3176 *Macromolecules* **2001,** *34,* 3176−3181

Cationic Polymerization of Cyclopentadiene with $SnCl_4$: Control of Molecular Weight and Narrow Molecular Weight Distribution[1]

Makoto Ouchi, Masami Kamigaito, and Mitsuo Sawamoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Received September 25, 2000

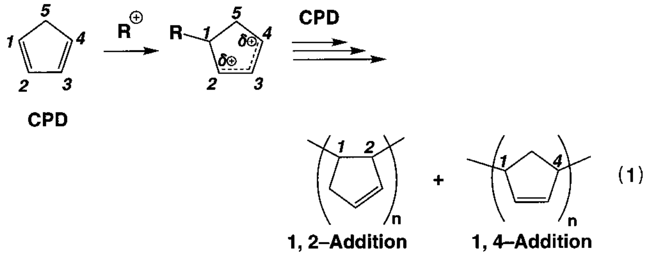
ABSTRACT: Precise control of molecular weights and their distributions (MWD) in cationic polymerization of cyclopentadiene (CPD) has been achieved with a three-component initiating system: the HCl adduct of CPD or a vinyl ether (initiator), $SnCl_4$ (Lewis acid catalyst), and n-Bu_4NCl (additive), in dichloromethane at −78 °C. The number-average molecular weights of the polymers increased in direct proportion to monomer conversion as well as to the monomer-to-initiator mole ratio (up to 200), and the MWDs were narrow throughout the reactions ($M_w/M_n = 1.2-1.3$); those in the additive-free systems were clearly broader ($M_w/M_n > 2$). Weak bases such as diethyl ether and ethyl acetate were also effective additives, whereas THF inhibited the polymerization. The poly(CPD) was completely soluble in organic solvents, carried the initiator fragment at the α-end (nearly one per chain), and consisted of nearly equal amounts of 1,2- and 1,4-repeat units, free from other enchainments.

Introduction

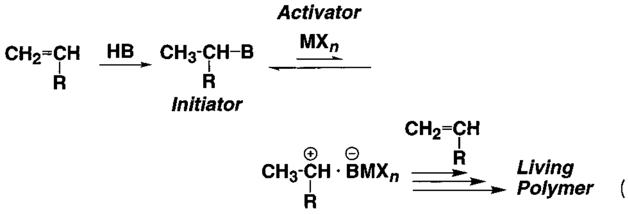
Hydrocarbon polymers with rigid cyclic repeat units have attracted much attention as new materials with high glass-transition temperature and low dielectric constant. The majority of such polymers have been obtained via addition (vinyl) polymerization of cyclic olefins,[2,3] cyclopolymerization of α,ω-dienes,[3] and ring-opening metathesis polymerization of bicyclic olefins.[4] The first of the three methods gives the most rigid backbones since cyclic units are directly connected to each other without spacers, whereas the second and the third generate polymers with one and two spacer carbons, respectively, in the main chain. The monomers for the addition polymerization include cyclic dienes, which afford rigid main chains of directly linked, unsaturated rings that may be hydrogenated into more stable saturated structures.[5]

Cyclopentadiene (CPD) is a representative cyclic diene that is easily obtained by the retro-Diels−Alder reaction of dicyclopentadiene and can be polymerized via cationic addition mechanism with conventional Lewis acids (metal halides) and stable carbocation salts (eq 1).[6] The growing species therein is most likely a relatively stable allylic carbocation and thus leads to 1,2- and 1,4-enchainments in the main-chain cyclic units. Despite its long history of research dating back to the 1920s,[7−11] the precise control of CPD cationic polymerization has been difficult, in terms of molecular weights and main-chain microstructure (1,2- vs 1,4-); occasional formation of insoluble products renders research more complicated. Some possibilities of molecular weight control were achieved with the Ph_3CSbCl_6 [12] or $H_2O/TiCl_3(OBu)$[13] system. Poor controllability is also seen in the transition-metal-catalyzed cationic polymerizations developed more recently.[14,15]

One of the most effective techniques to control polymer molecular weight and structures is living polymerization. Living cationic polymerization[16] has been achieved for various vinyl monomers, such as vinyl ethers, styrene derivatives, isobutene, indene, N-vinylcarbazole, and β-pinene, where the obtained polymers have controlled molecular weights and narrow molecular weight distributions (MWDs).[17] Most living cationic polymerizations employ binary systems that consist of a protonic acid (HB) or its derivative as an initiator and a Lewis acid (MX_n) as an activator or catalyst (eq 2). The Lewis acid activates the C−B bond in the initiator and polymer terminals to give a growing cationic species ($\sim\sim C^+$) accompanied by a counteranion (BMX_n^-). The choice of initiators, Lewis acids, and additives is crucial in achievement of living polymerization.[17]



(1)



(2)

