Macromolecules **2003,** *36,* 3498−3504

Revised Interpretation for *N*-Cyclohexylmaleimide Polymerization in the Presence of an Optically Active Cobalt(II) Complex: Polymerization Mediated by Anionic Species Formed through Monomer−Co(II) Complex−O_2 Interaction

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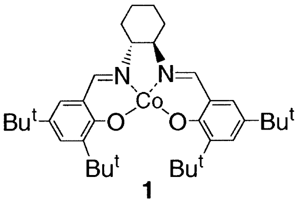
Received November 21, 2002; Revised Manuscript Received February 5, 2003

ABSTRACT: This report revises the interpretations of the reaction mechanism in the polymerization of *N*-cyclohexylmaleimide (CHMI) in the presence of α,α′-azobis(isobutyronitrile) (AIBN) and (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminatocobalt(II) (**1**) [*Macromolecules* **2000**, *33*, 1489]. Although we proposed that the reaction was mediated by a radical species and that the interaction between growing polymer radical with **1** induced chirality in the main chain in the earlier report, the results in the present article indicate that the systems reported in the earlier report were most probably contaminated by a small amount of air and that the polymerization proceeds via an anionic species that was produced by the interaction of the monomer, **1**, and O_2. The effect of the contamination was overlooked due to the lack of a control experiment using O_2 in the absence of AIBN in our earlier study. In this work, the polymerization of CHMI was performed in the presence and absence of **1**, O_2, α,α′-azobis(isobutyronitrile) (AIBN), and protonic additives (methanol and acetic acid). The results indicated the following: (1) the polymerization in a tetrahydrofuran−pyridine mixture occurs in the presence of **1** and a small amount of oxygen even without using AIBN; (2) the reaction does not take place in the presence of **1** alone or in the presence of **1** and AIBN under a strictly controlled N_2 atmosphere; (3) a small amount of AcOH completely inhibits the polymerization with **1** and O_2 while 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) does not kill the reaction; and (4) the polymer was likely to possess −OH or −OOH groups at the chain terminals (a telechelic structure). On the basis of these observations, we withdraw our earlier, wrong interpretation that the polymerization is mediated by a radical species and conclude that the polymerization and the observed stereochemistry are effected by an anionic mechanism.

Introduction

We recently reported that *N*-cyclohexylmaleimide (CHMI) afforded an optically active polymer by polymerization in a tetrahydrofuran (THF)−pyridine mixture in the presences of α,α′-azobis(isobutyronitrile) (AIBN) and (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminatocobalt(II) (**1**).[1] The results were interpreted by assuming a radical polymerization mechanism initiated by AIBN where the proposed interaction between the growing radical and **1** was responsible for the chiral induction. However, through the careful reinvestigations in the present study, we found that the polymerization was in effect mediated not by a radical species but by an anionic species formed by the interaction of CHMI, **1**, and O_2. The polymerization systems reported in the earlier communication were most probably contaminated by a small amount of air, and the contamination was overlooked due to the lack of a control polymerization using **1** in the presence of O_2 in our earlier study. We herein withdraw the mechanistic interpretation in the earlier communication, report the full details of the CHMI polymerizations in the presence and absence of **1**, O_2, AIBN, and protonic additives (methanol and acetic acid), and propose the revised polymerization mechanism involving an anionic growing species. The anionic mechanism was supported by copolymerization with methyl methacrylate and methyl acrylate using conventional anionic initiators. Anionic polymerization of N-substituted maleimides have been performed using the complexes of organolithiums[2] and organozincs[3] with the purpose of stereoregulation. Structural comparisons of the polymers obtained in this work with the polymer synthesized using the *n*-BuLi−(−)-sparteine (Sp) complex also supported the anionic mechanism.



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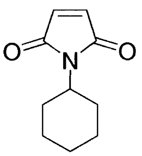

CHMI

Experimental Section

Materials. CHMI (TCI) was used as obtained; purity >99.2% (^1H NMR), mp 87.6−88.6 °C. Methyl methacrylate (MMA) and methyl acrylate (MA) (Wako Chemical) were purified by distillation, dried on CaH_2 under a N_2 atmosphere, and distilled under vacuum immediately before use. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) (Aldrich) was used as obtained. α,α′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Tetrahydrofuran (THF) was refluxed over sodium benzophenone ketyl, distilled and stored on $LiAlH_4$ under a N_2 atmosphere, and distilled under vacuum im-

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10.1021/ma025857q CCC: $25.00

Table 1. Polymerization of CHMI in THF−Pyridine[a]

run	[**1**]$_0$ (M)	[AIBN]$_0$ (M)	[TEMPO]$_0$ (M)	added gas	temp (°C)	conv[b] (%)	M_n[c]	M_w/M_n[c]
1	0	0.023	0		60	95	1060[d]	1.98[d]
2	0.023	0.023	0		60	*e*		
3	0.023	0.023	0	O_2	60	33	1970	2.01
4	0.023	0.023	0.10	O_2	60	23	2480	2.01
5	0.023	0	0		rt	∼0		
6	0.023	0	0	O_2	rt	70	11100	2.42
7	0.023	0	0	air	rt	64	6590	2.62
8	0.023	0	0.10	O_2	rt	52	7200	2.65

