J|A|C|S
COMMUNICATIONS

Synthesis of Rare-metal Absorbing Polymer by Three-component Polyaddition through Combination of Chemo-selective Nucleophilic and Radical Additions

Bungo Ochiai,[†] Takayuki Ogihara,[†] Masayuki Mashiko,[†] and Takeshi Endo*,[‡]

Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, Yamagata, Japan, and Molecular Engineering Institute, Kinki University, Fukuoka, Japan

Received September 8, 2008; E-mail: tendo@me-henkel.fuk.kindai.ac.jp

Three-component coupling polymerizations have produced versatile sequence-ordered polymers with easily tunable polymer backbones.[1−7] Successful three-component coupling polymerizations have been achieved by the combinations of "condensation and addition" or "condensation and condensation" reactions, or sequential additions[8] because the sufficiently chemoselective reactions typically require formations of a stable byproduct, such as salts, in either or both of the primary reactions, to give thermodynamic advantages to the first reactions. The condensation reactions unfortunately reduce the atom economy.[9] However, the aforementioned requirement impedes three-component polyaddition reactions, because the first additions typically consume the two reactive monomers and the resulting thermodynamically stable products may not attack the remaining most stable monomers. To construct three-component polyaddition by overcoming the thermodynamic problem, the polyaddition should involve two primary additions based on differing mechanisms, e.g., nucleophilic and radical additions. Accordingly, we focused on a nucleophilic addition of amines to cyclic dithiocarbonates affording mercaptothiourethanes,[10−12] whose mercapto group may react either nucleophilically or radically. This reaction gives the primary products the radical addition abilities in place of the decreased nucleophilicities.

We have chosen a diyne 1,4-diethynylbenzene (DEB) as a monomer for the radical addition process, because of its electron-sufficient character avoiding Michael-type nucleophilic additions of amines. A mixture of 5-phenoxymethyl-1,3-oxathiolan-2-thione (POTT, 1.20 mmol), 4,4′-trimethylenedipiperidine (TMDP, 500 μmol), DEB (500 μmol), and 2,2′-azobisisobutyronitrile (AIBN, 10 μmol) was heated at 60 °C in chlorobenzene (2.0 mL) for 48 h under a nitrogen atmosphere (Scheme 1, Table 1 run 1). A pale yellow polymer, which can be assignable to the desired structure composed from the addition of the three monomers (see Supporting Information, SI), was obtained in quantitative yield.[13] The amount of AIBN affected the yields and the solubility. The lower AIBN amount resulted in the lower yield (run 2), and the too high AIBN amount resulted in giving insoluble products (AIBN > 40 μmol). We attributed the formation of the insoluble polymers to the addition of the thiyl radicals to the double bond moieties in the main chain that competitively took place with the desired reactions. When the mixture was reacted for 24 h at 35 °C, the nucleophilic addition of TMDP to POTT took place to afford a bismercaptourethane quantitatively, although DEB was not consumed at all. The subsequent reaction at 60 °C for 24 h resulted in the addition of the mercapto group to DEB to produce alkenyl sulfide structures, which leads to production of the poly(thiourethane-phenylenevinylene sulfide) having the identical structure with the polymer obtained in run 1 [yield = 98%, M_n (M_w/M_n) = 6000 (2.64)]. The high selectivity of the polymerization was confirmed by the model reactions (see SI). First, the selectivity of the primary reactions is confirmed by the reactions of each of the two components under conditions similar to those for the polyaddition. As expected, only POTT and TMDP reacted to give the corresponding bis(mercaptourethane), while the mixture of POTT and DEB and that of TMDP and DEB did not react at all. The reaction of piperidine, which is a monofunctional analogue of TMDP, with POTT obeying second-order kinetics, and both reactants were consumed at identical rates. Second, the selectivity of the second radical addition was confirmed by the reaction of DEB with *n*-hexanethiol, which also obeyed second-order kinetics by identical consumption rates of the triple bond and the thiol moieties.

Scheme 1. Three-Component Polyaddition of Five-Membered Cyclic Dithiocarbonate, Diamine, and Diyne

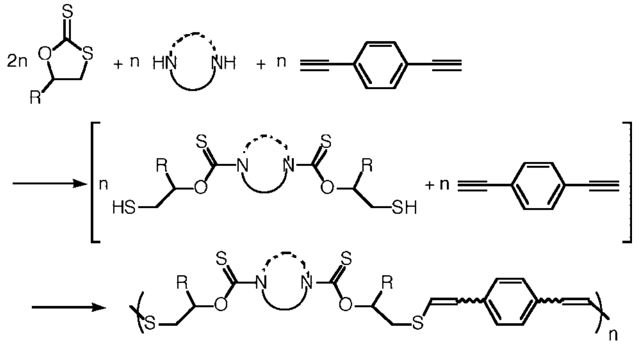

Table 1. One-Pot Three-Component Polyaddition of Five-Membered Cyclic Dithiocarbonate, Diamine, and Diyne[a]