Given this background, we became interested in precision control of CPD cationic polymerization for at least two reasons. First, there are few or no living cationic polymerizations of linear and cyclic aliphatic dienes, and thus fine molecular weight control therein is an interesting subject. Second, no general methods are available for controlling the 1,2- and 1,4-structures in the CPD main chain, and the selective formation of such units would be important in the chemistry of allylic-type growing carbocations and would also give interesting materials. This study was thus to develop living cationic polymerization of CPD with HB/Lewis acid initiating systems primarily for our first object in molecular weight control. The effects of additives and

10.1021/ma0016580 CCC: $20.00

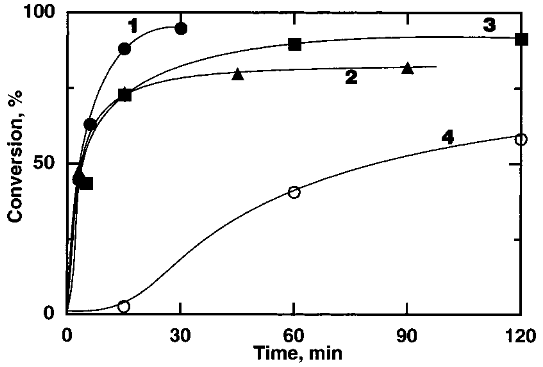
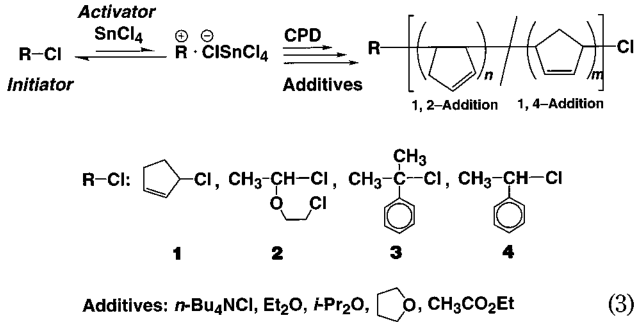


Figure 1. Time−conversion curves for the polymerization of CPD with R−Cl/$SnCl_4$ in toluene at −78 °C: $[M]_0 = 0.50$ M; $[R-Cl]_0 = 5.0$ mM; $[SnCl_4]_0 = 50$ mM. R−Cl: (●) **1**; (▲) **2**; (■) **3**; (○) **4**.

solvent polarity were also examined to optimize its control. This paper reports an example of precisely controlling polymer molecular weight and MWD in the cationic CPD polymerization using the HCl−CPD adduct (**1**)/$SnCl_4$ initiating system in the presence of an additive such as *n*-Bu_4NCl, diethyl ether, or ethyl acetate.



(3)

Results and Discussion

1. Search of Initiators. As potential initiators for living cationic polymerization of CPD, we first examined the hydrogen chloride adducts of CPD (**1**), 2-chloroethyl vinyl ether (**2**), α-methylstyrene (**3**), and styrene (**4**). The use of these adducts means that, in eq 2, the anion B^- is invariably the chloride, while the carbocationic parts differ in structure and reactivity. The polymerizations were carried out in toluene at −78 °C with $SnCl_4$ as the activator (MX_n in eq 2): $[CPD]_0/[initiator]_0/[SnCl_4]_0 = 500/5.0/50$ mM. All systems induced homogeneous polymerizations, whereas the rate depended upon the initiators (Figure 1). The CPD adduct **1** induced a fast and quantitative polymerization, whereas those with **2** and **3** proceeded at nearly the same rate as with **1** at the initial stage but subsequently slowed down. In contrast, **4** resulted in a much slower and incomplete CPD consumption.

Figure 2 shows the MWDs of the obtained polymers, as measured by size exclusion chromatography (SEC) calibrated with polystyrene. The SEC curves with **1** were relatively narrow and shifted to higher molecular weights with increasing CPD conversion. The adducts **2** and **3** also gave relatively narrow MWDs until ~50% conversion; however, they became broader at higher conversion. The MWDs with **4** were much broader due to slow initiation from **4**, which has a stronger and less active C−Cl bond than the others. Thus, **1** proved most suitable for controlling cationic polymerization of CPD with $SnCl_4$.