[a] Conditions: $[\mathrm{CHMI}]_0 = 2.3$ M, $[\mathrm{pyridine}]_0 = 0.35$ M, added gas = 5 mL, time = 24 h. [b] Determined by ^{1}H NMR analysis of the reaction mixture. [c] Determined by SEC (vs polystyrene). [d] THF-soluble part (51%). [e] Trace.

mediately before use. Toluene was purified by washing with H_2SO_4, distilled, dried by mixing with a small amount of *n*-BuLi, and distilled under a vacuum immediately use. Pyridine (WAKO) was dried on KOH, distilled, and stored on Molecular Sieve 3A under a N_2 atmosphere. Methanol (WAKO) and acetic acid (WAKO) were degassed under vacuum and purged with N_2 immediately before use. Fluorene (WAKO) was recrystallized from hexane (mp 117.9−118.3 °C). *n*-BuLi (Nacalai) (1.6 M, a hexane solution) was used as obtained. $Co(OAc)_2 \cdot 4H_2O$ (WAKO) and (*R*,*R*)-(−)-1,2-diaminocyclohexane (WAKO) were used as obtained. (−)-Spartein (Sp) (Aldrich) was distilled over CaH_2 under a reduced pressure and used as a dry toluene solution (1.08 M).

Synthesis of Complex 1. The literature method[4] was followed with modifications. 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (21.7 g, 92.8 mmol) (Aldrich) dissolved in ethanol (340 mL) was mixed with a solution of (*R*,*R*)-(−)-1,2-diaminocyclohexane (5.30 g, 46.4 mmol) (WAKO) in ethanol (160 mL). The mixture was diluted with 200 mL of ethanol and refluxed for 1 h. Removal of solvent afforded (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (25.4 g, 100%) as a yellow solid. ^{1}H NMR δ: 13.71 (s, 2H), 8.30 (s, 2H), 7.30 (d, $J = 2.3$ Hz, 2H), 6.99 (d, $J = 2.3$ Hz, 2H), 3.35−3.29 (m, 2H), 2.0−1.4 (m, 8H), 1.41 (s, 18H), 1.24 (s, 18H). HRMS (ESI). Calcd for $C_{36}H_{55}N_2O_2$ ($M + H^+$): 547.4264. Found: 547.4236.

$Co(OAc)_2 \cdot 4H_2O$ (2.26 g, 9.06 mmol) (WAKO) dissolved in a mixture of H_2O (7 mL) and ethanol (70 mL) was added to a solution of (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (4.96 g, 9.06 mL) in toluene (70 mL), and the reaction mixture was refluxed for 2 h. Solvent was removed under reduced pressure to give a solid, crude material. The crude material was dissolved in $CHCl_3$ (30 mL), and hexane (600 mL) was added to the solution with stirring. This mixture afforded a deep red solid poduct (**1**) on standing at −20 °C for 12 h. The product was collected with a centrifuge, washed with hexane (5 mL), and dried under vacuum. TLC analysis (Silica Gel 60 F_{254} (Merck), hexanes−ethyl acetate 9/1) showed a single spot and indicated the absence of free ligand. Yield 2.18 g (40%). HRMS (ESI). Calcd for $C_{36}H_{52}CoN_2O_2$: 603.3361. Found: 603.3323.

Polymerization Using 1−O₂. The reactions were carried out in a glass ampule sealed with a glass-made three-way stopcock attached to the ampule via a ground joint. The joint was completely sealed with high-vacuum grease. The ampule was flame-dried under high vacuum and flushed with N_2 immediately before use. A typical procedure is described for run 6 in Table 1. CHMI (1.000 g, 5.58 mmol) and **1** (33.6 mg, 0.0558 mmol) were placed in a glass ampule, dried under high vacuum for 30 min at room temperature, and purged with N_2. THF (1.30 mL) and a THF solution of pyridine (8.49 M THF solution, 0.10 mL, 0.85 mmol) were introduced with a syringe, and the monomer and **1** were completely dissolved. Oxygen (purity 99.9%, 5 mL) was bubbled through the solution in a ca. 3 s period using a syringe. After the reaction mixture was allowed to stand for 24 h, a part of the reaction mixture (0.60 mL) was poured into methanol (40 mL). The methanol-insoluble part was collected with a centrifuge and dried under vacuum at 40 °C for 10 h (0.184 g, 67%). The monomer conversion ratio was 70% by ^{1}H NMR analysis of an aliquot (ca. 0.1 mL) of the reaction mixture dissolved in $CDCl_3$ (0.6 mL) based on the intensity of the olefinic proton signal (s, 6.6 ppm) using the solvent signal (m, 3.7 ppm) as an internal reference.

