Control of Regioselectivity and Main-Chain Microstructure in Cationic Polymerization of Cyclopentadiene[1]

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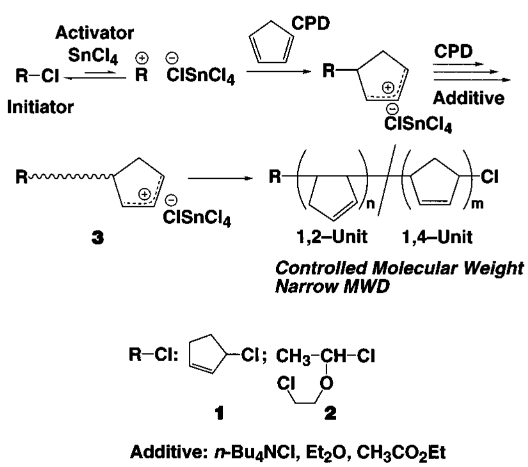
ABSTRACT: The control of regioselectivity in the cationic polymerization of cyclopentadiene (CPD) was examined with initiating systems consisting of the HCl adduct of CPD (**1**; initiator) and a Lewis acid (activator/catalyst). Among a series of metal halides as catalysts, weak Lewis acids such as ZnX_2 (X = Cl, Br, I) gave the highest [1,4]-contents (64, 70, and 76%, respectively). In particular, the **1**/$ZnBr_2$ system induced controlled polymerization to give poly(CPD)s with narrow molecular weight distributions (MWDs) (M_w/M_n = 1.3−1.5) and relatively high regioselectivity ([1,4] = 70%). In contrast, $SnCl_4$, $TiCl_4$, and other strong Lewis acids resulted in less controlled microstructures ([1,4] = 45−50%). Other reaction parameters, e.g., solvents, additives, and temperatures, did not dramatically affect regioselectivity, giving 55−60% [1,4]-contents almost invariably.

Introduction

Cyclopentadiene (CPD) is one of the most representative and inexpensive cyclic dienes, and its polymer is a candidate for new hydrocarbon-polymeric materials with rigid cyclic repeat units. CPD can be polymerized by cationic catalysts to give two rigid main-chain cyclic units, 1,2- and 1,4-enchainments, due to the allylic growing carbocation.[2] Despite the long research history that dates back to the 1920s,[3−7] fine control of molecular weights and microstructures of the polymers is difficult, and the products thus far reported are invariably of low molecular weights and poorly controlled architectures. There are a few studies trying to control the enchainments whereas they suffer from other structures in addition to 1,2- and 1,4-enchainments due to side reactions.[8,9]

Quite recently, however, we have succeeded in controlling molecular weights and molecular weight distributions (MWDs) in cationic polymerization of CPD by using an initiating system consisting of an HCl adduct (**1** or **2**; initiator) and $SnCl_4$ (activator/catalyst) in the presence of an additive such as n-Bu_4NCl, diethyl ether, or ethyl acetate (eq 1).[10,11] These polymerizations



(1)

are considered to proceed via the allylic carbocation (**3**) reversibly generated from its dormant, chlorine-capped species, to give polymers with controlled molecular weights and narrow MWDs (M_w/M_n = 1.2−1.3).

However, even these systems failed to control another critical factor of CPD cationic polymerization, the regioselectivity for the main chain, giving nearly equal amounts of 1,2- and 1,4-units as do conventional systems.[7] Another problem in cationic CPD polymerization is the formation of irregular main-chain structures (due to cation rearrangement) and insoluble products (due to the in-chain double bonds).[3,7,9,10] Thus, the regioselective cationic polymerization of CPD has not been attained yet,[3−13] which is in contrast to some metal-catalyzed coordination polymerizations of cyclopentene that generate crystalline, highly isotactic *cis*-1,3-polymers.[14−20]

This study was thus aimed to develop a regioselective cationic polymerization of CPD with our binary initiating systems [**1**/MX_n (Lewis acid)], in relation to the effects of reaction conditions such as solvents, temperatures, additives, and Lewis acids (Scheme 1). As with other vinyl monomers,[21−23] these reaction parameters may affect the nature of the growing CPD (allylic) carbocation and, in turn, the regioselectivity in propagation. For example, in cationic polymerizations of isobutyl vinyl ether, the meso dyad content (isotacticity) can be varied from 60% to 90% with designed Lewis acids.[23] No stereochemical control via catalyst design, however, has been found in cationic polymerizations of CPD and related cyclic or linear conjugated dienes.

