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Synthesis of Novel Hydrocarbon Polymers Containing 6-Membered Rings in the Main Chain : Living Anionic Polymerization of 1,3-Cyclohexadiene

Itaru Natori*, Kimio Imaizumi

Corporate Research and Development Administration (Europe), Asahi Chemical Industry, London Office, Gainsborough House Suite 607, 81 Oxford Street, London W1R 1RB, U.K.

SUMMARY:The *n*-butyllithium (n-BuLi) / *N,N,N',N'*-tetrametylethylene-diamine (TMEDA) system (the molar ratio of TMEDA to *n*-BuLi higher than 4/4) has been found to polymerize 1,3-cyclohexadiene (1,3-CHD) to produce "living" polymer having narrow molecular weight distribution with well-controlled polymer chain length. Binary and ternary block copolymers with narrow molecular weight distribution could be synthesized from 1,3-cyclohexadiene, styrene, and butadiene with very high efficiency. These polymers and their hydrogenated derivatives have excellent thermal, mechanical, chemical, and optical properties for the new industrial materials.

Introduction

The synthesis of hydrocarbon polymers containing 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. In particular, directly connected cyclohexane rings are selected as the most favorable compound out of all alicylic monomeric unit as target of polymer chain for ideal hydrocarbon polymers. Thus, the most important problem to be solved was the method of direct connection of cyclohexane rings in the main chain. For example, the polymerization of 1,3-cyclohexadienen (1,3-CHD) expected to provide a preferable prepolymer of poly(cyclohexane) which has directly connected cyclohexene rings. If well-controlled polymerization of 1,3-CHD will be possible, directly connected cyclohexane rings with well-defined structure can be prepared by the hydrogenation of poly(1,3-cyclohexadiene) (Figure 1).

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*e-mail : a8710317@ut.asahi-kasei.co.jp

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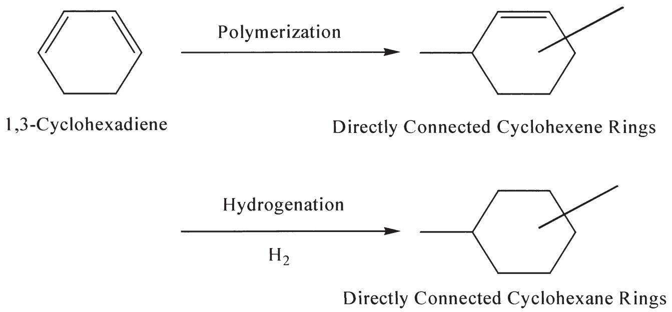

Figure 1. Synthesis of hydrocarbon polymers with directly connected cyclohexane rings. Polymerization of 1,3-cyclohexadiene and hydrogenation of poly(1,3-cyclohexadiene).

However, the polymerization of 1,3-CHD has been reported to be difficult in the studies under various conditions including the case of anionic polymerization with alkyllithium as initiator. The obtained polymers were of low molecular weight or in low yield 1). In our investigation, the new polymerization technology for 1,3-CHD was examined by using various polymerization methods. Finally, a specific initiator system for living anionic polymerization of 1,3-CHD was found for the first time 2).

In this paper, we report the first successful example of living anionic polymerization of 1,3-CHD, and then the block copolymerization with styrene (St) and butadiene (Bd). Furthermore, the microstructure and properties of 1,3-CHD homopolymer, block copolymers, and their hydrogenated derivatives are also described.

Living Anionic Polymerization of 1,3-Cyclohexadiene

In the previous paper, we reported the first successful example of living anionic polymerization of 1,3-cyclohexadiene with *n*-BuLi/TMEDA system as initiator2a). The molar ratio of *n*-BuLi and TMEDA composing the initiator system strongly influenced the anionic polymerization of 1,3-CHD 2d). The polymerization attained the living nature as the ratio of TMEDA increased. When the ratio of TMEDA to *n*-BuLi was higher than 4/4, obtained polymers had very narrow molecular weight distribution. On the other hand, no polymeric product was obtained in the polymerization initiated by *n*-BuLi in the absence of TMEDA($[1,3\text{-CHD}]_0/[\text{Li}]_0=125$, 120 min, 40℃). These results suggest that the propagation ends of living poly(1,3-cyclohexadiene) is composed of 1/1 molar ratio of Li and TMEDA (Table 1) 2d).

