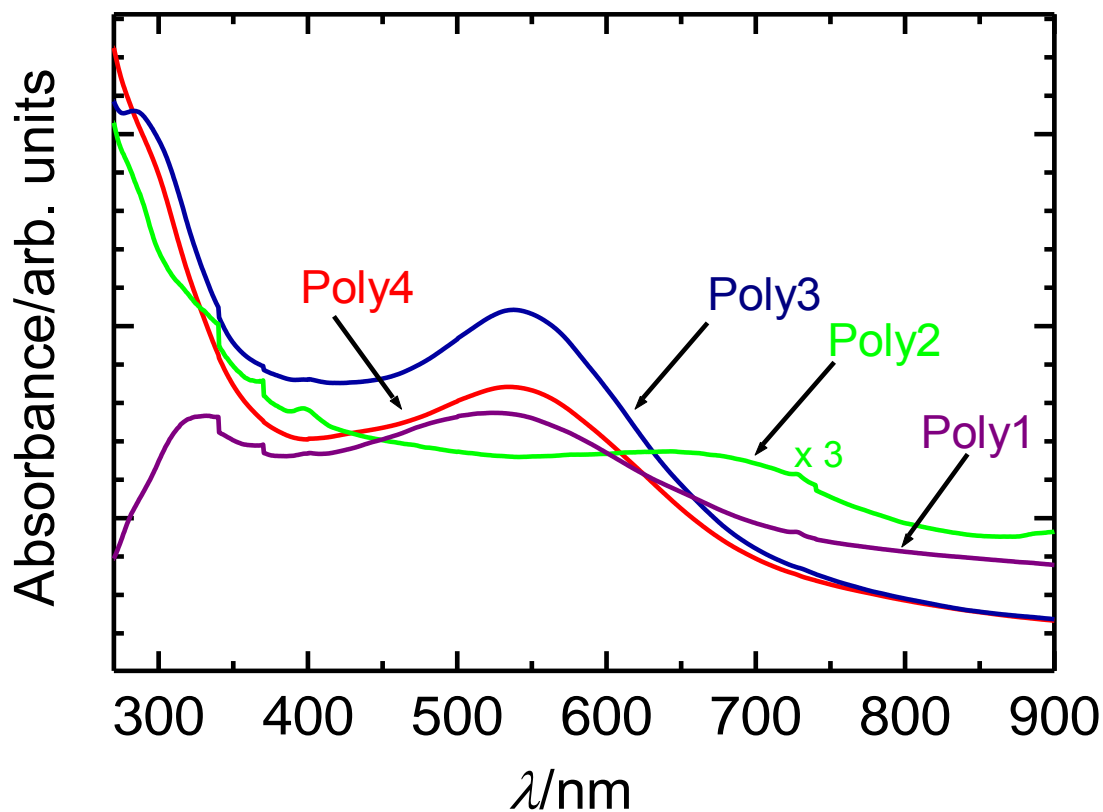


Figure 4. UV-VIS optical absorption spectra of the polymers in *N*-methyl pyrrolidone solutions.

4. CONCLUSIONS

Ullmann polycondensation reaction for formation of tertiary amine allows network copolymers consisting of arylene (EDOT, pyridine, and thiophene) and aniline units. The structures were confirmed using IR absorption spectroscopy measurements. Surface structure of the polymers was observed using a SEM. The π -conjugated network polymers thus obtained may be useful for thermo-resistance materials, sensors, and antistatic organic materials.

INSTRUMENTS

IR spectroscopy measurements were conducted using a FT-IR 550 spectrometer (JASCO, Japan). ESR spectroscopy measurements were carried out using a JEOL JES TE-200 spectrometer with 100 kHz modulation. SEM observations were carried out with JEOL JSM-521. UV-VIS absorption spectroscopy measurements were conducted using a V-630 (JASCO).

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