Futurum
Tsukuba Science Journal

An Attempt of Migita-Kosugi-Stille Type Polycondensation at Room Temperature

Polymer Synthesis

Kyoka Komaba, Hiromasa Goto*

Department of Material Science, Faculty of Pure and Applied Sciences,
University of Tsukuba, Tsukuba Ibaraki 305-8573, Japan.
*Correspondence: gotoh@ims.tsukuba.ac.jp

ABSTRACT

In this research, preparation of conjugated polymers was attempted with Migita-Kosugi-Stille cross coupling type polycondensation at room temperature. The polymers thus synthesized in this study were characterized with infrared absorption spectroscopy (IR), UV-vis absorption spectroscopy (UV-vis) and fluorescence spectroscopy.

Keywords: Conjugated polymer, Migita-Kosugi-Stille cross coupling

Introduction

Ito and Shirakawa et al. discovered synthesis of polyacetylene film in 1975[1]. After that, many types of conductive polymers have been synthesized. Conductive polymers are now applied for organic solar cells, transistors, organic light-emitting diodes[2–4]. Migita-Kosugi-Stille coupling is one of the effective reactions to synthesize conjugated polymers as precursor of conducting polymers[5].

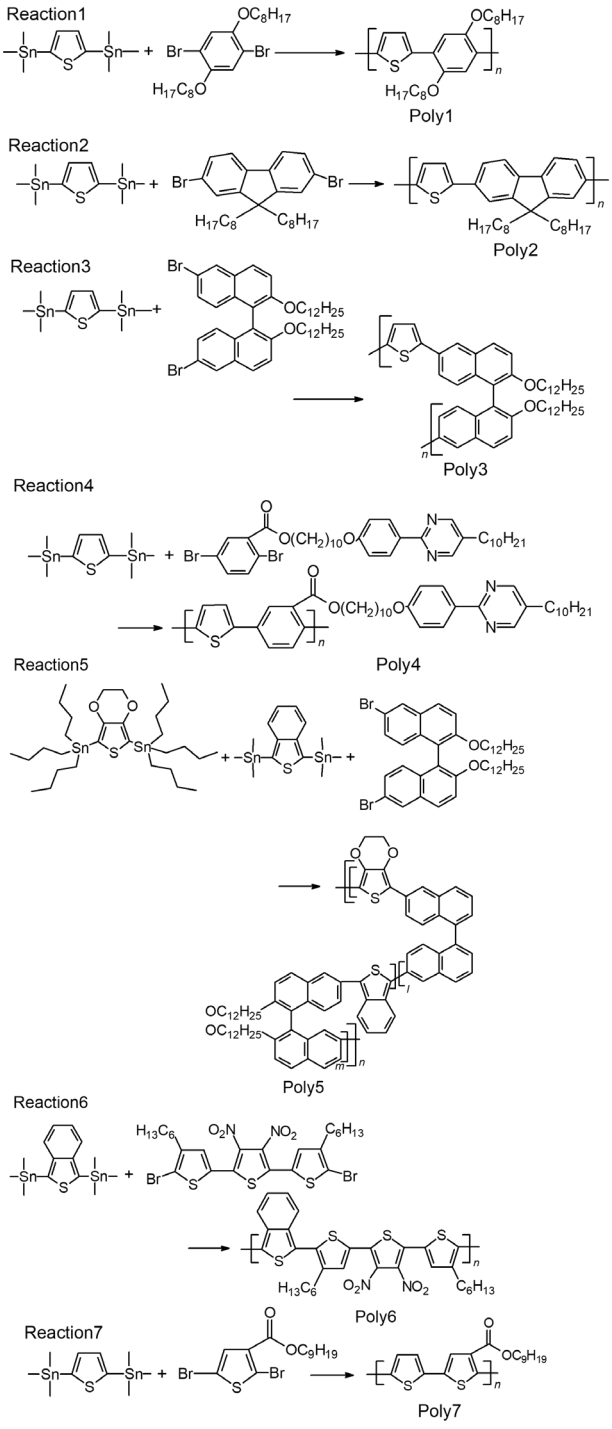
In this research, we attempted to synthesize conjugated polymers by Migita-Kosugi-Stille coupling at room temperature. This reaction has been usually conducted at high temperature.

Experimental section

Migita–Kosugi–Stille type polycondensation reactions in the presence of a palladium catalyst were carried out (Scheme 1). The monomers were synthesized in previous research[6]. Dialkyl-stannylated monomers (monoA), dihalided monomers (monoB), bis(triphenylphosphine)palladium(II) dichloride (0.07 g) and iodine (0.02 g) were dissolved in tetrahydrofuran (0.5 mL). The mixture was stirred at room temperature (~25 °C) overnight. The mixtures were poured into a large volume of methanol. The precipitates were centrifuged and the solvent was removed under reduced pressure to afford polymers. Molecular weights were < 1000 g/mol from the results of gel permeation chromatography in tetrahydrofuran against polystyrene calibration at room temperature.