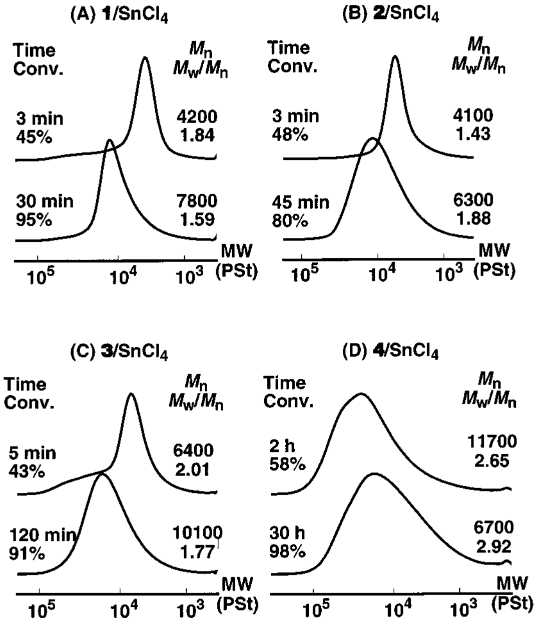


Figure 2. MWD curves of poly(CPD) obtained with R−Cl/$SnCl_4$ in toluene at −78 °C: $[M]_0 = 0.50$ M; $[R-Cl]_0 = 5.0$ mM; $[SnCl_4]_0 = 50$ mM. R−Cl: (A) **1**; (B) **2**; (C) **3**; (D) **4**.

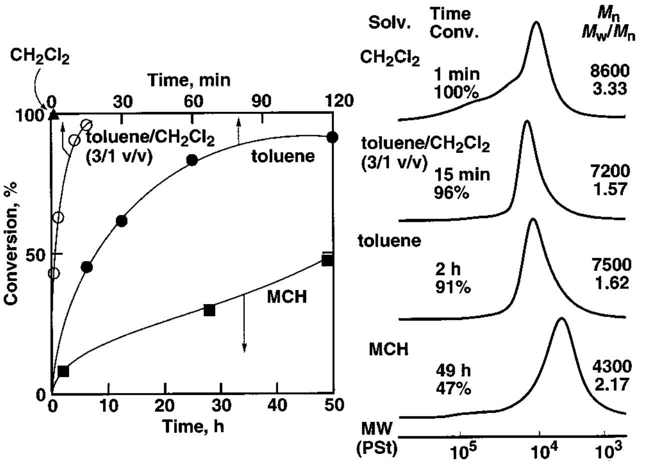


Figure 3. Time−conversion and MWD curves for the polymerization of CPD with **1**/$SnCl_4$ at −78 °C: $[M]_0 = 0.50$ M; $[\mathbf{1}]_0 = 5.0$ mM; $[SnCl_4]_0 = 5.0$ mM [or 50 mM in methylcyclohexane (MCH)]. Solvent: (▲) CH_2Cl_2; (○) toluene/CH_2Cl_2 (3/1 v/v); (●) toluene; (■) MCH.

2. Effects of Solvents. In general, cationic polymerization is affected by solvent polarity, and thus the effect of solvent was examined in the CPD polymerization with **1**/$SnCl_4$ at −78 °C (Figure 3). The higher the solvent polarity, the faster the rate of polymerization. Addition of CH_2Cl_2 to toluene (toluene/CH_2Cl_2 = 3/1 v/v) increased polymerization rate, reaching 96% conversion in 15 min. The polymerization in pure CH_2Cl_2 was very fast and completed within 1 min, while one in methylcyclohexane (MCH), a less polar solvent, was much slower even with 10 times more $SnCl_4$ (50 mM) employed. The MWDs of the polymers were fairly narrow in toluene or its mixture with CH_2Cl_2. The multimodal MWD obtained with pure CH_2Cl_2 solvent is probably due to a highly active, dissociated growing carbocation, which can attack a double bond in another polymer chain to generate comblike and partially cross-linked

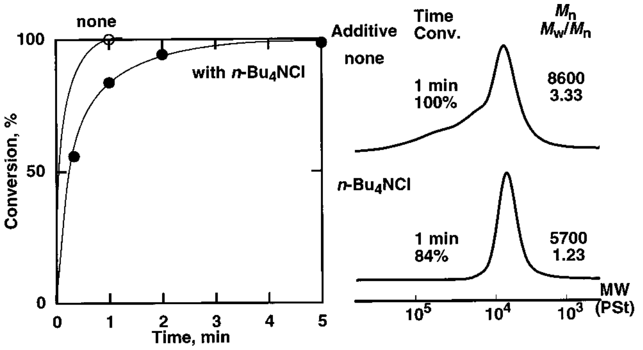


Figure 4. Effect of added *n*-Bu$_4$NCl on CPD polymerization with **1**/SnCl$_4$ in CH$_2$Cl$_2$ at −78 °C: [CPD]$_0$ = 500 mM; [**1**]$_0$ = 5.0 mM; [SnCl$_4$]$_0$ = 5.0 mM; [*n*-Bu$_4$NCl]$_0$ = 5.0 mM. Additive: (○) none; (●) *n*-Bu$_4$NCl.

polymers. In contrast to the polymerization with SnCl$_4$ in CH$_2$Cl$_2$ reported previously,[9] however, no insoluble gels formed with the **1**/SnCl$_4$ system. Overall, therefore, less polar media are better suited for control of CPD polymerization.