Anionic Polymerization Using 9-Fluorenyllithium (FlLi). The glassware setup was the same as that for the polymerization using **1**−O_2. A typical procedure is described for run 3 in Table 4. Fluorene (166 mg, 1.00 mmol) was placed in a glass ampule, dried under high vacuum for 30 min, and purged with N_2. THF (1.25 mL) was introduced using a syringe and fluorene was dissolved. To the solution was added *n*-BuLi (1.6 M hexane solution, 0.63 mL, 1.0 mmol) at room temperature. The resulting FlLi solution (0.50 M) was used as an initiator after standing for 10 min at room temperature. CHMI (500 mg, 2.79 mmol) was placed in a glass ampule, dried under high vacuum for 30 min, and purged with N_2. THF (1.47 mL) and MA (0.25 mL, 2.8 mmol) were introduced using a syringe, and the monomer was dissolved. The polymerization was initiated by adding the FlLi solution (0.11 mL, 0.053 mmol) to the monomer solution cooled at 0 °C. After 24 h of reaction, an aliquot (0.1 mL) of reaction mixture was sampled out with a syringe and dissolved in 0.6 mL of $CDCl_3$, and the solution was subjected to ^{1}H NMR and SEC analysis.

Anionic Polymerization Using *n*-BuLi−Sp. The literature method[2] was followed with modifications. The glassware setup was the same as that for the polymerization using **1**−O_2. To dry toluene (1.7 mL) placed in a glass ampule was added *n*-BuLi (1.6 M hexane solution, 0.69 mL, 1.1 mmol) and Sp (1.1 M toluene solution, 1.2 mL, 1.3 mmol). The resulting solution (0.30 M) was used as an initiator solution after standing for 10 min at room temperature. CHMI (1.02 g, 5.68 mmol) was placed in a glass ampule, dried under high vacuum for 1 h, and purged with argon. Toluene (19.9 mL) was introduced using a syringe to dissolve the monomer. The polymerization was initiated by adding the *n*-BuLi−Sp solution (0.43 mL, 0.13 mmol) to the monomer solution cooled at 0 °C. After 2 h, the polymerization was quenched by the addition of methanol (0.2 mL), and the reaction mixture was poured into methanol (500 mL). The methanol-insoluble part was collected with a centrifuge and dried under vacuum at 50 °C for 2 h (0.382 g, 38%). M_n 6300, M_w/M_n 2.63.

Measurements. The ^{1}H NMR spectra were recorded on a JEOL JNM ECP500 or LA400 spectrometer (500 and 400 MHz, respectively, for ^{1}H measurement). CD spectra were obtained with a JASCO J-720L spectrometer. SEC analyses of polymers were performed using a chromatographic system consisting of a Hitachi L-7100 pump, an L-7420 UV detector (254 nm), an L-7490 RI detector, and a JASCO OR990 polarimetric detector equipped with TOSOH TSK gel G3000H$_{HR}$ (styrene−divinylbenzene gel; particle size 5 μm; molecular weight range up to 6×10^4) and G6000H$_{HR}$ (styrene−divinylbenzene gel; particle size 5 μm; molecular weight range up to 4×10^7) columns connected in series (eluent, THF; flow rate, 1.0 mL/min). MALDI-mass spectra were taken on a Voyager DE-STR spectrometer equipped with a N_2 laser (337 nm, 3 ns pulse width, frequency up to 20 Hz) under vacuum (sample chamber pressure 5.5×10^{-7} Torr) using reflector mode (acceleration voltage 20 000 V). The exciting laser power was set to 3000. Samples were prepared by mixing a *N*,*N*-dimethylformamide solution of polymer (concentration 10 mg/mL, 1 μL), aqueous 2,5-dihydroxybenzoic acid (concentration 10 mg/mL, 10 μL) as matrix, and aqueous potassium iodide (concentration 1 mg/mL, 1 μL) and drying the mixed solution in a sample well on a gold-plated sample slide under air flow. ESI MS spectra were recorded using a JEOL JMS-700 spectrometer in the positive measurement mode. TGA analyses were performed on a SEIKO TG/DTA-6200 system under a N_2 atmosphere at a heating rate of 20 °C/min. Temperature and heat capacity were calibrated using In as a standard sample (T_m 156.6 °C, heat capacity 28.59 mJ/mg).

Results and Discussion

Polymerization Behavior and Polymer Structure. In our earlier communication,[1] we reported that

Table 2. Polymerization of CHMI in THF[a]

run	$[\mathbf{1}]_0$ (M)	$[\mathrm{AIBN}]_0$ (M)	$[\mathrm{TEMPO}]_0$ (M)	added gas	temp (°C)	conv[b] (%)	M_n[c]	M_w/M_n[c]
1	0	0.023	0		60	>99	1410[d]	4.11[d]
2	0.023	0.023	0		60	57	4840	1.57
3	0.023	0.023	0.10		60	~0		
4	0.023	0	0	O_2	rt	~0		

[a] Conditions: $[\mathrm{CHMI}]_0$ = 2.3 M, added gas = 5 mL, time = 24 h. [b] Determined by ^{1}H NMR analysis of the reaction mixture. [c] Determined by SEC (vs polystyrene). [d] THF-soluble part (51%).

CHMI afforded an optically active polymer by polymerization in a tetrahydrofuran (THF)–pyridine mixture using AIBN in the presence of **1**. However, through the repeated reactions using **1** and AIBN in THF–pyridine under the same conditions as we reported in the communication, we found that the polymerization had poor reproducibility with varying polymer yield in the range of 0–13%. In contrast, the conventional radical polymerization using AIBN and the anionic polymerization with *n*-BuLi–Sp were completely reproducible. Through reinvestigations into the reaction in the presence of **1** and AIBN, we noticed that a crude reaction mixture that had failed in giving a polymer on heating for 24 h and was left in the ampule with the stopcock removed in the fume hood at room temperature after the experiment became gradually viscous due to polymer formation. On the basis of this observation, we suspected that the inert atmosphere was contaminated with a small amount of air in the earlier study, and the contamination played a role in promoting the polymerization. To make this point clear and reveal the nature of polymerization, the systematic experiments were carried out as described below.