Table 1. Polymerization of 1,3-cyclohexadiene by the *n*-BuLi/TMEDA Systems [a]

No.	Iinitiator system	Yield (%)	Mn	Mcalc.[b]	Mw/Mn
1	n-BuLi	0			
2	n-BuLi/TMEDA(4/2)	72	16,000	7,200	1.52
3	n-BuLi/TMEDA(4/3)	100	11,100	10,000	1.12
4	n-BuLi/TMEDA(4/4)	100	10,600	10,000	1.07
5	n-BuLi/TMEDA(4/5)	100	11,600	10,000	1.06
6	n-BuLi/TMEDA(4/6)	100	10,800	10,000	1.08
7	n-BuLi/TMEDA(4/7)	100	10,100	10,000	1.06
8	n-BuLi/TMEDA(4/8)	100	11,300	10,000	1.07

[a] $[1,3\text{-CHD}]_0/[\text{Li}]_0=125$. [Monomer(s)]/[Solvent]=10/90. Polymerization was carried out in cyclohexane. Reaction temp. 40℃. Reaction time 120min. Mn and Mw/Mn were estimated by GPC, using polystyrene as standards. [b] Mcalc: $\text{FW}(C_6H_8) \times 125 \times \text{Yield}(\%) \times 10^{-2} = 10{,}000 \times \text{Yield}(\%)$.

The characteristics of living anionic polymerization of 1,3-CHD initiated by some *n*-BuLi/TMEDA systems (4/5), (4/2), and (4/0.5) in cyclohexane was examined in further detail ($[1,3\text{-CHD}]_0/[\text{Li}]_0=250$, 240 min, 40℃) .

The results are shown in Figures 2 and 3.

Figure 2

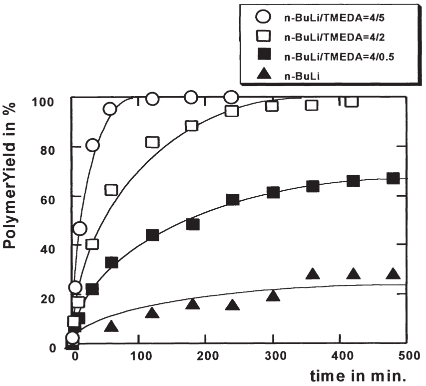

Figure 3

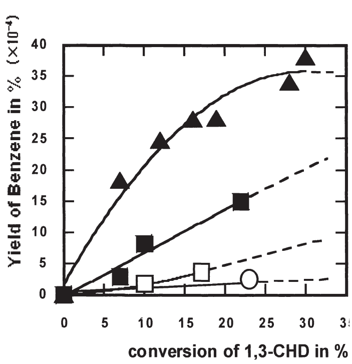

Figure 2. Conversion-time relationship of the polymerization of 1,3-CHD with some *n*-BuLi/TMEDA systems in cyclohexane at 40℃. $[1,3\text{-CHD}]_0/[\text{Li}]_0=250$, the ratio of *n*-BuLi/TMEDA(4/5), (4/2) and (4/0.5).
Figure 3. The relationship between the conversion of 1,3-CHD and the amount of benzene fromed in the anionic polymerization of 1,3-CHD initiated by some *n*-BuLi/TMEDA systems and *n*-BuLi in cyclohexane at 40℃. $[1,3\text{-CHD}]_0/[\text{Li}]_0=250$, the ratio of *n*-BuLi/TMEDA(4/5), (4/2), and (4/0.5).

Figure 2 clearly shows that the rate of polymerization and polymer yield increased with the ratio of TMEDA to *n*-BuLi. On the other hand, the polymer yield was considerably low in the absence of TMEDA and the increase in polymer yield was not observed after 360 min. The molecular weight distribution of obtained polymers became narrower with the ratio of TMEDA to *n*-BuLi (*n*-BuLi/TMEDA (4/5) : Mn=18,700, Mw/Mn =1.09, conversion 100%; (4/2) : Mn=28,200, Mw/Mn=1.41, conversion 100%; (4/0.5) : Mn=16,300, Mw/Mn=2.42, conversion 77%; *n*-BuLi : Mn=3,500, Mw/Mn=2.27, conversion 30%). The yield of benzene was found to decrease with the ratio of TMEDA to *n*-BuLi (Figure 3). The formation of benzene is considered to be the results of the decomposition of cyclohexadienyllithium (CHDLi) with hydride elimination and the abstraction of the allylic hydrogen of 1,3-CHD by CHDLi, respectively1). Obviously, in the polymerization of 1,3-CHD with the *n*-BuLi/TMEDA (4/5) system, there is neither transfer reaction nor termination reaction by the abstraction of allylic hydrogen of 1,3-CHD by organolithium species.