3. Effects of Additives: Control of CPD Polymerization. Control of polymerization in polar media like CH$_2$Cl$_2$ may be possible adding of an ammonium salt or a base, as demonstrated in cationic polymerizations of vinyl ethers,[18−20] styrene derivatives,[21] and isobutene.[22,23] These additives presumably suppress ionic dissociation or stabilize the growing carbocation; another possibility is the modification of Lewis acid (catalyst) by those nucleophiles. As shown in Figure 4, addition of an ammonium chloride, *n*-Bu$_4$NCl, retarded the polymerization in CH$_2$Cl$_2$ and gave poly(CPD)s with much narrower MWDs ($M_w/M_n \sim 1.2$) than those in the salt-free systems.

The number-average molecular weights (M_n) of the polymers increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one polymer chain forms per CPD−HCl adduct molecule, although the M_n's were based on polystyrene calibration (Figure 5). Therefore, *n*-Bu$_4$NCl is an effective additive for controlling the molecular weights and MWDs in cationic polymerizations of CPD. Initiator **2** also gave polymers with controlled molecular weights and narrow MWDs in conjunction with *n*-Bu$_4$NCl.

A series of oxygen-based nucleophiles such as diethyl ether (Et$_2$O), isopropyl ether (*i*-Pr$_2$O), ethyl acetate (EA), and tetrahydrofuran (THF) were also added to potentially control the polymerization with **1**/SnCl$_4$ in CH$_2$Cl$_2$ at −78 °C (Figure 6).[19,20] Et$_2$O and EA retarded the polymerization moderately, with the conversion reaching 95% in 2 h and 93% in 16 h, respectively. With both

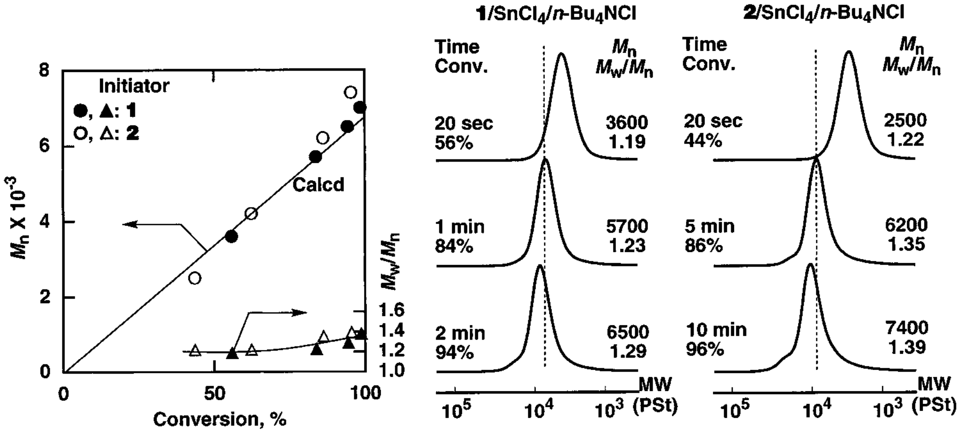


Figure 5. M_n, M_w/M_n, and MWD curves of poly(CPD) obtained with **1** (●, ▲) or **2** (○, △)/SnCl$_4$ in the presence of *n*-Bu$_4$NCl in CH$_2$Cl$_2$ at −78 °C: [CPD]$_0$ = 500 mM; [**1** or **2**]$_0$ = 5.0 mM; [SnCl$_4$]$_0$ = 5.0 mM; [*n*-Bu$_4$NCl]$_0$ = 5.0 mM. The diagonal bold line indicates the calculated M_n assuming the formation of one polymer chain per **1** molecule.