run	R in dithiocarbonate	diamine	AIBN (μmol)	temp (°C)	yield (%)[b]	M_n (M_w/M_n)[c]
1	PhOCH$_2$	TMDP	10	60	>99	11 000 (5.13)
2	PhOCH$_2$	TMDP	5	60	85	3200 (2.43)
3	PhOCH$_2$	TMDP	20	60	>99	12 000 (6.81)
4	PhOCH$_2$	TMDP	40	60	37[d]	2400 (1.45)
5	PhOCH$_2$	TMDP	10	80	>99	8800 (4.52)
6	PhOCH$_2$	DAP	10	60	>99	3500 (2.57)
7	PhOCH$_2$	DAD	10	60	94	4500 (2.66)
8	PhCOOCH$_2$	TMDP	10	60	94	6200 (2.61)

[a] DOX: 1,4-dioxane, TMDP: 4,4′-trimethylenedipiperidine, DAP: 1,3-diaminopropane, DAD: 1,12-diaminododecane. [b] Isolated yield after precipitation with methanol. [c] Estimated by SEC (THF, polystyrene standard). [d] THF soluble part. Insoluble product was also produced.

The use of primary diamines, 1,3-diaminopropane (DAP) and 1,12-diaminododecane (DAD), also gave corresponding polymers, although the molecular weights were lower (runs 6 and 7). These polymers were also confirmed to have structures originating from the three-component polyaddition. The lower molecular weights

---

[†] Yamagata University.
[‡] Kinki University.

10.1021/ja8070978 CCC: $40.75

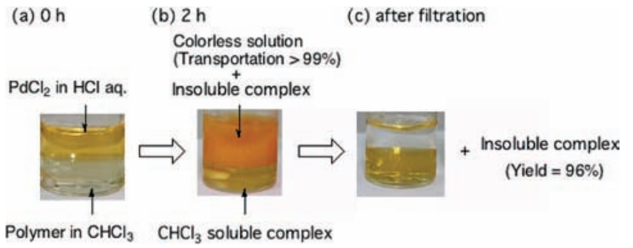

Figure 1. Photo images of the reaction mixture of $PdCl_2$ in 1 N HCl_{aq} (30 mL, 2.0 mmol/L) and a polymer obtained from POTT, DEB, and TMDP in $CHCl_3$ (30 mL, 2.0 mmol-unit/L) (a) after mixing, (b) after stirring for 2 h, and (c) after filtration.

may be ascribed to the slower first addition of the primary amines than the cyclic secondary amines (see SI). A polymer carrying the ester group in the side chain was also obtained using the corresponding dithiocarbonate, (2-thioxo-1,3-oxathiolane-5-yl)methyl benzoate, without TMDP attacking the ester moieties (run 8). The resulting poly(thiourethane-phenylenevinylene sulfide)s have high refractive indexes (the n_D value of the film of the polymer obtained in run 1 is 1.61 at 23.8 °C), photoluminescent properties (λ_{em} = 400 nm by excitation with 336 nm of UV light in DMF), and rare-metal extraction ability.

Specific ligation with soft metals is a unique character of sulfur containing groups.[14−19] Accordingly, we examined the metal absorpotion ability of the polymer obtained using POTT, DEB, and TMDP ($M_n = 5100$, $M_w/M_n = 2.30$). When an aqueous 1 N HCl solution of $PdCl_2$ (30 mL, 2.0 mmol/L) was mixed with a chloroform solution of the polymer obtained in run 1 (30 mL, 2.0 mmol-unit/L, [Pd]/[C=S] = 0.5), a precipitate formed between the layer and the color of the aqueous solution originating from the Pd salt disappeared. The total transportation efficiency of the Pd salt from the aqueous phase to the solid and the $CHCl_3$ layer was 96% (Figure 1). The yield of the insoluble product was also 96%, and a negligible amount of solid was isolated by pouring the $CHCl_3$ solution to *n*-hexane. This fact demonstrated that most of the transported palladium complex was in the precipitated product and that the Pd salt in the aqueous phase was easily collected by simple mixing and filtration. The absorbed Pd atom in $PdCl_2$ to the polymer was 129 mg/g (1.22 mmol/g), which is much higher than the case for commercial Pd absorbing polymers.[19] When a more dilute $PdCl_2$ solution (30 mL, 1.0 mmol/L) was used, the transportation efficiency exceeded 99%. A gold salt ($NaAuCl_4$) was also absorbed, and the transportation efficiency was quantitative. We attributed the better efficiency of the gold salt to the improved solubility of the complex in $CHCl_3$ that forms a negligible amount of precipitate between the layers.

In summary, the transformation of the addition process from nucleophilic to radical enabled the one-pot three-component coupling polyaddition. The appropriate choice of the three-components will afford polymers with desired functions such as solubility and luminescence, especially owing to the variety of dithiocarbonates easily prepared from CS_2 and epoxides.[20] The resulting polymer extracted Pd and Au salts from their aqueous solution in a facile manner, and the efficiencies are high. The advantages as metal scavenger are variable solubility, high absorption ability, and ease of the isolation process.