Block Copolymerization of 1,3-Cyclohexadiene and Styrene 2b)

The living prepolymer of 1,3-CHD was prepared by the polymerization with the *n*-BuLi/TMEDA (4/5) system ($[1,3\text{-CHD}]_0/[\text{Li}]_0=125$, 120min, 40℃, 100% conversion). Styrene (St) was then added into the above reaction mixture ($[\text{St}]_0/[\text{Li}]_0=384$). After 120 min, the conversion of St was 100%. 1,3-CHD was added into the above binary block copolymer solution ($[1,3\text{-CHD}]_0/ [\text{Li}]_0=125$) to continue the reaction. The conversion of 1,3-CHD after 300 min was 96%. The number average molecular weight (Mn) and molecular weight distribution (MWD) of this ternary block copolymer were 64,000 and Mw/Mn=1.14, respectively (Figure 4). The obtained 1,3-CHD-St-1,3-CHD ternary block copolymer was soluble in cyclohexane, tetrahydrofuran (THF), and chloroform. A transparent colorless strong plastic film could be obtained by casting from the cyclohexane solution of this polymer.

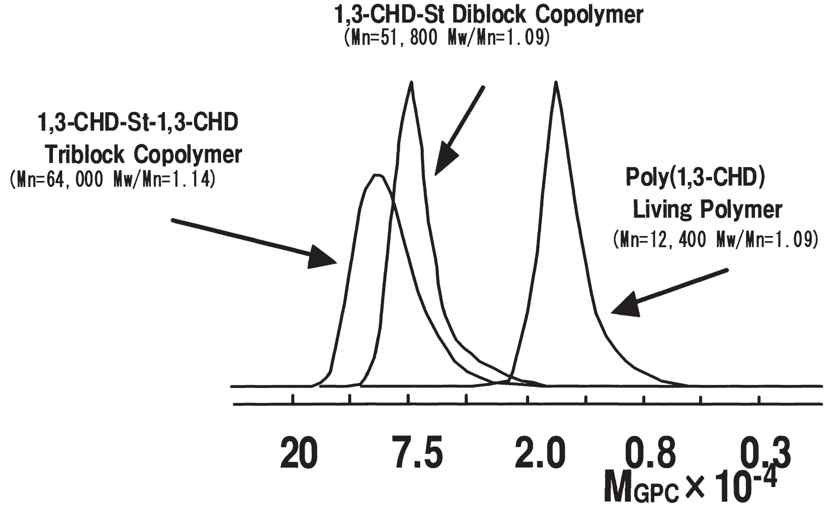

Figure 4. Block copolymerization of 1,3-cyclohexadiene and styrene.

Block Copolymerization of 1,3-Cyclohexadiene and Butadiene [2b)]

The living prepolymer of 1,3-CHD was prepared by the polymerization with the *n*-BuLi/TMEDA (4/5) system ($[1,3\text{-CHD}]_0/[\text{Li}]_0=125$, 120min, 40℃, 96% conversion). Butadiene (Bd) was then added into the above reaction mixture ($[\text{Bd}]_0/[\text{Li}]_0=370$). After 60 min, the conversion of butadiene was 99%. 1,3-CHD was added into the above binary block copolymer solution ($[1,3\text{-CHD}]_0/[\text{Li}]_0=125$) to continue the reaction. The conversion of 1,3-CHD after 300 min was 95%. The number average molecular weight (Mn) and molecular weight distribution (MWD) of this ternary block copolymer were 41,000 and Mw/Mn=1.15, respectively. The obtained 1,3-CHD-Bd-1,3-CHD ternary block copolymer was soluble in cyclohexane, tetrahydrofuran (THF), and chloroform. A transparent colorless tough elastic film could be obtained by casting from the cyclohexane solution of this polymer.

Microstructure of Poly(1,3-cyclohexadiene) [2d)]

Poly(1,3-cyclohexadiene) has a structure of the main chain consisting of units formed by 1,2-addition (1,2-unit) and 1,4-addition (1,4-unit) (Figure4). The ratio of 1,2-unit and 1,4 -unit can be determined by 2D-NMR(H-H COSY method) [2d)]. As for the polymer initiated by the *n*-BuLi/TMEDA systems, the content of the 1,2-units in the polymer chain increased with the ratio of TMEDA to *n*-BuLi. When the ratio of TMEDA to *n*-BuLi was higher than 4/4, the content of the 1,2-units was almost the same (51〜54%).

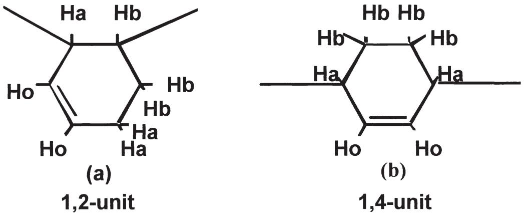

Figure 5. Structural formulas of 1,2-unit (a) and 1,4-unit (b).