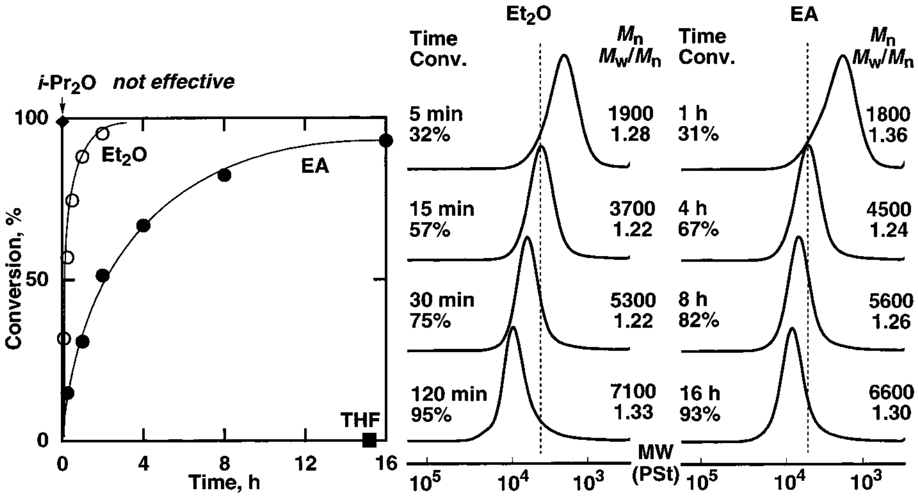


Figure 6. Time−conversion and MWD curves of poly(CPD) obtained with **1**/SnCl$_4$ in the presence of additives in CH$_2$Cl$_2$ at −78 °C: [CPD]$_0$ = 500 mM; [**1**]$_0$ = 5.0 mM; [SnCl$_4$]$_0$ = 10 mM, 1 vol % additive ([Et$_2$O]$_0$ = 96 mM, [EA]$_0$ = 100 mM, [*i*-Pr$_2$O]$_0$ = 71 mM, [THF]$_0$ = 120 mM). Additive: (○) Et$_2$O; (●) EA; (◆) *i*-Pr$_2$O; (■) THF.

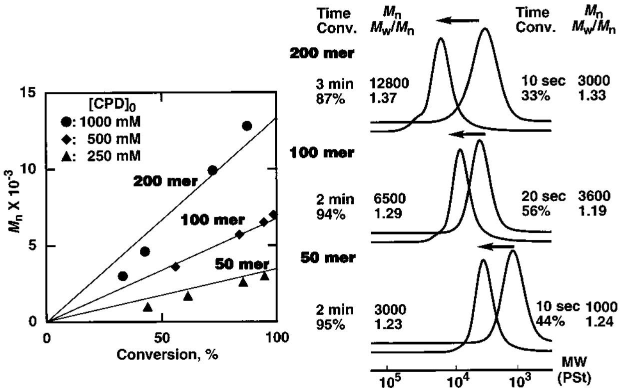


Figure 7. M_n, M_w/M_n, and MWD curves of poly(CPD) obtained with **1**/$SnCl_4$ in the presence of n-Bu_4NCl in CH_2Cl_2 at −78 °C: $[CPD]_0 = 1000$ (●), 500 (◆), 250 (▲) mM; $[\mathbf{1}]_0 = 5.0$ mM; $[SnCl_4]_0 = 5.0$ mM; $[n\text{-}Bu_4NCl]_0 = 5.0$ mM. The diagonal bold line indicates the calculated M_n assuming the formation of one polymer chain per **1** molecule.

additives, the MWDs were as narrow as those obtained with n-Bu_4NCl. The M_n increased linearly with conversion and agreed with the calculated values. The polymerization with i-Pr_2O, a weaker and more hindered base, was fast and uncontrolled, similar to that in the absence of additives. In contrast, no polymers were obtained with THF, a stronger base. Thus, the **1**/$SnCl_4$ initiating system afforded poly(CPD) with controlled molecular weight and narrow MWD in the presence of bases such as n-Bu_4NCl, Et_2O, and EA.

Figure 7 demonstrates further control of molecular weights and their distributions with increasing monomer-to-initiator ratio ($[M]_0/[\text{initiator}]_0$). Thus, in the **1**/$SnCl_4$/$n$-$Bu_4NCl$ initiating system, the amount of **1** was fixed ($[\mathbf{1}]_0 = 5.0$ mM), whereas the initial monomer concentration was varied ($[M]_0 = 250$, 500, and 1000 mM for $DP_n = 50$, 100, and 200, respectively) (Figure 7). M_n increased linearly with monomer conversion and agreed well with the calculated values. These results also show that **1** in fact serves as an initiator to form polymer with controlled molecular weights.

The living nature of the polymerization with the **1**/$SnCl_4$ initiating system in the presence of n-Bu_4NCl or Et_2O was then examined in monomer-addition experiments; thus, CPD was polymerized with these systems, and a fresh feed of CPD was added to the reaction mixture when the initial charge had been almost consumed. Although the second-phase polymerization proceeded, it was slower than the first and terminated at 50−70% conversion of the added CPD, to give products with a bimodal SEC curve with a small shoulder at lower molecular weights. This indicates that part of the growing carbocations react with the double bond of a polymer chain, rather than monomer, to be inactivated at the latter stage of the first-phase polymerization where most of the monomer has been consumed. Thus, the cationic polymerizations of CPD with these systems cannot be defined as "living polymerizations", despite the observed molecular weight increase and narrow MWDs, which show a long lifetime of the intermediate and near absence of side-reactions.

4. Polymer Analysis. The structure of the poly(CPD) obtained with **2**/$SnCl_4$/n-Bu_4NCl in CH_2Cl_2 was examined by ^{1}H NMR spectroscopy (Figure 8). The vinyl ether adduct **2** was used herein for easy detection of the initiator fragment. The poly(CPD) shows large characteristic signals of main-chain repeat units, i.e., olefinic (*e*) and aliphatic protons (*f*−*i*). The aliphatic protons consist of roughly four parts due to 1,2- and 1,4-structures, as known in conventional cationic polymerization of CPD.[24] The 1,2-unit content was 46% based on peak areas $[(1 - f/e) \times 100]$.[24] The regioselectivity was almost the same in both n-Bu_4NCl and salt-free systems.