This paper reports that 1,4-enchainment can be varied between 51 and 76% using various catalysts. The **1**/$ZnBr_2$-system especially induces controlled cationic polymerization to give poly(CPD)s with controlled molecular weights, narrow MWDs (M_w/M_n = 1.2−1.3), and relatively high regioselectivity ([1,4] = 70%).

Results and Discussion

1. Effect of Solvents, Additives, and Temperature. (a) Solvents. In cationic polymerizations of vinyl monomers, the stereochemistry of the polymers depends on solvent polarity, which affects the ionic dissociation of the growing carbocation.[23−25] Therefore, we carried out CPD polymerization with the **1**/$SnCl_4$ initiating

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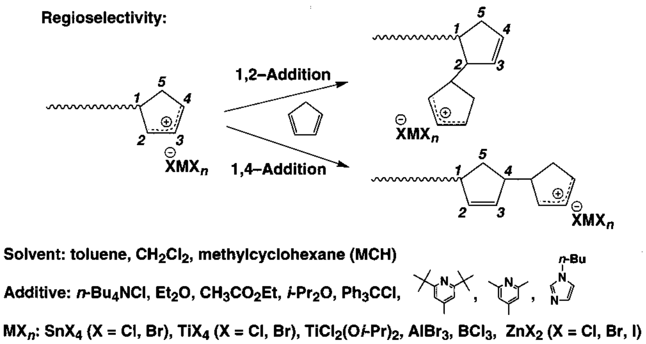
Scheme 1



system at −78 °C in toluene, methylcyclohexane (MCH), and CH_2Cl_2 (Table 1, entries 1−3, and Figure 1, parts A−C). The higher the solvent polarity was, the faster the polymerization. The molecular weight and MWDs of the polymers also depended on the solvents.

The microstructures of the obtained poly(CPD) was analyzed by ^{1}H NMR spectroscopy. Figure 2 shows a representative ^{1}H NMR spectrum of a sample obtained with **1**/$SnCl_4$ in toluene at −78 °C (for entry 1, Table 1). Characteristic signals appear in two regions, one for the olefinic protons (D; $a^{1,2}$ and $a^{1,4}$) around 5.5−6.0 ppm and the other for the aliphatic protons ($b^{1,2}$, $c^{1,2}$, $d^{1,2}$, $b^{1,4}$, and $c^{1,4}$) around 1.5−3.0 ppm. The latter region consists of three well-resolved parts; i.e., 1.4−1.8 ppm (A; $c^{1,4}$), 1.8−2.2 ppm (B; $d^{1,2}$), and 2.2−2.8 ppm (C; $c^{1,2}$, $b^{1,2}$, and $b^{1,4}$). The 1,2- and 1,4-contents (hereafter, [1,2] and [1,4], respectively) can be calculated from their integrated signal intensities by the following two methods[4]

$$\text{Method 1: } [1,2], \% = [(B + C - A)/(A + B + C)] \times 100$$

$$\text{Method 2: } [1,2], \% = [1 - (A/D)] \times 100$$

where A, B, C, and D represent the peak intensities of the four signals.

If a poly(CPD) sample consists of two “regular” main-chain units, 1,2- and 1,4-, the olefinic/aliphatic proton ratio $D/(A + B + C)$ should be 0.5. If the ratio deviates from 0.5, the polymer contains other structures, such as those from the isomerization of the growing carbocation and saturated units via chain transfer or termination. The observed ratios for all of the poly(CPD) are close to 0.50, which indicates the absence of such side reactions under our reaction conditions with **1**/$SnCl_4$. The regioselectivity did not depend on the solvents, where the [1,2] contents were around 45%.

(b) Additives. The effect of additives, which interact with growing carbocation[26] or Lewis acid activator,[27] were also examined in the **1**/$SnCl_4$ system in CH_2Cl_2 at −78 °C (Table 1, entries 4−11, and Figure 1, parts D−K). In addition to n-Bu_4NCl,[10] weak Lewis bases including diethyl ether, ethyl acetate, Ph_3CCl and 2,6-di-*tert*-butyl-4-methylpyridine effectively controlled molecular weights and MWDs (M_w/M_n = 1.3−1.4) (Figure 1, parts D−H). However, diisopropyl ether, 2,4,6-trimethylpyridine, and 1-butylimidazole gave broader and multimodal MWDs (Figure 1, parts I−K), though some of them were effective in living cationic polymerization of styrene.

