

Living Radical Polymerization of 7,7,8,8-Tetrakis(ethoxycarbonyl)quinodimethane

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ARTICLE INFO

Article history:

Received 20 November 2013

Received in revised form 24

January 2014

Accepted 29 January 2014

Available online 5 April 2014

Keywords:

Living Radical Polymerization 7,7,8,8-Tetrakis(ethoxycarbonyl)quinodimethane

ABSTRACT

The living radical polymerizations (LRP) of 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (TECQ) were investigated using various LRP methods, such as atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer radical polymerization (RAFT) and telluride-mediated radical polymerization (TERP). The living homo-polymerization of TECQ were not successfully achieved by any LRP methods because of high reactivity of TECQ which cause various side reactions except the addition of monomer to living radicals. On the other hand, the copolymerization of TECQ and isobutyl vinyl ether (IBVE), which was an electron-donating monomer, proceeded in a living polymerization manner by TERP method, and gave the alternating copolymer of TECQ and IBVE with narrow molecular weight distribution.

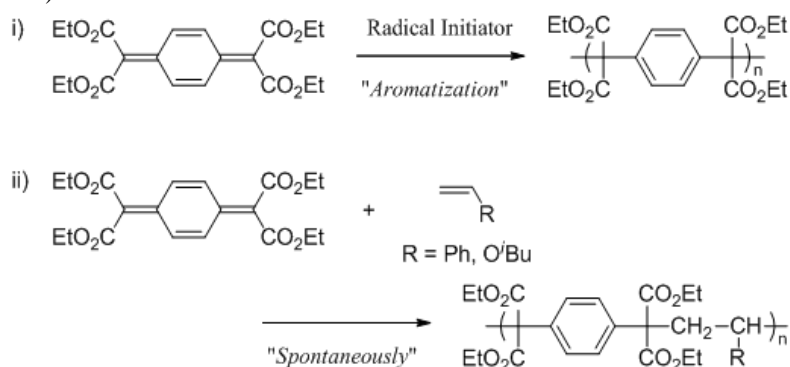
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To Cite This Article: K. Takashi, U. Takahiro, K. Masataka and I. Takahito., Living Radical Polymerization of 7,7,8,8-Tetrakis(ethoxycarbonyl)quinodimethane. *Aust. J. Basic & Appl. Sci.*, 8(4): 859-862, 2014

INTRODUCTION

Living polymerization is one of precision polymerization methods with no termination and transfer reaction through propagation reaction. Particularly, living radical polymerization (LRP) have attracted much attention in the field of polymer manufacturing, because LRP have both features, that is, high versatility of monomer and the tolerance of functional group based on traditional radical polymerization and precision control of polymer structure based on living polymerization.

Previously, we investigated the polymerization behavior of 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (TECQ) and found two important properties, that is, i) the radical polymerizations of TECQ proceed through the aromatization of quinoid skeleton, ii) the spontaneous alternating copolymerizations occur between TECQ and electron-donating monomers (EDMs) such as styrene (St) and isobutyl vinyl ether (IBVE), as shown in Scheme 1 (Iwatsuki, S., Itoh, T., and Yokotani, I., 1983). However, the living radical polymerization of TECQ has not been investigated yet. In this work, living radical homopolymerization and copolymerization of TECQ were investigated using various LRP methods including atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer radical polymerization (RAFT) and telluride-mediated radical polymerization (TERP).



Scheme 1: Polymerization behaviors of TECQ.

Experimental Section:**Measurements:**

^1H NMR and ^{13}C NMR spectra were measured with a JOEL JNM-EX270 (270 MHz for ^1H) spectrometer in chloroform-*d* with tetramethyl silane as internal standard. Infrared (IR) spectra were recorded on a JASCO FT / IR-4100 spectrometer. The number-average molecular weights (M_n) of the polymers were estimated by gel permeation chromatography (GPC) on a JASCO PU-2080 equipped with JASCO UV-2075 ultraviolet (254 nm) detector and TOSOH TSK gel G2500H₈ and TSK gel G3000H₈ using THF as an eluent at a flow rate of 1.0 ml/min and polystyrene standards for calibration.

Synthesis of TECQ:

TECQ was synthesized by the same procedure reported previously (Itoh, T., Nomura, S., Uno, T. and Kubo, M., 2002): yellow needles by recrystallization from hexane (25% yield); mp 141.5-143.8 °C; IR (KBr, cm^{-1}): ν = 2912 (CH), 1680 (C=O), 1543 (C=C), 1197 (C-O); ^1H NMR (270 MHz, CDCl_3 , δ , ppm): 7.45 (s, 4H, CH), 3.86 (s, 12H, CH_3); ^{13}C NMR (67.5 MHz, CDCl_3 , δ , ppm): 165.1 (C=O), 139.2 (=C<), 130.1 (C-H), 125.6 (=C<), 52.7 (CH_3); elemental analysis calcd (%) for $\text{C}_{16}\text{H}_{16}\text{O}_8$: H 4.80, C 57.14, O 38.06; found: H 4.78, C 56.93, O 38.29.

