Communications to the Editor

Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the *n*-Butyllithium/*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine System

Itaru Natori[†]

Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan, and Chemicals Research and Development II, Asahi Chemical Industry, 1-3-1 Yakoh, Kawasaki-ku, Kawasaki-city, 210 Japan

Received September 9, 1996

Revised Manuscript Received January 28, 1997

The synthesis of hydrocarbon polymers with an alicyclic structure in the main chain is one of the most interesting subjects in basic and practical aspects, since a dramatic improvement of thermal stability, chemical stability, and mechanical strength is expected for such polymers.

Although the synthesis of the above-mentioned polymers by the polymerization of cycloolefins,[1] bicyclic olefins,[2] and cyclodiolefins[3,4] has been reported, examples of polymers with directly connected alicyclic structures have been limited to those of cycloolefins or cyclodiolefins by addition polymerization. However, in all of these cases, polymers with narrow molecular weight distribution and controlled molecular weight have not yet been obtained. Among the monomers examined, a number of studies on the polymerization of 1,3-cyclohexadiene, one of the typical cyclodiolefins, has been carried out by ionic polymerization, radical polymerization, and coordination polymerization. In contrast to butadiene and isoprene, however, the polymerization of 1,3-cyclohexadiene was found difficult in all these studies including the case of anionic polymerization with *n*-butyllithium (*n*-BuLi) as initiator. Obtained polymers were of low molecular weight or in low yield.[4]

In the polymerization initiated with *n*-BuLi, the formation of 1,4-cyclohexadiene and benzene was observed, due to abstraction of the allylic hydrogen of 1,3-cyclohexadiene by organolithium species competing with the propagation reaction.[5] Thus, there have been no successful examples of living anionic polymerization of 1,3-cyclohexadiene so far.

Recently, we have studied the organometallic system consisting of alkyllithium and amine as initiator for the polymerization of 1,3-cyclohexadiene. As a result, a specific organometallic system consisting of *n*-butyllithium (*n*-BuLi) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was found to be particularly active as initiator for the polymerization of 1,3-cyclohexadiene. The present communication describes the first successful example of living anionic polymerization of 1,3-cyclohexadiene by this initiator (Scheme 1).

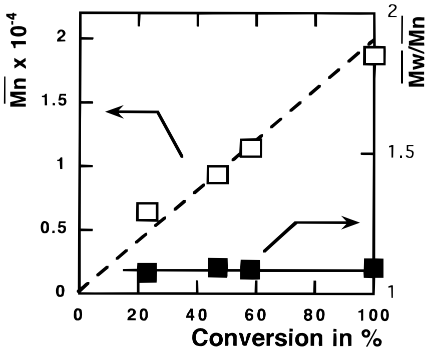
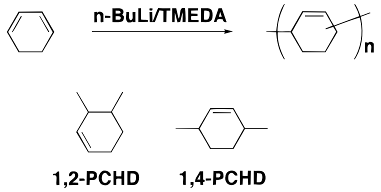


Figure 1. Polymerization of 1,3-cyclohexadiene with *n*-BuLi/TMEDA (4/5) system in cyclohexane at 40 °C ([1,3-cyclohexadiene]$_0$/[*n*-BuLi]$_0$ = 5000/20) with a M_n(M_w/M_n) conversion relationship. M_n, M_w/M_n were obtained by GPC calibrated with standard polystyrenes. Dashed line represents the degree of polymerization of the polymer calculated from the mole ratio of the monomer reacted to the initiator, assuming that every initiator (*n*-BuLi) produces one polymer molecule.