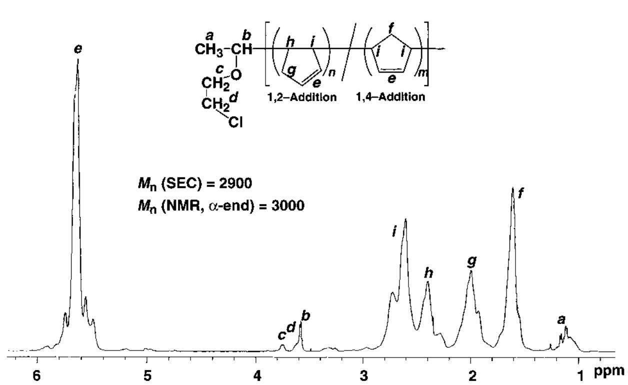


Figure 8. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of poly(CPD) ($M_n = 2900$, $M_w/M_n = 1.15$) obtained with **2**/$SnCl_4$ in the presence of n-Bu_4NCl in CH_2Cl_2 at −78 °C: $[CPD]_0 = 500$ mM; $[\mathbf{2}]_0 = 5.0$ mM; $[SnCl_4]_0 = 5.0$ mM; $[n\text{-}Bu_4NCl]_0 = 5.0$ mM.

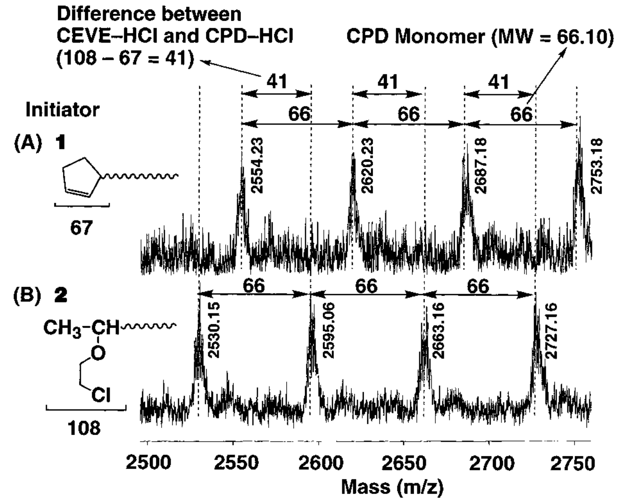


Figure 9. MALDI-TOF-MS spectrum of poly(CPD) obtained with **1**/$SnCl_4$ (A) and **2**/$SnCl_4$ (B) in the presence of n-Bu_4NCl in CH_2Cl_2 at −78 °C: $[CPD]_0 = 500$ mM; [**1** or **2**]$_0$ = 5.0 mM; $[SnCl_4]_0 = 5.0$ mM; $[n\text{-}Bu_4NCl]_0 = 5.0$ mM. (A) $M_n = 3700$, $M_w/M_n = 1.14$; (B) $M_n = 2900$, $M_w/M_n = 1.15$.

In addition to these major peaks, there appeared small but distinct absorptions assignable to the initiator fragment (*a*−*d*). The M_n(NMR) was determined from the relative peak area of the main-chain repeat units (*e*) to the initiator moiety (*b*−*d*) and was very close to that by SEC [M_n(NMR) = 3000, M_n(SEC) = 2900]. This also suggests that **2** initiates one living polymer chain per molecule.

The poly(CPD) obtained with **1**/$SnCl_4$/n-Bu_4NCl and **2**/$SnCl_4$/n-Bu_4NCl was further analyzed by matrix-assisted laser desorption−ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) (Figure 9). Both spectra consist of a single series of sharp peaks separated by a 66 Da interval each, corresponding to the molecular weight of CPD monomer. These indicate the virtual absence of significant side reactions such as chain transfer. Furthermore, there is 41 Da difference between the sharp peaks in the two spectra, which agrees with the mass difference between the initiators **1** and

2 whose fragments are to be affected to the α-end. This result also indicates that one initiator generates one polymer chain and that every polymer chain contains the initiator moiety at the α-end. The terminal structure predicted from the absolute mass is an olefin, which is due to chlorine elimination induced by the laser, similar to the Cl-terminated polymers obtained with transition-metal-catalyzed living radical polymerization,[25] or due to hydrogen chloride elimination during the workup process.