In contrast, none of the additives affected the regioselectivity; i.e., all polymers showed about 45% [1,2] and 55% [1,4] contents (Table 1). Thus, it was difficult to control the regioselectivity by changing the solvent polarity or by adding salts and Lewis bases in the cationic polymerization with **1**/$SnCl_4$.

(c) Temperature. The regioselectivity was not affected by the polymerization temperature (0 to −78 °C), either. Rather unusual in cationic polymerization, the overall polymerization rate with **1**/$SnCl_4$ in toluene did not clearly depend on temperature (conversion: 50% in 15 min; 80−100% in 120 min), though there were some differences in time−conversion profiles for the temperatures. The olefinic/aliphatic proton ratios were also close to 0.50; a slight decrease at 0 °C (47%) might indicate some side reaction at higher temperature, although the regioselectivities were similar, 55−60% [1,4] units.

2. Effect of Lewis Acids. In addition to varying external reaction parameters such as solvent and temperature, we employed various Lewis acids (MX_n) in conjunction with **1** in toluene or CH_2Cl_2 at −78 °C. The Lewis acids were SnX_4 (X = Cl, Br), TiX_4 (X = Cl, Br), $TiCl_2(O\textit{i}\text{-Pr})_2$, $AlBr_3$, BCl_3, and ZnX_2 (X = Cl, Br, I). The results are summarized in detail in Table 2.

(a) Molecular Weight Control. Entries 1−5, Table 2, show the data for the polymerizations in nonpolar solvent (toluene). Strong Lewis acids such as TiX_4 (X = Cl, Br) and $AlBr_3$ induced rapid polymerizations (90% conversion within 10 min) to give broad MWDs. On the other hand, the polymerization was slower (75% in 30 min, 100% in 5 h) with a weak Lewis acid (BCl_3) and resulted in a broad MWD. Other weak Lewis acids such as $SnBr_4$, $TiCl_2(O\textit{i}\text{-Pr})_2$, and ZnX_2 (X = Cl, Br, I) were not active enough to induce polymerization in toluene.

The Lewis acids had marked effects in polar CH_2Cl_2 (Figure 3 and entries 6−12, Table 2). Strong Lewis acids such as TiX_4 (X = Cl, Br) and $AlBr_3$ gave insoluble gels due to cross-linking as previously reported for their cationic polymerizations in the absence of **1**. In contrast, weaker Lewis acids such as $SnBr_4$, $TiCl_2(O\textit{i}\text{-Pr})_2$, and ZnX_2 (X = Cl, Br, I), which were not active in toluene, induced polymerizations in CH_2Cl_2, despite their low activities. Although most of the Lewis acids gave bimodal or multimodal SEC curves, $ZnCl_2$ and $ZnBr_2$ led to narrow MWDs that are similar to that for the controlled CPD polymers with **1**/$SnCl_4$/n-Bu_4NCl (Figure 1, trace D).[10]

The polymerization with $ZnBr_2$ was quantitative and produced polymers with narrow MWDs (M_w/M_n = 1.3−1.5) (Figure 4). Also, the M_n increased in direct proportion to monomer conversion, as in the polymerization with **1**/$SnCl_4$/n-Bu_4NCl in CH_2Cl_2 at −78 °C.[10] Thus, **1**/$ZnBr_2$ effectively controlled the molecular weights in cationic polymerization of CPD in a salt/additive free solvent.

(b) Regioselectivity with Lewis Acids. Table 2 also summarizes the 1,2- and 1,4-microstructures of poly(CPD) samples obtained with a series of Lewis acids at −78 °C. The olefinic/aliphatic proton ratios [$D/(A + B + C)$] are nearly independent of the catalysts and close to 0.50, as expected for main chains composed exclusively of regular 1,2- and 1,4-units.