The results of the polymerization in a THF–pyridine mixture in the presence and absence of **1**, AIBN, O_2, and air are summarized in Table 1. Under the conventional radical polymerization condition with AIBN as initiator, a polymer was obtained in a high yield (run 1). In contrast, only a trace amount of polymer was obtained in the presence of **1** (run 2) although we reported in the eariler communication that an optically active polymer was produced in 72% yield under the same conditions. In this reaction, **1** seems to inhibit the radical polymerization. However, when 5 mL of O_2 was quickly bubbled through the sample solution, a polymer was obtained in 33% yield (run 3). Further, polymerization occurred even without AIBN when O_2 or air was injected to the solution of CHMI and **1** at room temperature while **1** alone did not promote polymerization of CHMI (runs 5–7).

To obtain information on the nature of growing species, the effect of TEMPO on the reaction was investigated. The polymerization in the presence of **1** and O_2 and that in the presence of **1**, O_2, and AIBN were not inhibited with TEMPO (runs 4 and 8), indicating that the interaction with O_2, **1**, and CHMI leads to a growing species that is not a free radical. A free-radical growing species would be quickly terminated by TEMPO. On the basis of the results described so far, it would be reasonable to conclude that the reaction systems we reported in the earlier communication was contaminated with a small amount of air and that the reaction was promoted by the interaction of **1**, CHMI, and O_2 in the air.

A different polymerization behavior was observed in a pure THF solution in the absence of pyridine (Table 2). In the polymerization using AIBN, a polymer was obtained in both the presence and absence of **1** where the former case led to a lower polymer yield (runs 1 and 2). The reaction in the presence of **1** was completely inhibited by TEMPO, indicating that the polymerization was mediated by a free-radical species (run 3). In addition, no polymerization took place in a pure THF solution containing only CHMI and **1** upon injecting O_2 (run 4). Hence, it is assumed that coordination of pyridine to the cobalt center of **1** is indispensable in the polymerization involving **1** and O_2 in the reaction mechanism.

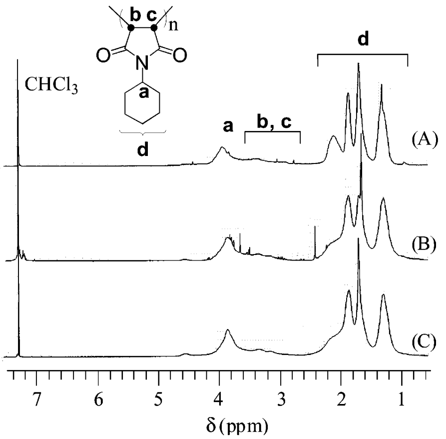


Figure 1. ^{1}H NMR spectra of poly(CHMI)s: (A) conventional radical polymerization with AIBN, (B) anionic polymerization using *n*-BuLi–(–)-sparteine at 0 °C, and (C) polymerization using Co(II) complex **1** and O_2 (500 MHz, $CDCl_3$, room temperature).

There have been reports on the polymerization of vinyl monomers using a cobalt(II) species and O_2 leading to a polymer containing alternating peroxy (–O–O–) and vinyl monomeric units in the main chain.[5,6] If this is the case for the CHMI polymerization in the presence of **1** and O_2 in THF–pyridine, the polymer should be clearly distinguished by spectroscopies from the polymer prepared with AIBN whose main chain consists only of vinyl monomeric units, and also it may thermally decompose through bond-breaking of the peroxy moiety. Upon these working hypotheses, the structures of the polymers obtained from runs 1 and 6 of Table 1 were examined by ^{1}H NMR and thermolysis.

Figure 1 shows the ^{1}H NMR spectra of the two polymers along with that of the polymer anionically prepared using the *n*-BuLi–Sp complex according to the literature[2] (M_n 6300, M_w/M_n 2.63). There was no clear difference in the NMR spectra of the three polymers (Figure 1) in the cyclohexyl $-CH_2-$ (1–2.4 ppm) and the main chain –CH and N–CH (2.6–4.6 ppm) regions, indicating that the polymer prepared using **1**–O_2 in THF–pyridine has the same chemical structure as those of the anionically and radically obtained polymers having no –O–O– bondings in the main chain. The slight difference in the peak shape around 2 ppm may reflect the difference in the tacticity of the polymers.

In the TGA experiments under a N_2 atmosphere, the polymers from runs 1 and 6 of Table 1 indicated very similar thermolysis profiles (Figure 2). The two polymers decomposed at similar onset temperatures around ca. 400 °C. In addition, the polymer from run 6 of Table 1 showed no decrease in molecular weight when heated at 130 °C for 2 h under a N_2 flow. These results support the conclusion from the NMR studies that the polymer from run 6 of Table 1 does not contain –O–O– bondings in the main chain.