Scheme 1



A typical example of the synthesis of the 1,3-cyclohexadiene polymer is shown as follows. First, cyclohexane (2570 mL), *n*-BuLi (20 mmol as a 1.44 M *n*-hexane solution), and TMEDA (10 mmol) were placed in a 5 L stainless steel autoclave equipped with an electromagnetic induction stirrer. The solution was stirred for 10 min at room temperature (~25 °C) under dry nitrogen atmosphere (about 4 kg/cm^2), then was warmed up to 70 °C, and was stirred for another 10 min and cooled to 40 °C. Additional TMEDA (15 mmol) and 1,3-cyclohexadiene (5.0 mol) were supplied to this solution in the autoclave, and polymerization was carried out under a dry nitrogen atmosphere at 40 °C for 120 min. At an appropriate time interval, part of the reaction mixture was taken out and was poured into a large amount of acetone to precipitate the polymer, which was separated by filtration. The product was dried in vacuum for 8 h at 50 °C, to give a white, powdery polymer. The polymer was soluble in cyclohexane, tetrahydrofuran (THF), and chloroform. A transparent colorless film could be obtained by casting from the cyclohexane solution of this polymer.

The produced polycyclohexadiene showed a sharp GPC chromatogram (THF) and had a narrow molecular weight distribution (MWD) (M_w/M_n = 1.08−1.09, polystyrene standard). In the example of the synthesis described above ([1,3-cyclohexadiene]$_0$/[*n*-BuLi]$_0$ = 5000/20), the conversion of 1,3-cyclohexadiene estimated by gas chromatography to polycyclohexadiene was 23% (5 min), 47% (10 min), 58% (15 min), and 99% (120 min), respectively. The number average molecular weight

---

[†] All correspondence should be directed to the Asahi Chemical Industry address.

S0024-9297(96)01331-9 CCC: $14.00 © 1997 American Chemical Society

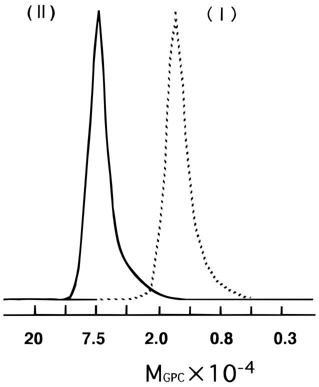


Figure 2. Block copolymerization of 1,3-cyclohexadiene and styrene with a *n*-BuLi/TMEDA (4/5) system ([1,3-cyclohexadeien]$_0$/[styrene]$_0$/[*n*-BuLi]$_0$=1250/3840/10). GPC chromatograms of the prepolymer of 1,3-cyclohexadiene (**I**, $M_n = 12\,400$, $M_w/M_n = 1.09$) and the block copolymer of 1,3-cyclohexadiene and styrene (II, $M_n = 51\,800$, $M_w/M_n = 1.09$). M_n, M_w/M_n were obtained by GPC calibrated with standard polystyrenes.

(M_n) of these polymers increased linearly with conversion of 1,3-cyclohexadiene to polycyclohexadiene, retaining the narrow MWD (Figure 1). The degree of polymerization of the polymers was in good agreement with the mole ratio of the monomer reacting with the initiator, indicating that every initiator (*n*-BuLi) produces one polymer molecule. The polycyclohexadiene obtained by the polymerization for 120 min had a structure of the main chain consisting of units formed by 1,2-addition (1,2-PCHD) and 1,4-addition (1,4-PCHD). The ratio of 1,2- and 1,4-units was 52/48 as estimated by 2D-NMR. In order to confirm the living character of the polymerization of 1,3-cyclohexadiene with the *n*-BuLi/TMEDA system, we attempted the synthesis of the block copolymer of 1,3-cyclohexadiene and styrene with narrow molecular weight distribution (MWD).

For the polymerization of the first stage, the system of *n*-BuLi (10 mmol)/TMEDA (12.5 mmol) was added to the solution of 1,3-cyclohexadiene (1.25 mol) in cyclohexane (3000 mL), and the polymerization was carried out under dry nitrogen atmosphere at 40 °C for 120 min. The conversion of 1,3-cyclohexadiene to polycyclohexadiene after 120 min was 100%. The number average molecular weight (M_n) and molecular weight distribution (MWD) of the cyclohexadiene prepolymer were $M_n = 12\,400$ and $M_w/M_n = 1.09$, respectively (Figure 2(I)). For the polymerization of the second stage, styrene (3.84 mol) was added into the above reaction mixture and the polymerization was continued under dry nitrogen atmosphere at 40 °C. The conversion of styrene after 180 min was 100%, and the corresponding product was obtained in an almost quantitative yield, which was confirmed to consist of 1,3-cyclohexadiene units and styrene units by ^{1}H-NMR. This block copolymer showed a sharp GPC chromatogram (THF), and the number average molecular weight (M_n) of the polymer increased from $M_n = 12\,400$ to $M_n = 51\,800$ (polystyrene standard), retaining narrow MWD ($M_w/M_n = 1.09$). (Figure 2(II))