In contrast, Lewis acids affected the regioselectivity ([1,4] content) in both toluene and in CH_2Cl_2. Specifically, marked effects were observed in CH_2Cl_2, where weak Lewis acids such as ZnX_2 are still active due to the polar nature of the solvent. For example, Figure 5 shows the main-chain aliphatic proton regions in the ^{1}H NMR spectra of poly(CPD) obtained in CH_2Cl_2 (see also Table 2, entries 6−12). The 1,4-unit contents

Table 1. Effects of Solvent and Additive on CPD Polymerization with 1/SnCl$_4$ at −78 °C[a]

entry	[SnCl$_4$]$_0$, mM	solvent	additive	[additive]$_0$, mM	time, min	convn, %	M_n(calcd) $\times 10^{-3}$ [b]	M_n $\times 10^{-3}$	M_w/M_n	method 1, % [1,2]	method 1, % [1,4]	method 2, % [1,2]	method 2, % [1,4]	$D/(A+B+C)$[c]
1	5.0	toluene	none	0	120	91	6.1	7.5	1.62	46	54	45	55	0.49
2	50	MCH[d]	none	0	2940	47	3.2	4.3	2.17	46	54	45	55	0.49
3	5.0	CH_2Cl_2	none	0	1	100	6.7	8.6	3.33	47	53	45	55	0.48
4	5.0	CH_2Cl_2	n-Bu_4NCl	5.0	2	94	6.3	6.5	1.29	46	54	46	54	0.50
5	10	CH_2Cl_2	Et_2O	96	120	95	6.3	7.1	1.33	44	56	45	55	0.51
6	10	CH_2Cl_2	EtAc[e]	100	960	93	6.2	6.6	1.30	46	54	46	54	0.51
7	5.0	CH_2Cl_2	Ph_3CCl	5.0	3	87	5.8	5.5	1.29	46	54	46	54	0.50
8	5.0	CH_2Cl_2	DTBMP[f]	4.5	1	97	6.5	7.7	1.41	48	52	47	53	0.50
9	10	CH_2Cl_2	i-Pr_2O	71	1	99	6.6	6.6	3.67	47	53	45	55	0.48
10	5.0	CH_2Cl_2	TMP[g]	4.5	1	86	5.8	5.8	2.54	48	52	47	53	0.49
11	5.0	CH_2Cl_2	BIZ[h]	4.5	1	100	6.7	8.0	2.44	47	53	46	54	0.49

[a] [CPD]$_0$ = 500 mM; [**1**]$_0$ = 5.0 mM; [SnCl$_4$]$_0$ = 5.0−50 mM; [additive]$_0$ = 0−100 mM. [b] M_n(calcd) = ([CPD]$_0$/[**1**]$_0$) × 66.1 × convn + 67.1. [c] The olefinic/aliphatic proton ratios by ^{1}H NMR. [d] Methylcyclohexane. [e] Ethyl acetate. [f] 2,6-Di-*tert*-butyl-4-methylpyridine. [g] 2,4,6-Trimethylpyridine. [h] 1-Butylimidazole.

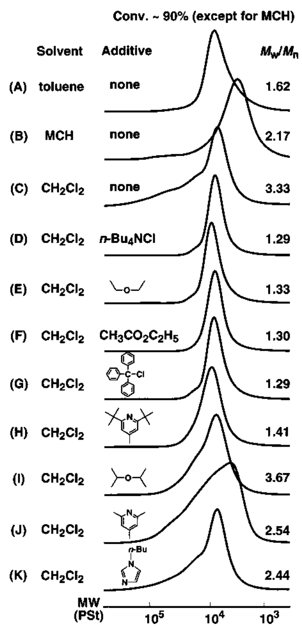


Figure 1. SEC curves and [1,2]/[1,4] contents of poly(CPD) obtained with **1**/SnCl$_4$ at −78 °C: See Table 1 for reaction conditions.

determined from these spectra are compared more visually in Figure 6 as a function of Lewis acids in CH_2Cl_2.

As already discussed, strong Lewis acids such as $SnCl_4$ and $TiCl_4$ give poor regioselectivity (around 55%), irrespective of solvent polarity, additives, and molecular weight control (the so-called living nature of the relevant polymerizations). The 1,4-content (51%) is similarly low with CH_3SO_3H, a protonic acid sometimes employed for CPD cationic polymerization.[28]

With weaker Lewis acids (last four entries in Figure 5), the signals of the 1,2-units clearly weaken and, in turn, those of the 1,4-units become increasingly sharper and stronger in the order of ($SnCl_4$ < $TiCl_4$ < $TiCl_2(Oi\text{-}Pr)_2$ < $ZnCl_2$ < $ZnBr_2$ < ZnI_2). In particular, ZnI_2 led to a 76% 1,4-content, to our knowledge, the highest reported thus far for cationically prepared poly(CPD). $ZnBr_2$ also gives a relatively high 1,4-content (70%), the second highest just below the iodide version. This dual controllability in both MWD and 1,4-content indicates that the **1**/$ZnBr_2$ initiating system may lead to a regioselective *and* living cationic polymerization of CPD, although we have not optimized the reaction conditions yet. The regioselectivity with weak Lewis acids in comparison to strong Lewis acids is most probably due to formation of tight ion pairs. However, we have not clarified why the 1,4-enchainment predominates with these catalysts.