In conclusion, we have synthesized poly(CPD) with controlled molecular weights and narrow MWDs via cationic polymerization of CPD with **1** or **2**/$SnCl_4$ initiating systems in the presence of *n*-Bu_4NCl, Et_2O or EA in CH_2Cl_2 at −78 °C. Our forthcoming paper will discuss another aspect of CPD polymerization, control of regioselectivity for the 1,2- and 1,4-structure.[26]

Experimental Section

Materials. Unless otherwise specified, all of the chemicals were purchased from Wako Company, Japan. CPD was obtained by the retro-Diels−Alder reaction of dicyclopentadiene (Tokyo Kasei; >95%) at 165 °C over calcium hydride and distilled from calcium hydride. It was stored at −84 °C and used within 1 month. The purity and the absence of dicyclopentadiene in CPD were confirmed by NMR before use (purity >99%). CH_2Cl_2 (>99%) was dried overnight over calcium chloride and distilled from phosphorus pentoxide and then from calcium hydride before use. Methylcyclohexane (MCH) (Tokyo Kasei; >99%), carbon tetrachloride (internal standard for gas chromatography; >99%), ethyl acetate (EA) (>99%), and 1-phenylethyl chloride (**4**; >97%) were dried overnight over calcium chloride and distilled twice from calcium hydride. Toluene (>99%), diethyl ether (Et_2O) (>99%), and tetrahydrofuran (THF) (>99%) were dried overnight over calcium chloride and distilled from sodium benzophenone ketyl. $SnCl_4$ and BCl_3 (both Aldrich; 1.0 M solution in CH_2Cl_2), $TiCl_4$ (Aldrich; >99.9%), *n*-Bu_4NCl (Tokyo Kasei; >98%), and isopropyl ether (*i*-Pr_2O) (Aldrich; anhydrous; 99%) were used as received.

Synthesis of HCl Adducts 1−3. The HCl adducts **1**−**3** were synthesized by bubbling dry HCl gas into a solution of the respective vinyl compounds (CPD, CEVE, and αMeSt).[27] The synthesis of HCl−CPD adduct **1** is outlined below as a typical example. Dry HCl gas was bubbled into 1.0 M toluene solution (36 mL) of CPD (3.0 mL; 0.036 mol) at −78 °C. The gas was generated by dropping concentrated sulfuric acid onto powdery sodium chloride and dried by passing it through a column packed with calcium chloride. After 30 min, the excess HCl in the reaction mixture was removed by bubbling dry nitrogen gas at 0 °C for 30 min, and the clean and quantitative formation of adduct **1** was confirmed by ^1H NMR spectroscopy. ^1H NMR (500 MHz, $CDCl_3$): δ 2.65−3.15 (*m*, $-CH_2-CH_2-$, 4 H), 5.46 (*m*, $CH-Cl$, 1 H), 6.35−6.50 (*m*, $-CH{=}CH-$, 2 H). The concentration of **1** was determined by titrating the chloride by the Volhard method.[28] The observed value (0.89 M) further confirmed the quantitative formation of **1** from CPD.

Polymerization Procedures. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure in CH_2Cl_2 is given below: The reaction was initiated by sequential addition of prechilled solutions of **1** (0.02 mmol; 0.40 mL of 0.050 M in CH_2Cl_2) and mixture solutions (0.40 mL) of $SnCl_4$ (0.050 M in CH_2Cl_2; 0.02 mmol) and *n*-Bu_4NCl (0.050 M in CH_2Cl_2; 0.02 mmol) via dry syringes into a monomer solution (in CH_2Cl_2; 3.2 mL) containing CPD (0.165 mL; 2.0 mmol) and CCl_4 (0.165 mL). The total volume of the reaction mixture was 4.0 mL. After stirring at −78 °C for 20 s, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia, to precipitate white powder. 3-*tert*-Butyl-4-hydroxy-5-methylphenyl sulfide (0.014 mmol; 0.005 g) was then added as an antioxidant immediately after quenching. Monomer conversion was 56%, which was calculated from its residual concentration measured by gas chromatography with CCl_4 as an internal standard. The quenched reaction mixture was washed with dilute hydrochloric acid and with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to yield 0.08 g (60%) of polyCPD: $M_n = 3600$, $M_w/M_n = 1.19$.

Measurements. The MWD of the polymers were measured by size exclusion chromatography (SEC) in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: 20−1000 Å; 8.0 nm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index detector. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemicals; M_n = 580−1 547 000; $M_w/M_n \leq 1.1$) as well as the styrene monomer. ^1H NMR spectra of the produced polymers were recorded in $CDCl_3$ on a JEOL LNM-LA500 spectrometer, operating at 500.2 MHz. MALDI-TOF-MS spectra were measured on a Perseptive Biosystems Voyager-DE STR equipped with a 2 m linear flight tubes and a 337 nm nitrogen laser (pulse width, 3 ns), along with a delayed extraction capability. All experiments were carried out at an accelerating potential of 20 kV. In general, mass spectra from 256 laser shots were accumulated summed to produce a final spectrum. Angiotensin I (human; MW = 1296.5) (BACHEM) and insulin (bovine pancreas 28.3; MW = 5733.50) (Nacalai) were used as internal standards to calibrate the mass scale. Samples for MALDI-TOF-MS analysis were prepared by mixing the poly(CPD), a matrix (1,8-dihydroxy-9(10*H*)-anthracenone; dithranol), and a cationizing agent (silver trifluoroacetate) in THF. For example, a poly(CPD) sample (approximately 10 mg/mL) was dissolved in THF. The matrix and the cationizing agent were also dissolved separately in THF (30 and 10 mg/mL, respectively). A 30 μL portion of the poly(CPD) solution, 90 μL of the matrix solution, and 30 μL of the cationizing agent were mixed in a glass vial. Then 0.5 μL portions of the mixture were deposited onto 10−20 wells of the gold-coated sample plate and dried in air at room temperature.