Supporting Information Available: Experimental procedures, details of the model reactions, and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Miyaki, N.; Tomita, I.; Endo, T. *Macromolecules* **1996**, *29*, 6685. (b) Miyaki, N.; Tomita, I.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem* **1997**, *35*, 1211. (c) Miyaki, N.; Tomita, I.; Endo, T. *Macromolecules* **1997**, *30*, 4504. (d) Choi, C.-K.; Tomita, I.; Endo, T. *Chem. Lett.* **1999**, 1253. (e) Choi, C.-K.; Tomita, I.; Endo, T. *Macromolecules* **2000**, *33*, 1487. (f) Ishibe, S.; Tomita, I. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3403.

(2) (a) Takenoya, K.; Yokozawa, T. *Macromolecules* **1998**, *31*, 2906. (b) Yokozawa, T.; Niimi, L.; Takenoya, K. *Macromol. Chem. Phys.* **1998**, *199*, 2453. (c) Niimi, L.; Shiino, K.; Hiraoka, S.; Yokozawa, T. *Macromolecules* **2002**, *35*, 3490. (d) Niimi, L.; Serita, K.; Hiraoka, S.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1236.

(3) Leung, L. M.; Chan, W. H.; Leung, S. K.; Fung, S. M. *J. Macromol. Sci. Pure Appl. Chem.* **1994**, *A31*, 495–505.

(4) (a) Oi, S.; Nemoto, K.; Matsuno, S.; Inoue, Y. *Macromol. Rapid Commun.* **1994**, *15*, 133. (b) Oi, S.; Fukae, Y.; Nemoto, K.; Inoue, Y. *Macromolecules* **1996**, *29*, 2694.

(5) Pawlow, J. H.; Sadow, A. D.; Sen, A. *Organometallics* **1997**, *16*, 5659.

(6) Aitken, R. A.; Hill, L.; Massil, T.; Hursthouse, M. B.; Malik, K. M. A. *Tetrahedron* **1997**, *53*, 10441.

(7) Kanbara, T.; Kawai, Y.; Hasegawa, K.; Morita, H.; Yamamoto, T. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3739.

(8) (a) Saegusa, T.; Kobayashi, S.; Kimura, Y. *Macromolecules* **1977**, *10*, 68. (b) Saegusa, T.; Furukawa, J.; Kimura, Y.; Kobayashi, S. *Polym. Bull.* **1979**, *1*, 243. (c) Choi, W.; Nakajima, M.; Sanda, F.; Endo, T. *Mactomol. Chem. Phys* **1998**, *199*, 1909.

(9) (a) Trost, B. M. *Science* **1991**, *254*, 1471. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.

(10) (a) Moriguchi, T.; Endo, T. *Macromolecules* **1995**, *28*, 5386. (b) Ochiai, B.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5097.

(11) (a) Choi, W.; Sanda, F.; Kihara, N.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 79. (b) Choi, W.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1189. (c) Choi, W.; Nakajima, M.; Sanda, F.; Endo, T. *Macromol. Chem. Phys.* **1998**, *199*, 1909.

(12) Suzuki, A.; Nagai, D.; Ochiai, B.; Endo, T. *Macromolecules* **2004**, *37*, 8823.

(13) The polyaddition of POTT, DEB, and TMDP under the theoretical molar ratio (i.e., 2.0:1.0:1.0) also gave the corresponding polymer with the identical structure in 95% yield, which equals to the atom efficiency. In spite of the very high atom efficiency, the molecular weight was lower ($M_n = 5100$, $M_w = 11\ 700$) probably because of the difficulty to maintain the complete equivalencies of the three substances.

(14) El-Shekiel, A.; Al-Karbooly, A.; Al-Yusufy, P. *J. Inorg. Organomet. Polym.* **2001**, *11*, 105.

(15) Bearinger, J. P.; Terrettaz, S.; Michel, R.; Tirelli, N.; Vogel, H.; Texor, M.; Hubbell, J. A. *Nat. Mater.* **2003**, *2*, 259.

(16) Kagaya, S.; Sato, E.; Masore, I.; Hasegawa, K.; Kanbara, T. *Chem. Lett.* **2003**, *32*, 622.

(17) Napoli, A.; Valentini, M.; Tirelli, N.; Muller, M.; Hubbell, J. A. *Nat. Mater.* **2004**, *3*, 183.

(18) Mellace, A.; Hanson, J. E.; Griepenburg, J. *Chem. Mater.* **2005**, *17*, 1812.

(19) http://www.sigmaaldrich.com/aldrich/brochure/al_dd_quadraqure_flyer.pdf.

(20) Kihara, N.; Hara, N.; Endo, T. *J. Org. Chem.* **1993**, *58*, 6198.

JA8070978