3. DSC Analyses of Poly(CPD)s. The success of the controlled polymerization of CPD in terms of molecular weight and main-chain microstructure promoted us to investigate the thermal property of the polymers by differential scanning calorimetry (DSC) (Figure 7). We employed three poly(CPD) samples with controlled molecular weights and narrow MWDs but low regioselectivity (M_n = 2700, 6600, 10100; [1,4] = 55% each) obtained with **1**/$SnCl_4$/n-Bu_4NCl, and another sample (M_n = 5100; [1,4] = 70%) with a higher regioselectivity with **1**/$ZnBr_2$ in CH_2Cl_2 at −78 °C.

Figure 7 shows that the T_g increased with increasing M_n for the three samples with the same 1,4-content. When the molecular weights are similar (6100 vs 5100), T_g decreased sharply with increasing 1,4-content, most likely due to an increased flexibility of the five-membered ring in the main chain.

In conclusion, enchainment in cationic polymerization of CPD with the **1**/Lewis acid system is not affected by solvents, additives, or temperature but is dramatically affected by Lewis acids. Specifically, weak Lewis acids such as $TiCl_2(Oi\text{-}Pr)_2$ and ZnX_2 (X = Cl, Br, I) induced regioselective polymerization with relatively high 1,4-contents; the highest 1,4-content was obtained with ZnI_2 ([1,4] = 76%).

Experimental Section

Materials. Unless otherwise specified, all of the chemicals were purchased from Aldrich. 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.[10] It was stored at −84 °C and used within 1 month. The purity of CPD and the absence of dicyclopentadiene was confirmed by NMR before use (purity >99%). CH_2Cl_2 (Wako; >99%) was dried overnight over calcium chloride, distilled from phosphorus pentoxide and then from calcium hydride before use. Methylcyclohexane (Tokyo Kasei; >99%), carbon tetrachloride (Wako; internal standard for gas chromatography; >99%), ethyl acetate (Wako; >99%) and 1-butylimidazole (98%) were dried overnight over calcium chloride, distilled twice from calcium hydride. Toluene (Wako; >99%) and diethyl ether (Wako; >99%) were dried overnight over calcium chloride and distilled from sodium benzophenone ketyl. The following materials were used as received: $SnCl_4$, $SnBr_4$ and BCl_3 (all 1.0 M solution in CH_2Cl_2); $TiCl_4$ (>99.9%); $TiBr_4$ and $AlBr_3$ (both >99.99%); $ZnCl_2$ (1.0 M solution in Et_2O); $ZnBr_2$ and ZnI_2 (both >99.999%); CH_3SO_3H (Nacalai Tesque; 99%); n-Bu_4NCl and Ph_3CCl (both Tokyo Kasei; >98%); 2,6-di-*tert*-butyl-4-