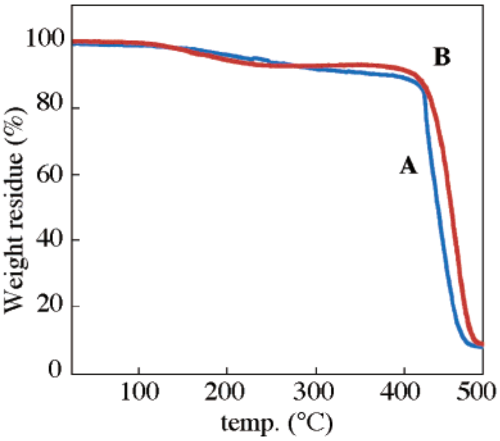


Figure 2. TGA profiles of poly(CHMI)s obtained by radical polymerization using AIBN (run 1 in Table 1) (A) and by polymerization using **1** and O_2 (run 6 in Table 1) (B).

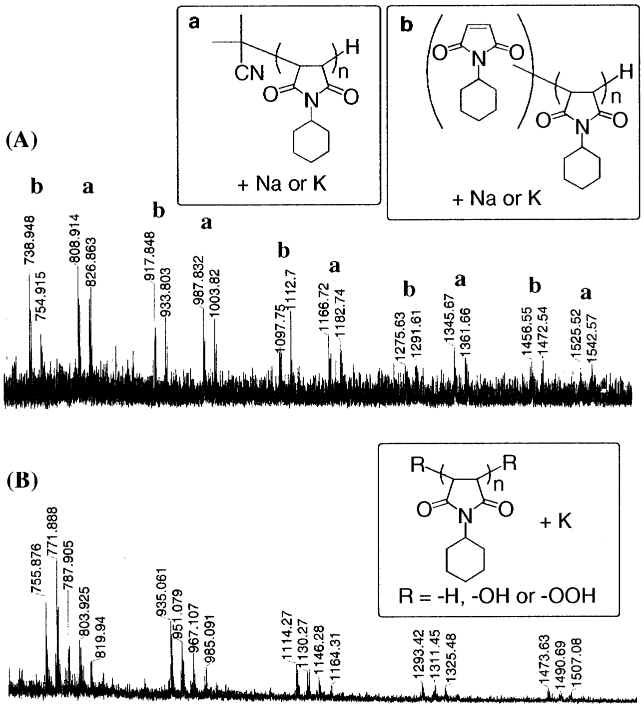
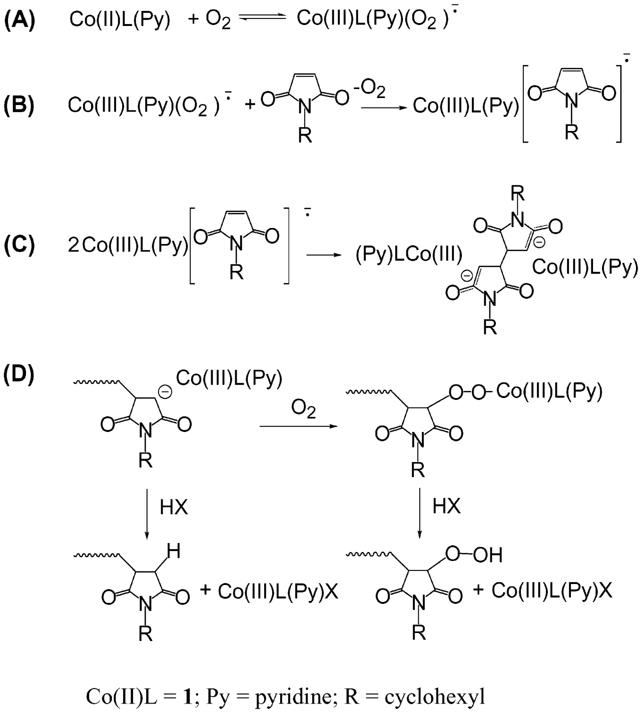


Figure 3. MALDI−mass spectra of poly(CHMI)s obtained by radical polymerization using AIBN (run 1 in Table 1) (A) and by polymerization using **1** and O_2 (run 6 in Table 1) (B). The spectra were obtained using 2,5-dihydroxybenzoic acid as matrix.

The structure of the two polymers was further analyzed by means of MALDI−mass spectrometry (Figure 3). The mass spectrum of the polymer from run 1 of Table 1 (radical polymerization using AIBN) indicated two series of peaks corresponding to different types of structure (Figure 3A). The first series of peaks with mass numbers = ca. 809 (827), 988 (1004), 1167 (1183), 1346 (1362), ... may correspond to the structure of a poly(CHMI) having a 1-cyano-1-methylethyl group at a chain terminal ($M_{\rm n} = 68 + 179n$). The molecular ions seem to be accompanied by an Na or a K (mass numbers in parentheses). This indicates that the 1-cyano-1-methylethyl radical effectively added to CHMI monomer, leading to a growing radical. The fact that there were no peaks corresponding to a polymer having two terminal 1-cyano-1-methylethyl groups demonstrates that the growing chain is not terminated through recombination on through primary radical termination.