Acknowledgment. M.O. is grateful to the Japan Society for the Promotion of Sciences (JSPS) for JSPS Research Fellowships for Young Scientists and also to the Ministry of Education, Science, Culture, and Sports, Japan, for the partial support of this work by the Grant-in-Aid for Scientific Research (No. 9828).

References and Notes

(1) This work was presented in part at the 49th Annual Meeting of the Society of Polymer Science, Nagoya, Japan, May 2000; Paper ID17: Ouchi, M.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **2000**, *49* (2), 162.
(2) Okuda, J.; Mülhaupt, R. In *Synthesis of Polymers (Materials Science and Technology Series)*; Schlüter, A.-D., Ed.; Wiley-VCH: Weinheim, Germany, 1999; Chapter 5.
(3) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223.
(4) Grubbs, R. H.; Khosravi, E. In *Synthesis of Polymers (Materials Science and Technology Series)*; Schlüter, A.-D., Ed.; Wiley-VCH: Weinheim, Germany, 1999; Chapter 3.
(5) Recently, Natori et al. reported living anionic polymerization of 1,3-cyclohexadiene and subsequent hydrogenation to produce high-T_g polymers: (a) Natori, I. *Macromolecules* **1997**, *30*, 3696. (b) Natori, I.; Imaizumi, K.; Yamagishi, H.; Kazunori, M. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1657.
(6) For a review on cationic polymerization; see: Kennedy, J. P. *Cationic Polymerization of Olefins: A Critical Inventory*; Wiley-Interscience: New York, 1975.
(7) Staudinger, H.; Bruson, H. A. *Ann.* **1926**, *447*, 110.
(8) Aso, C.; Kunitake, T.; Ishimoto, Y. *J. Polym. Sci., Part A-1* **1968**, *6*, 1163.
(9) Sigwalt, P.; Vairon, J. P. *Bull. Soc. Chim. Fr.* **1964**, 482.
(10) Momiyama, Z.; Imanishi, Y.; Higashimura, T. *Chem. High Polym.* **1966**, *23*, 56.

(11) Aso, C.; Kunitake, T.; Ishimoto, Y. *J. Polym. Sci., Part A-1* **1968**, *6*, 1175.
(12) Sauvet, G.; Vairon, J. P.; Sigwalt, P. *C. R. Acad. Sci. Paris* **1967**, *265*, 1090.
(13) Vairon, J. P.; Sigwalt, P. *Bull. Soc. Chim. Fr.* **1971**, 559.
(14) McCann, M.; Coda, E. M. G. *J. Mol. Catal. A: Chem.* **1996**, *109*, 99.
(15) Kühn, F. E.; Ismeier, J. R.; Schon, D.; Xue, W.-M.; Zhang, G.; Nuyken, O. *Macromol. Rapid Commun.* **1999**, *20*, 555.
(16) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265.
(17) For recent reviews on living cationic polymerization, see: (a) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111. (b) Kennedy, J. P.; Iván, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser: Munich, 1992. (c) *Cationic Polymerizations*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996.
(18) Kamigaito, M.; Maeda, Y.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1993**, *26*, 1643.
(19) Aoshima, S.; Higashimura, T. *Polym. Bull.* **1986**, *15*, 417.
(20) Kishimoto, Y.; Aoshima, S.; Higashimura, T. *Macromolecules* **1989**, *22*, 3877.
(21) Ishihama, Y.; Sawamoto, M.; Higashimura, T. *Polym. Bull.* **1990**, *24*, 201.
(22) Kaszas, G.; Puskas, J.; Kennedy, J. P. *Polym. Bull.* **1988**, *20*, 413.
(23) Perneker, T.; Kennedy, J. P. *Polym. Bull.* **1991**, *26*, 305.
(24) Aso, C.; Kunitake, K.; Ito, Y.; Ishimoto, Y. *J. Polym. Sci., Part B: Polym. Lett.* **1966**, *4*, 701.
(25) Nonaka, H.; Ouchi, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 2083.
(26) Ouchi, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules*, in press.
(27) Katayama, H.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1995**, *28*, 3747.
(28) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1990**, *23*, 4896.

MA0016580