Homopolymerization:

ATRP (Yang, H., Jiang, B., Huang, W., Zhang, D., *et al.*, 2009): In a typical experiment, TECQ (210.3 mg, 0.536 mmol), $\text{Cu}^{\text{I}}\text{Br}$ (7.7 mg, 0.0536 mmol) as a catalyst, 4,4'-dinonyl-2,2'-bipyridine (dNbpy) (32.8 mg, 0.0804 mmol) as a ligand and anisole (0.50 ml) as a solvent were charged in a flask. The flask was deoxygenated by bubbling N_2 for 30 min. *tert*-Butyl 2-bromoisobutyrate (*t*-BBiB) (0.01 ml, 0.0536 mmol) as initiator was added to the flask and then placed in an oil bath thermostated at 60 °C for 120 h. The reaction was stopped by exposing to the air. The polymer was isolated by precipitation in hexane, and filtered by Al_2O_3 column using THF as eluent to remove copper catalyst.

RAFT (Nicolay, R., 2012): In a typical experiment, TECQ (101.6 mg, 0.256 mmol), 2,2'-azobisisobutyronitrile (AIBN) (0.11 mg, 6.5×10^{-4} mmol) as an initiator, 2-cyano-2-propyl benzodithioate (CPBDT) (2.5×10^{-4} ml, 1.3×10^{-3} mmol) as a RAFT reagent and anisole (0.26 ml) as a solvent were charged in a flask. The flask was deoxygenated by bubbling N_2 for 30 min, degassed by the freeze-thaw method (repeated four times), and then placed in an oil bath thermostated at 60 °C for 48 h. The reaction was stopped by placing the flask in liquid nitrogen, and the polymer was isolated by precipitation in hexane.

TERP (Yamago, S., Ikeda, K., Nakajima, M., Yoshida, J., 2003): In a typical experiment, TECQ (156.9 mg, 0.400 mmol), AIBN (0.33 mg, 2.0×10^{-3} mmol) as an initiator, diphenyl ditelluride (DPDT) (0.98 mg, 2.4×10^{-3} mmol) as a deactivator and anisole (0.40 ml) as a solvent were charged in a flask. The flask was deoxygenated by bubbling N_2 for 30 min, degassed by the freeze-thaw method (repeated four times), and then placed in an oil bath thermostated at 60 °C for 40 h. The reaction was stopped by placing the flask in liquid nitrogen, and the polymer was isolated by precipitation in hexane.

Table 1: Homopolymerization of TECQ by ATRP system ^{a)}.

Ligand	Time / h	Conv. / %	M_n	MWD
dNbpy	120	28.5	2,800	1.19
PMDETA	36	25.9	3,000	1.67
Me_6TREN	24	78.5	13,700	1.29
$\text{Me}_6\text{TREN}^{\text{b)}$	24	98.4	18,200	1.25

a) Conditions: [TECQ] = 1.0 mol/l in anisole, temp. = 60 °C,

[TECQ] / [*t*-BBiB] / [$\text{Cu}^{\text{I}}\text{Br}$] / [Ligand] = 10 / 1 / 1 / 1.1.

b) Without initiator (*t*-BBiB).

TERP Copolymerization with EDMs:

In a typical experiment, TECQ (156.9 mg, 0.400 mmol), AIBN (0.33 mg, 2.0×10^{-3} mmol), DPDT (0.98 mg, 2.4×10^{-3} mmol) and anisole (0.40 ml) were charged in a flask. The flask was deoxygenated by bubbling N_2 for 30 min. Isobutyl vinyl ether (IBVE) (0.01 ml, 0.0536 mmol) as electron-donating monomer was added to the flask, and degassed by the freeze-thaw method (repeated four times), and then placed in an oil bath thermostated at 60 °C for 24 h. Aliquots of reaction mixture (1.9 ml) were taken by a syringe through a septum at predetermined intervals and the reaction was stopped by exposing to the air, and the polymer was isolated by precipitation in hexane.