Co(II)L = **1**; Py = pyridine; R = cyclohexyl

Figure 4. Proposed mechanism of CHMI polymerization using **1** and O_2.

The second series of peaks with mass numbers = 739 (755), 918 (934), 1098 (1113), 1276 (1292), 1457 (1473), ... may correspond to a poly(CHMI) bearing a CHMI monomer with the intact vinyl group at the chain terminal ($M_{\rm n} = 179 + 179n + 1$). In this case also, the mass peaks seem to reflect molecular ions carrying an Na and a K (mass numbers in parentheses). From the mass spectral data, the chain reaction may proceed through chain transfer to monomer to a certain extent.

In contrast to the polymer synthesized using AIBN, the one synthesized using **1** and O_2 showed a series of group peaks. Each group consisted of three to five peaks that were separated by a mass number of 16. The lowest-mass peak in each group seems to correspond to a polymer molecular ion consisting only of CHMI units with no terminal group, and the rest may correspond polymer molecular ions bearing one to four oxygen atoms. The molecular ions seem to carry a K in this case. These results indicate that the polymer synthesized with **1** and O_2 contains up to four oxygen atoms per chain. Because it was shown that there is no −O−O− bonding in the main chain as described in the preceding section, the oxygen atoms are assumed to be present at the chain terminal as an −O−OH or an −OH group. Therefore, at least, part of the poly(CHMI) synthesized using **1**−O_2 is considered to have a telechelic structure with an −OOH or an −OH groups at the both chain terminals.

Proposed Reaction Mechanism. On the basis of the findings so far described, we propose the revised reaction mechanism (Figure 4). The first step of the series of reactions will be complexation of O_2 with **1** (step A). Such a reaction is known for cobalt(II) complexes having Schiff base type ligands, and crystal structures have been shown in some examples.[7,8] The next step will be single-electron transfer from the **1**−O_2 complex to CHMI (step B). This type of reaction has been reported for reduction of a benzoquinone using the $Co(CN)_5(II)-O_2$ complex.[9] In step B, it is not clear whether O_2 is

Table 3. Effect of Protonic Additive on the Polymerization of CHMI[a]

run	$[\mathbf{1}]_0$ (M)	$[\mathrm{AIBN}]_0$ (M)	protonic additive	added gas	temp (°C)	conv[b] (%)	M_n[c]	M_w/M_n[c]
1	0	0.023	none		60	95	1060[d]	1.98[d]
2	0	0.023	MeOH		60	90	1100[e]	1.85[e]
3	0	0.023	AcOH		60	32	1120	1.38
4	0.023	0	none	O_2	rt	70	11100	2.42
5	0.023	0	MeOH	O_2	rt	25	910	1.18
6	0.023	0	AcOH	O_2	rt	f		

[a] Conditions: $[\mathrm{CHMI}]_0 = 2.3$ M, $[\mathrm{pyridine}]_0 = 0.35$ M, $[\mathrm{additive}]_0 = 0.50$ M, added gas = 5 mL, time = 24 h, solvent = THF. [b] Determined by ^{1}H NMR analysis of the reaction mixture. [c] Determined by SEC (vs polystyrene). [d] THF-soluble part (51%). [e] THF-soluble part (66%). [f] Trace.

completely freed or it stays within the anion radical complex structure. Two molecules of the resulting CHMI anion radical may couple to afford a dianion type species having two trivalent Co species generated from **1** as a countercation (step C). This species would add CHMI monomers, leading to a polymer. The growing species is expected to have an anionic character, and therefore it is not quenched with TEMPO.

This anionic reaction mechanism was supported by the polymerization in the presence of protonic additives (Table 3). The polymer yield was largely suppressed in the presence of MeOH, leading to the formation of a small amount of oligomers, and no polymerization took place in the presence of acetic acid (runs 4–6) while MeOH had virtually no effect on the polymerization using AIBN (run 2). The decrease in polymer yield of the radical polymerization with AIBN in the presence of acetic acid may mean that acetic acid suppressed polymerization through hydrogen radical transfer to the growing radical (run 3). These results indicate that the growing species has an anionic character, but its nucleophilicity is lower than other carbanion species such as those in the anionic polymerization systems of acrylic monomers or styrene where the reaction is readily quenched with MeOH.

Uptake of O_2 into the polymer chain seems to be a part of termination step of the polymerization in addition to protonation of the anionic species (step D). A Co–O–O–C bonding at the chain terminal will result through the reaction of the growing species with O_2. The terminal Co–O–O–C group may heterolytically decompose with water in the atmosphere or with MeOH used in the product purification process to afford a terminal –O–O–H group that may be converted into a terminal –OH group through –O–O– bond breaking. These assumptions are consistent with the mass numbers observed in Figure 3B.

The reaction in step A in Figure 4 has been proposed also for the Co(II) phthalocyanine complex–pyridine (Co(II)Pc(Py))/O_2 system which was used as an initiator for oxidative polymerization of vinyl monomers giving an alternating copolymer of O_2 with a vinyl monomer.[6] While Co(III)Pc(Py)–$O_2^{\bullet}$ was proposed to react with a monomer (M) to give $^{\bullet}$OOM$^{\bullet}$ species and Co(II)Pc(Py) in the oxidative polymerization,[6] we assume that the Co(III)L(Py)–$O_2^{\bullet}$ derived from **1** transfers an electron to CHMI in the present reaction systems (step B) based on the fact that the obtained polymer has a vinyl homopolymeric structure. The mechanism would change depending on the monomer: for a more electron-poor monomer, the electron-transfer mechanism will be more plausible.