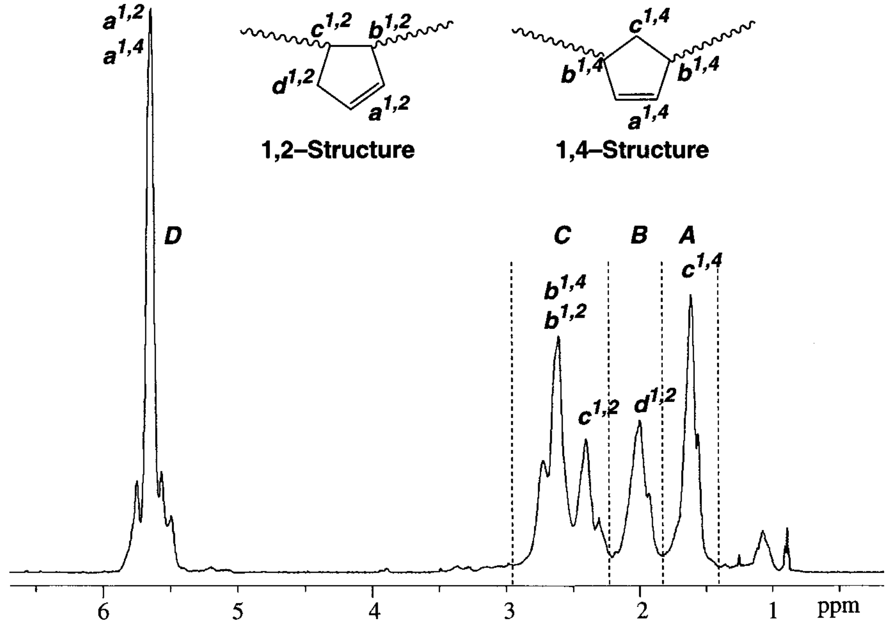


Figure 2. [1]H NMR spectra (500 MHz, $CDCl_3$) of poly(CPD)s ($M_n = 7500$, $M_w/M_n = 1.62$, [1,2]/[1,4] = 45/55) obtained with **1**/$SnCl_4$ in toluene at −78 °C: $[CPD]_0 = 0.50$ M; $[\mathbf{1}]_0 = 5.0$ mM; $[SnCl_4]_0 = 5.0$ mM; entry 3, Table 1.

Table 2. Effects of Lewis Acids on CPD Polymerization with 1 (Initiator) at −78 °C[a]

entry	MX_n	$[MX_n]_0$, mM	solvent	time	convn, %	M_n(calcd) $\times 10^{-3}$[b]	$M_n \times 10^{-3}$	M_w/M_n	method 1, % [1,2]	method 1, % [1,4]	method 2, % [1,2]	method 2, % [1,4]	$D/(A+B+C)$[c]
1	$SnCl_4$	5.0	toluene	2 h	91	6.1	7.5	1.62	46	54	45	55	0.49
2	$TiCl_4$[d]	5.0	toluene	1 min	98	6.5	7.7	3.25	44	56	43	57	0.49
3	$TiBr_4$[d]	5.0	toluene	10 min	95	6.3	4.7	2.34	49	51	48	52	0.49
4	$AlBr_3$[d,e]	0.5	toluene	5 min	93	6.2	6.7	2.94	45	55	43	57	0.49
5	BCl_3	5.0	toluene	5 h	100	6.7	9.2	2.49	42	58	41	59	0.50
6	$SnCl_4$	5.0	CH_2Cl_2	1 min	100	6.7	8.6	3.33	47	53	45	55	0.48
7	$SnBr_4$	5.0	CH_2Cl_2	15 min	70	4.7	(4.7)[g]	(24.4)[g]	47	53	46	54	0.50
8	$TiCl_2(Oi\text{-}Pr)_2$	5.0	CH_2Cl_2	1 day	87	5.8	8.7	1.99	41	59	41	59	0.50
9	BCl_3	5.0	CH_2Cl_2	4 min	77	5.2	(3.1)[g]	(4.93)[g]	45	55	44	56	0.50
10	$ZnCl_2$[f]	100	CH_2Cl_2	26 days	63	4.2	4.8	1.37	36	64	36	64	0.50
11	$ZnBr_2$[f]	100	CH_2Cl_2	5 days	92	6.1	8.7	1.37	31	69	30	70	0.50
12	ZnI_2[e]	100	CH_2Cl_2	14 days	86	5.8	(11.2)[g]	(15.3)[g]	26	74	24	76	0.48

[a] $[CPD]_0 = 500$ mM; $[\text{initiator}]_0 = 5.0$ mM; $[MX_n]_0 = 0.5{-}100$ mM. [b] $M_n(\text{calcd}) = ([CPD]_0/[\mathbf{1}]_0) \times 66.1 \times \text{convn} + 67.1$. [c] The olefinic/aliphatic proton ratios by [1]H NMR. [d] These Lewis acids gave insoluble polymers in CH_2Cl_2. [e] Dissolved in *n*-hexane. [f] Dissolved in Et_2O. [g] Bimodal MWD; see Figure 3.