RESULTS AND DISCUSSION**Homopolymerization:**

Homopolymerizations of TECQ were investigated by three LRP systems, ATRP, RAFT and TERP under various conditions. The results of ATRP of TECQ using three kinds of multidentate ligands, 4,4'-dinonyl-2,2'-

bipyridine (dNbpy), *N,N,N',N',N''*-pentamethyl-diethylenetriamine (PMDETA), and tris[2-(dimethylamino)ethyl]amine (Me₆TREN), are summarized in Table 1. In the case using dNbpy and PMDETA as a ligand, the rate of polymerizations were very slow, and the polymers were obtained in low yield. On the other hand, ATRP using Me₆TREN gave the polymers with high molecular weight in good yield. However, the number-average molecular weight (M_n) of obtained polymer was about three times higher than the theoretical value calculated from the feed ratio of monomer and initiator. Furthermore, the polymer with almost same molecular weight and MWD also obtained in the absence of initiator (*t*-BBiB). From these results, it was suggested that the polymerization using Me₆TREN proceeded via not ATRP mechanism but anionic polymerization mechanism by the nucleophilic addition of Me₆TREN to TECQ monomer.

Table 2: Homopolymerization of TECQ by RAFT^{a)} and TERP^{b)} systems.

Reagent	Time / h	Conv. / %	M_n	MWD
CPBDT	48	34.4	3,100	1.40
CPBDT	168	55.1	3,200	1.31
DPDT	40	19.8	3,400	1.42
DPDT	90	53.5	3,100	1.46

a) Conditions: [TECQ] = 1.0 mol/l in anisole, temp. = 60 °C, [TECQ] / [AIBN] / [CPBDT] = 400 / 1 / 2.

b) Conditions: [TECQ] = 1.0 mol/l in anisole, temp. = 60 °C, [TECQ] / [AIBN] / [DPDT] = 200 / 1 / 1.2.

The results of RAFT and TERP of TECQ are summarized in Table 2. Although the monomer conversions increased with increasing polymerization time, the molecular weights of obtained polymers did not increase. This indicates that the both RAFT and TERP of TECQ did not proceed in living polymerization manner. From the ¹H NMR measurement, it was found that the polymers obtained by RAFT and TERP were not homopolymer of TECQ but alternating copolymer with oxygen (Itoh, T., Nomura, S., Uno, T., and Kubo, M., 2003), indicating that the spontaneous copolymerization with contaminant molecular oxygen proceeded in preference to RAFT and TERP mechanisms.

Copolymerization with EDMs:

The living homopolymerization of TECQ were not successfully achieved by any LRP methods because of high reactivity of TECQ. Therefore, the copolymerizations of TECQ with electron-donating monomers (EDMs) such as styrene (St) and isobutyl vinyl ether (IBVE) were investigated by TERP system using AIBN as an initiator and DPDT as a deactivator, and the results are summarized in Table 3. The GPC trace of polymer obtained by copolymerization with St showed bimodal peaks, indicating that two kinds of polymers, copolymer of TECQ with St and homopolymer of St, were formed. On the other hand, TERP copolymerizations with IBVE gave the copolymers with narrow MWD. Furthermore, the conversion of monomers and the molecular weight of resultant copolymers increased with increasing polymerization time.

In order to investigate the reaction mechanism of copolymerization of TECQ and IBVE by TERP system, more detailed analysis was carried out by taking samples at regular intervals during the reaction. Figure 1 shows the kinetic plot of the copolymerization of TECQ and IBVE. The linear semilogarithmic plot of monomer conversion versus time proves its consumption is first-order and implies a constant radical concentration during the reaction. This result strongly suggests that the copolymerization of TECQ and IBVE by TERP system proceeds in living polymerization manner.

Table 3: Copolymerizations of TECQ with electron-donating monomers (EDMs) by TERP system^{a)}.

[TECQ]/[EDM]	Time / h	Conv. / %	M_n	MWD
1:1 (St)	24	68.7	8,700	3.07
1:4 (IBVE)	24	34.2	6,800	1.27
1:4 (IBVE)	48	47.7	7,600	1.32
1:4 (IBVE)	72	57.0	8,200	1.39
1:4 (IBVE)	96	67.4	8,700	1.55
1:4 (IBVE)	120	73.6	9,300	1.72

a) Conditions: [TECQ] = 0.5 mol/l in anisole, temp. = 60 °C, [TECQ] / [AIBN] / [DPDT] = 200 / 1 / 2.

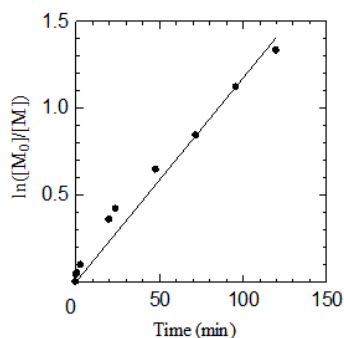


Fig. 1: Kinetic plot of the copolymerization of TECQ and IBVE by TERP system.

Conclusion:

The living radical polymerizations of TECQ were investigated by three LRP systems. The living homopolymerizations of TECQ were not achieved by any LRP systems because of high reactivity of TECQ. On the other hand, it was suggested that the copolymerization of TECQ and IBVE by TERP system proceeds in living polymerization manner. Detailed studies of copolymerizations by other LRP systems are now in progress.

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