Copolymerization with Acrylic Monomers. Polymerization of methyl acrylate (MA) and methyl methacrylate (MMA) and copolymerization of CHMI with MA and MMA using **1**–O_2 were carried out (Table 4). The results supported the anionic nature of the propagating species in the CHMI polymerization using **1**–O_2.

The attempted homopolymerizations of MA and MMA using **1**–O_2 under the same conditions as those for run 6 in Table 1 failed in affording a polymer. This may mean that the second step in the proposed initiation mechanism in Figure 4 requires a monomer that is electron-poor enough to accept an electron from **1**–O_2 complex. Monomers with only one electron-withdrawing carbonyl group attached to the vinyl group may not be able to form an anion radical through the interaction with **1**–O_2.

In addition, in the attempted copolymerization of CHMI with MA and MMA using **1**–O_2, only the homopolymers of CHMI were produced (runs 5 and 6), while in the radical copolymerization with AIBN, both monomers were quantitatively consumed (runs 1 and 2). This polymerization behavior is very similar to that of the anionic copolymerization using 9-fluorenyllithium (FlLi), a typical anionic initiator (runs 3 and 4). These results confirm that the growing species in the CHMI polymerization with **1**–O_2 has anionic nature, but its nucleophilicity is not high enough to polymerize MA and MMA.

Livingness of the Polymerization Initiated with 1 and O_2. The time vs conversion and the conversion vs M_n plots for the polymerizations under the same conditions as runs 1 and 6 in Table 1 are shown in Figure 5. The polymerization initiated with **1** and O_2 is slower than that of the conventional radical polymerization. A clear difference in the conversion vs M_n profile was observed for the two systems; M_n gradually decreased as the polymerization proceeded in the system with AIBN while M_n increased with conversion in the system with **1**–O_2. The latter system seems to have living character, and this observation is consistent with the proposed anionic mechanism.

Chiral Induction and Main-Chain Stereostructure. The stereochemistry of the present polymerization systems was compared with that of the conventional anionic polymerization systems. The main chain of the

Table 4. Copolymerization of CHMI with Methyl Acrylate or Methyl Methacrylate[a]

run	comonomer	initiator	solvent	temp (°C)	CHMI conv[b] (%)	comonomer conv[b] (%)	M_n[c]	M_w/M_n[c]
1	MA	AIBN	THF–pyridine	60	>99	98	1840	2.35
2	MMA	AIBN	THF–pyridine	60	98	>99	4320	6.02
3	MA	FlLi	THF	0	>99	~0	3420	4.10
4	MMA	FlLi	THF	0	>99	d	4540	3.99
5	MA	**1**–O_2	THF–pyridine	rt	74	~0	14700	3.55
6	MMA	**1**–O_2	THF–pyridine	rt	74	~0	14700	2.53

[a] Conditions: $[\mathrm{CHMI}]_0 = 1.2$ M, $[\mathrm{comonomer}]_0 = 1.2$ M, $[\mathrm{initiator}]_0 = 0.023$ M, $[\mathrm{pyridine}]_0 = 0.35$ M, added gas = 5 mL, time = 24 h. [b] Determined by ^{1}H NMR analysis of the reaction mixture. [c] Determined by SEC (vs polystyrene). [d] Trace.

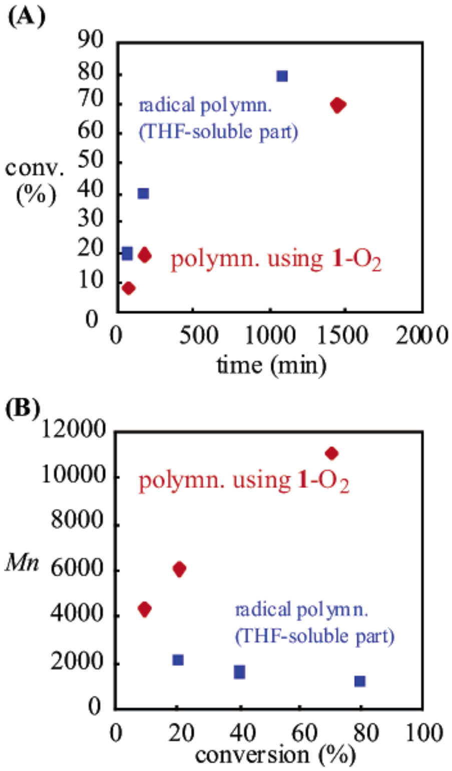
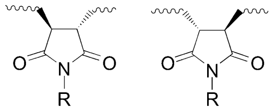


Figure 5. Conversion vs time (A) and M_n vs conversion plots (B) for CHMI polymerization systems: radical polymerization using AIBN in THF−pyridine at 60 °C ($[CHMI]_0$ = 2.3 M, $[AIBN]_0$ = 0.023 M) (blue) and polymerization using **1** and O_2 in THF−pyridine at room temperature ($[CHMI]_0$ = 2.3 M, $[Co(II)]_0$ = 0.023 M, O_2 = 5 mL) (red). Products were partially insoluble in THF in the radical polymerization.