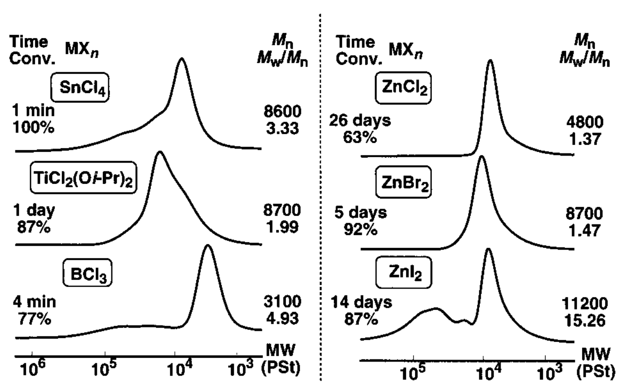


Figure 3. SEC curves of poly(CPD) obtained with **1**/MX_n in CH_2Cl_2 at −78 °C: $[CPD]_0 = 0.50$ M; $[\mathbf{1}]_0 = 5.0$ mM; $[MX_n]_0 = 5.0$ or 100 mM (for ZnX_2).

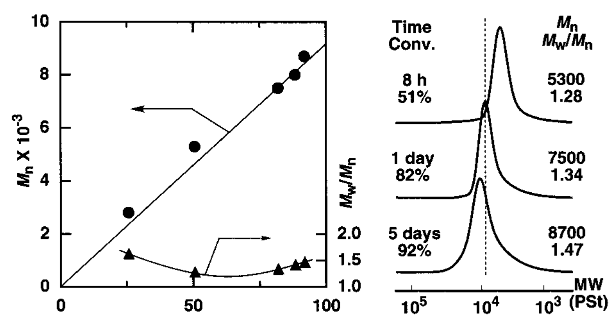


Figure 4. M_n, M_w/M_n, and SEC curves of poly(CPD) obtained with **1**/$ZnBr_2$ in CH_2Cl_2 at −78 °C: $[CPD]_0 = 0.50$ M; $[\mathbf{1}]_0 = 5.0$ mM; $[ZnBr_2]_0 = 100$ mM.

methylpyridine (98%); 2,4,6-trimethylpyridine (99%); and isopropyl ether (anhydrous; 99%). $TiCl_2(Oi\text{-}Pr)_2$ was prepared and purified as already reported.[29] The HCl adduct **1** was synthesized by bubbling dry HCl gas into a solution of CPD as already reported.[10,30]

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 with the **1**/$ZnBr_2$ system is given below: The reaction was initiated by sequential addition of prechilled solutions of **1** (0.015 mmol; 0.30 mL of 0.050 M in CH_2Cl_2) and $ZnBr_2$ (0.3 mmol; 0.30 mL of 1.0 M in Et_2O) via dry syringes into a monomer solution (in CH_2Cl_2; 2.4 mL) containing CPD (1.5 mmol; 0.124 mL) and CCl_4 (0.124 mL). The total volume of the reaction mixture was thus 3.0 mL. After the reaction mixture was stirred at −78 °C for 8 h, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia, to precipitate a white powder.

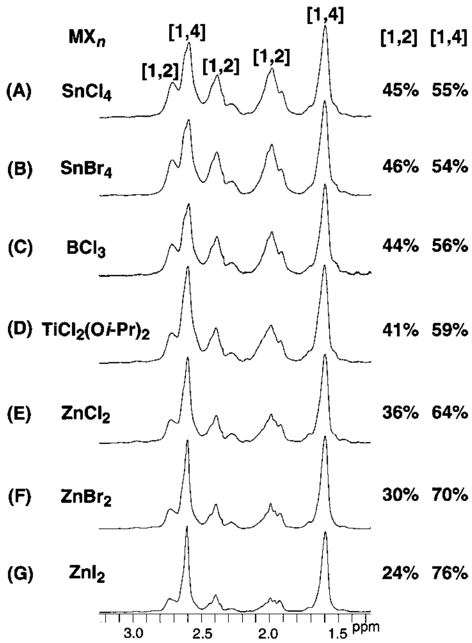


Figure 5. [1]H NMR spectra (500 MHz, $CDCl_3$) around 1.3−3.2 ppm of poly(CPD) obtained with various Lewis acids coupled with **1** in CH_2Cl_2 at −78 °C. See Table 2 for reaction conditions.