Table 1 Synthesis.

Entry	monoA	monoB	Yield
Reaction1	0.05 g	0.05 g	8.4 mg, 19.9 %
Reaction2	0.05 g	0.05 g	2.7 mg, 6.2 %
Reaction3	0.05 g	0.05 g	4.3 mg, 9.5 %
Reaction4	0.028 g	0.05 g	17 mg, 38.7%
Reaction5	0.05 g, 0.05 g	0.05 g	8.3 mg
Reaction6	0.05 g	0.05 g	33 mg, 69.2 %
Reaction7	0.07 g	0.07 g	16 mg, 18.3 %



Scheme 1. Synthesis.

Results and discussion

IR spectroscopy

Chemical structure of the polymers was confirmed with the infrared (IR) spectra (Figure 1). Table 2 shows assignments of IR spectra. The C–H vibrations were observed at ca. 2900 cm^{-1} for all the polymers. The C–H bending mode connected to the α carbon of the thiophene ring and δ_{C-S-C} was shown for the monomers at ca. 900 cm^{-1}. While, the signals derived from this were not detected for the products, indicating the reactions were progressed.

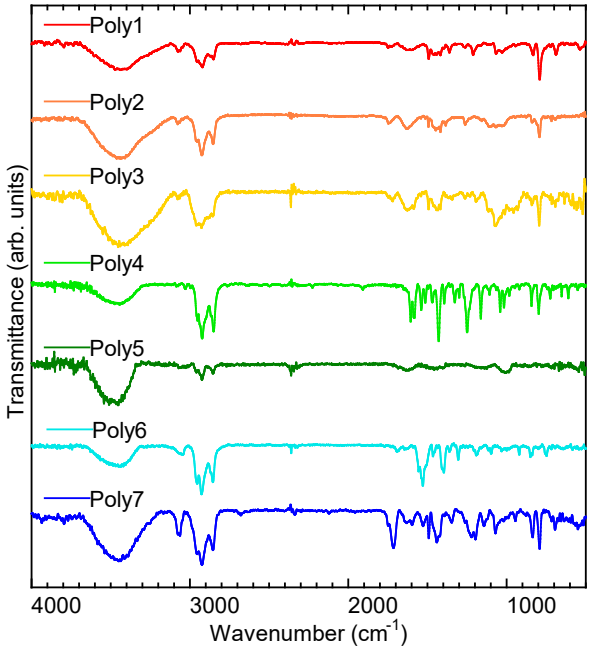


Figure 1. Infrared absorption spectra.

Table 2 Assignments of infrared (IR) spectra for the polymers.

Entry	$\nu_{C=O}$	$\nu_{C=N}$	ν_{NO2}	$\nu_{C=C}$	δ_{C-H}	ν_{C-O}
Poly1	–	–	–	1492	1361	1211 1066
Poly2	–	–	–	1493	1384	–
Poly3	–	–	–	1493		1075
Poly4	1605	1583	–	1514 1470	1394	1249 1040
Poly5	–	–	–	–	–	1000
Poly6	–	–	1529 1306	1464	1396	–
Poly7	1606	–	–	1493	1382	–

ν: stretching vibration, δ: vending vibration

Optical properties

UV-vis and fluorescence spectra of the polymers were obtained in tetrahydrofuran solution (Figure 4).

All the polymers show absorption bands from 390 to 430 nm derived from π–π* transition main chains.

Fluorescence spectroscopy measurements were carried out upon irradiation of an excitation light at 400 nm.