Thermal, Mechanical, Chemical, and Optical Properties of Poly(1,3-cyclohexadiene) (PCHD) and Hydrogenated Poly(1,3-cyclohexadiene) [Poly(cyclohexane) :PCHE][2c)]

As described above, the novel hydrocarbon polymers containing 6-menbered rings directly connected in the main chain can be synthesized by living anionic polymerization of 1,3-cyclohexadiene. Various types of 1,3-CHD/Bd, 1,3-CHD/St, and 1,3-CHD-isoprene(Ip) block copolymers can be also synthesized by living anionic polymerization of 1,3-cyclohexadiene and styrene or butadiene (or isoprene).

As shown in Table 2, completely hydrogenated poly(1,3-cyclohexadiene) [poly-(cyclohexane) :PCHE] is composed of cyclohexane rings directly connected in the main chain, and has the highest glass transition temperature (Tg) among all hydrocarbon polymers. PCHE also has some excellent properties such as low specific gravity, high heat resistance, high flexural modulus, high transparency, low dielectric constant, and low water absorption. The refractive index is almost same as glass (SiO_2).

Table 2. Properties of poly(1,3-cyclohexadiene) (PCHD) and hydrogenated poly(1,3-cyclohexadiene)[poly(cyclohexane) : PCHE]

	PCHD	PCHE	PMMA	PC
Specific Gravity	1.03	0.99	1.19	1.19
Glass Transition Temperature (℃)	175	238	100	150
Heat Distortion Temperature (℃)	150	183	90	140
Flexural Modulus (GPa)	4.0	6.1	3.4	2.4
Transparency (%)	92	91	93	90
Reflective Index	1.43	1.51	1.58	1.49
Dielectric Constant (ε)	2.5	2.3	4.0	3.0
Water Absorption (%)	<0.01	<0.01	0.3	0.3

[a] PMMA : Poly(methyl methacrylate), PC : Polycarbonate

As a special optical property of PCHE, because there is no functional group in the polymer chain of PCHE, it has an outstanding wavelength dependence for optical uses among all other amorphous polymers (Figure 6).

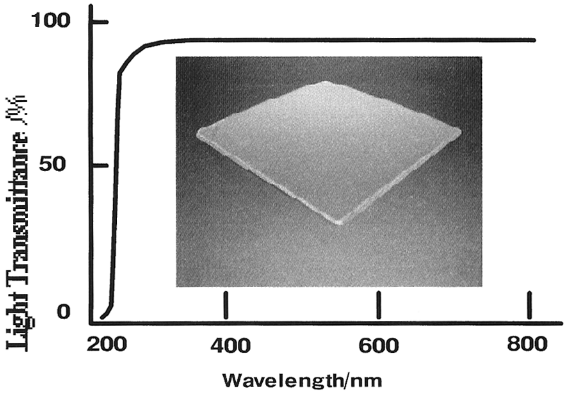

Figure 6. Photograph and wavelength dependence of PCHE.

Completely hydrogenated poly(1,3-cyclohexadiene)s such as hydrogenated 1,3-CHD-Bd-1,3-CHD triblock copolymer has good weatherability for outdoor uses (Figure 7). This result suggests that poly(cyclohexane) structure has good UV resistance.

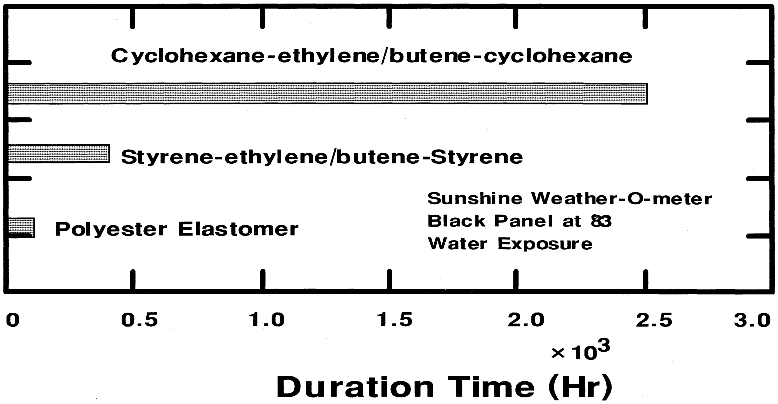

Figure 7. Weatherability of hydrogenated 1,3-cyclohexadiene-butadiene-1,3-cyclohexadiene triblock copolymer (PCHE-HBd-PCHE)

Conclusion

The *n*-BuLi/TMEDA system is an excellent initiator for the living anionic polymerization of 1,3-cyclohexadiene. The hydrocarbon polymers containing directly connected 6-membered rings in the main chain can be synthesized effectively by using this new technology. These novel hydrocarbon polymers and block copolymers have excellent properties to develop many high-performance industrial materials.

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