Thus, the polymerization of 1,3-cyclohexadiene with an *n*-BuLi/TMEDA system was confirmed to be a living anionic polymerization, by successful synthesis of the block copolymer of 1,3-cyclohexadiene and styrene. Further studies on the details of the polymerization and the properties of the polymer are in progress.

References and Notes

(1) Kaminsky, W.; Spiel, R. *Makromol. Chem.* **1989**, *190,* 515.

(2) (a) Gillion, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108,* 733. (b) Cannizzo, L. F.; Grubbs, R. H.; *Macromolecules* **1988**, *21*, 1961.

(3) (a) Reichel, B.; Marvel, C. S. *J. Polym. Sci., Part A* **1963**, *1*, 2935. (b) Yousufzai, A. H. K.; Endo, K.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1601.

(4) (a) Stuchlen, H.; Thayer, H.; Willis, P. *J. Am. Chem. Soc.* **1940**, *62*, 1717. (b) Ziegler, K. *Brennstoff. Chem.* **1949**, *30*, 181. (c) Marvel, C. S.; Hartzell, G. E. *J. Am. Chem. Soc.* **1959**, *81*, 448. (d) Brown, J. F.; White, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 5671. (e) Lefebvre, G.; Dawans, F. *J. Polym. Sci., Part A* **1964**, *2*, 3277. (f) Cassidy, P. E.; Marvel, C. S. *J. Polym. Sci., Part A* **1965**, *3*, 1553. (g) Imanishi, Y.; Yamane, T.; Kohjiya, S.; Okamura, S. *J. Macromol. Sci.-Chem.* **1969**, *A3(2)*, 223. (h) Imanishi, Y.; Matuzaki, K.; Yamane, T.; Kohjiya, S.; Okamura, S. *J. Macromol. Sci.-Chem.* **1969**, *A3(2)*, 249. (i) Dolgoplosk, B. A.; Beilin, S. I.; Korshak, Yu. V.; Chernenko, G. M.; Vardanyan, L. M.; Teterina, M. P. *Eur. Polym. J.* **1973**, *9*, 895. (j) Mango, L. A.; Lenz, R. W. *Makromol. Chem.* **1973**, *163*. 13. (k) Nagai, K.; Kon, M. *Kobunshi, Ronbunshu* **1977**, *34*, 333. (l) Nagai, K.; Machida, S.; Nonaka, T. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 773. (m) Nagai, K.; Machida, S. *J. Macromol. Sci.-Chem.* **1981**, *A16(5)*, 965. (n) Sen, A.; Lai, T. *Organometallics* **1982**, *1*, 415. (o) Sen, A.; Thomas, R. R. *Organometallics* **1982**, *1*, 1251. (p) Allcock, H. R.; Dudley, G. K.; Silverberg, E. N. *Macromolecules* **1994**, *27*, 1039.

(5) (a) Mango, L. A.; Lenz, R. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **1971**, *12*, 402. (b) Lussi, H.; Barman, J. *Helv. Chim. Acta* **1967**, *50*, 1233. (c) Sharaby, Z.; Jagur-Grodzinsky, J.; Maritan, M.; Vofsi, D. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 901. (d) Zhong, X. F.; Francois B. *Makromol. Chem.* **1990**, *191*, 2735. (e) Francois, B.; Zhong, X. F. *Makromol. Chem.* **1990**, *191*, 2743.

MA961331S