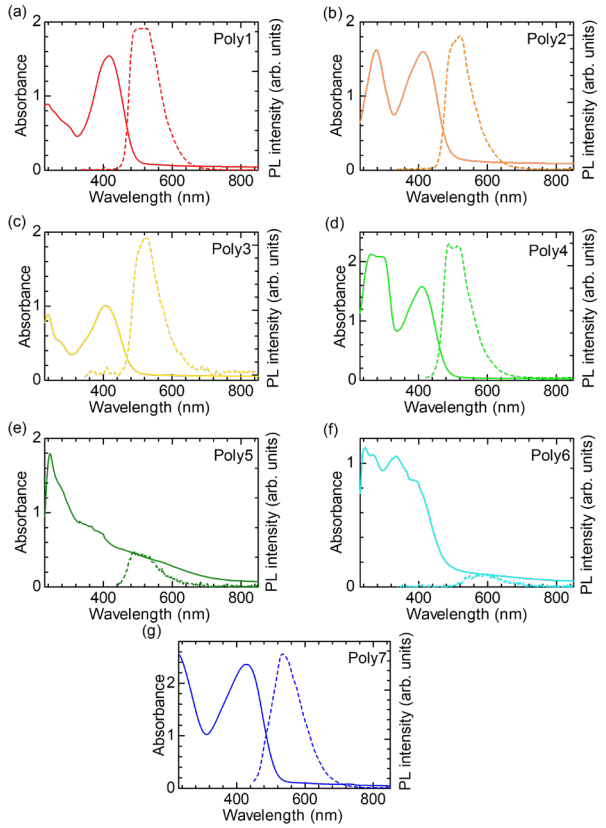


Figure 4. UV-vis spectra (solid line) and fluorescence spectra (PL, dashed line) of Poly1–Poly7 in tetrahydrofuran solution.

Table 3. UV-vis absorption and PL spectroscopy measurement results.

Entry	Absorption (nm)		PL (nm)
	Mru	Main chain	
Poly1	–	417	508
Poly2	277	412	521
Poly3	240	408	525
Poly4	261 300	412	489
Poly5	245	ca. 390	ca. 484
Poly6	242 333	397	ca. 479
Poly7	–	429	532

Mru: monomer repeat unit.

Conclusions

Migita-Kosugi-Stille type cross coupling polycondensation reactions were performed at room temperature. Although the molecular weights were somewhat low, the resultants prepared at room temperature as a simple and convenient method, showing beautiful colors caused by conjugated skeleton. A series of the products have possibility to apply opt-functional polymeric dyes.

Acknowledgement

We would like to thank the Glass Work Shop, University of Tsukuba. The pyrimidine type liquid crystal molecule was provided by Midori Kagaku (Midori Chemical Industry, Tokyo).

References

(1) Ito, T.; Shirakawa, H.; Ikeda, S. Thermal Cis–Trans Isomerization and Decomposition of Polyacetylene. *J. Polym. Sci. Polym. Chem. Ed.* **1975**, *13* (8), 1943–1950. https://doi.org/10.1002/pol.1975.170130818.

(2) Chang, C.-Y.; Huang, W.-K.; Chang, Y.-C.; Lee, K.-T.; Siao, H.-Y. High-Performance Flexible Tandem Polymer Solar Cell Employing a Novel Cross-Linked Conductive Fullerene as an Electron Transport Layer. *Chem. Mater.* **2015**, *27* (5), 1869–1875. https://doi.org/10.1021/acs.chemmater.5b00161.

(3) Du, Y.; Ding, Y.; Ge, F.; Wang, X.; Ma, S.; Lu, H.; Zhang, G.; Qiu, L. A Regular Ternary Conjugated Polymer Bearing π-Extended Diketopyrrole and Isoindigo Acceptor Units for Field-Effect Transistors and Photothermal Conversion. *Dyes Pigments* **2019**, *164*, 27–34. https://doi.org/10.1016/j.dyepig.2019.01.003.

(4) Di Nuzzo, D.; Kulkarni, C.; Zhao, B.; Smolinsky, E.; Tassinari, F.; Meskers, S. C. J.; Naaman, R.; Meijer, E. W.; Friend, R. H. High Circular Polarization of Electroluminescence Achieved via Self-Assembly of a Light-Emitting Chiral Conjugated Polymer into Multidomain Cholesteric Films. *ACS Nano* **2017**, *11* (12), 12713–12722. https://doi.org/10.1021/acsnano.7b07390.

(5) Amna, B.; Masood Siddiqi, H.; Hassan, A.; Ozturk, T. Recent Developments in the Synthesis of Regioregular Thiophene-Based Conjugated Polymers for Electronic and Optoelectronic Applications Using Nickel and Palladium-Based Catalytic Systems. *RSC Adv.* **2020**, *10* (8), 4322–4396. https://doi.org/10.1039/C9RA09712K.

(6) Kawabata, K.; Goto, H. Synthesis and Optical Properties of 1,1-Binaphthyl–Thiophene

Alternating Copolymers with Main Chain Chirality. *J. Mater. Chem.* **2012**, *22* (44), 23514–23524. https://doi.org/10.1039/C2JM35594A.

Accepted: 02-02-2022.

Citation:
Kyoka Komaba, Hiromasa Goto, An Attempt of Migita-Kosugi-Stille Type Polycondensation at Room Temperature, *Futurum - Tsukuba Science Journal,* **5**, 71–74 (2022).