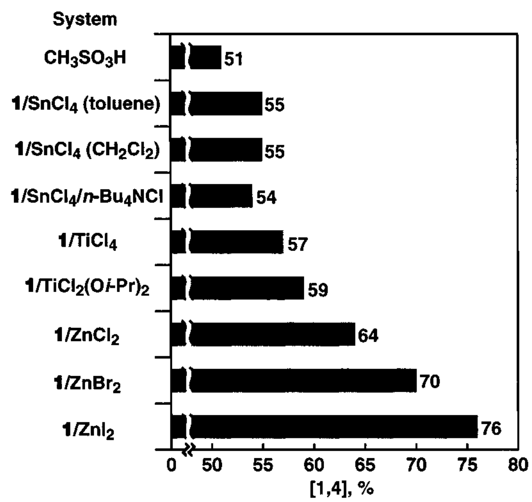


Figure 6. Content of 1,4-units in poly(CPD) obtained under various conditions. See Table 1 and Table 2 for reaction conditions.

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 51%, which was calculated from its residual concentration measured by gas chromatography using 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 0.05 g of poly(CPD): $M_n = 5300$, $M_w/M_n = 1.28$. The polymer yield by gravimetry agreed well with the gas-chromatographic conversion of the monomer. For polymerization in the presence of an additive, it was dissolved in the Lewis acid solution prior to initiation. The typical example for the polymerization procedure with *n*-Bu_4NCl is given below: The reaction was initiated by sequential addition of prechilled solutions of **1** (0.015 mmol; 0.30 mL of 0.050 M in CH_2Cl_2) and mixture solutions (0.30 mL) of $SnCl_4$ (0.050 M in CH_2Cl_2; 0.015 mmol) and *n*-Bu_4NCl (0.050 M in CH_2Cl_2; 0.015 mmol) via dry syringes into a monomer solution (in CH_2Cl_2; 2.4 mL) containing CPD (1.5 mmol; 0.124 mL) and CCl_4 (0.124 mL). The total volume of the reaction mixture was 3.0 mL. After stirring at

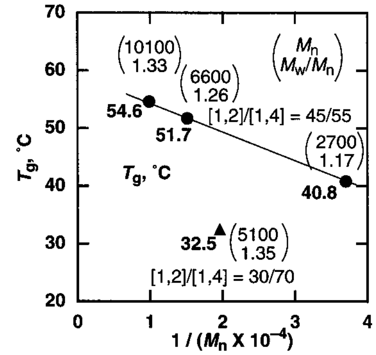


Figure 7. Dependence of molecular weight and main-chain microstructure on T_g of poly(CPD). The three samples (●: $M_n = 2700$, $M_w/M_n = 1.17$; $M_n = 6600$, $M_w/M_n = 1.26$; $M_n = 10100$, $M_w/M_n = 1.33$) with 45% [1,2] and 55% [1,4] were obtained with **1**/$SnCl_4$/*n*-Bu_4NCl in CH_2Cl_2 at −78 °C: $[CPD]_0 = 0.25$, 0.50, or 1.00 M; $[\mathbf{1}]_0 = 5.0$ mM; $[SnCl_4]_0 = 5.0$ mM; $[n\text{-}Bu_4NCl]_0 = 5.0$ mM. The sample (▲: $M_n = 5100$, $M_w/M_n = 1.35$) with 30% [1,2] and 70% [1,4] were obtained with **1**/$ZnBr_2$ in CH_2Cl_2 at −78 °C: $[CPD]_0 = 0.50$ M; $[\mathbf{1}]_0 = 5.0$ mM; $[ZnBr_2]_0 = 100$ mM.

−78 °C for 2 min, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia, to precipitate white powder. The similar procedures to the above example were carried out and 0.09 g (95%) of poly(CPD) was yielded: $M_n = 6500$, $M_w/M_n = 1.29$.

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. [1]H NMR spectra of the produced polymers were recorded in $CDCl_3$ on a JEOL LNM-LA500 spectrometer, operating at 500.2 MHz. The DSC measurements were performed on a Thermo Plus 2 Series (Rigaku, Tokyo) equipped with a DSC8230L module. Polymer solid samples (ca. 6 mg) were measured in an aluminum container under a dry nitrogen flow at a heating or cooling rate of 10 deg/min. α-Alumina was used as a standard.

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References and Notes

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(28) Polymerization conditions (the same as those in Table 2, footnote *a*): $[CPD]_0 = 500$ mM; $[CH_3SO_3H]_0 = 5.0$ mM; at -78 °C in CH_2Cl_2; time, 20 min; conversion = 78%; $M_n = 37\,000$; $M_w/M_n = 4.20$ (bimodal); [1,4] = 51%; $D/(A + B + C) = 0.49$.
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