polymers may have *cis*- and *trans*-monomeric units; the latter is chiral. Therefore, if a (*R*,*R*)-*trans*- or (*S*,*S*)-*trans*-monomeric unit is produced in excess, the polymer may be optically active. The polymers obtained using **1**−O_2 complex were optically active.



chiral *trans* monomeric units

Figure 6 shows the CD spectra of the polymer from run 6 in Table 1, the anionically obtained polymer, **1**, and (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (ligand of **1**). The first two samples showed clear CD bands in the imide chromophore region with a similar spectral shape. Complex **1** and its ligand showed CD bands with completely different patterns from those of the polymers, indicating that the chiroptical properties of the polymer sample synthesized with **1**−O_2 does not contain **1** or its ligand residue that may affect the chiroptical properties. These results demonstrate that in the polymerization with **1**−O_2 induced an excess (*R*,*R*)- or (*S*,*S*)-configuration in the main chain similar to the polymerization using the *n*-BuLi−Sp complex, a conventional anionic initiator.

The main-chain stereostructure was also examined by means of ^{13}C NMR spectroscopy (Figure 7). It has been pointed out that the signals around 40−45 ppm in ^{13}C NMR spectra of poly(RMI)s based on the main-chain methine carbons reflect the main-chain configuration (tacticity).[3b] In the ^{13}C NMR spectra, the polymer synthesized using the anionic initiator and that prepared using **1** and O_2 indicated a very similar spectral pattern while the polymer synthesized using AIBN had a different, broad spectral shape. This supports the idea that the optically active polymers have a (*R*,*R*)- or (*S*,*S*)-configuration in excess while the radically prepared, optically inactive polymer has an equal amount of (*R*,*R*)-

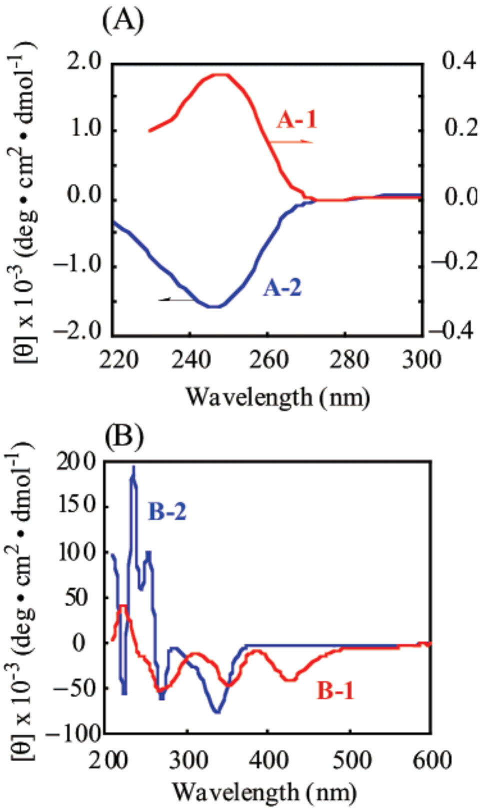


Figure 6. CD spectra of poly(CHMI)s prepared by polymerization with **1** and O_2 (run 6 in Table 1) (A-1) and by anionic polymerization with Sp-FlLi (A-2), and those of **1** (B-1) and (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (ligand of **1**) (B-2) (THF, room temperature).

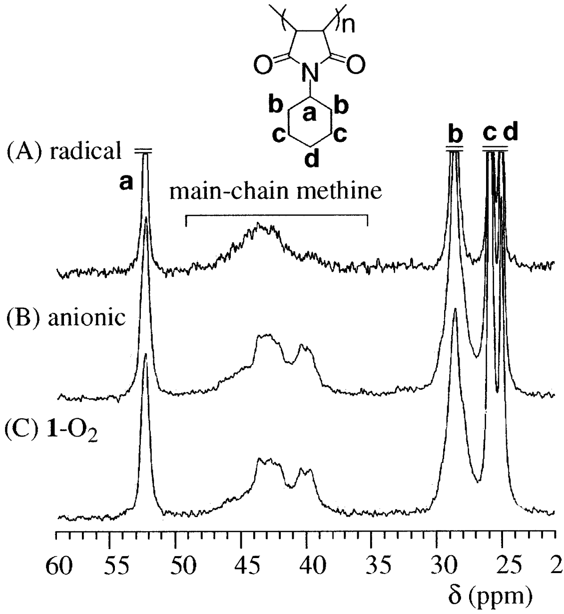


Figure 7. ^{13}C NMR spectra of poly(CHMI)s: (A) conventional radical polymerization with AIBN, (B) anionic polymerization using *n*-BuLi−Sp at 0 °C, and (C) polymerization using **1** and O_2 (125 MHz, $CDCl_3$, room temperature).

and (*S*,*S*)-configurations. Because the former two polymers and the latter polymer are diastereomeric, they may lead to different NMR spectral patterns.[10] The observed stereochemical characteristics are consistent with the revised conclusion that the reaction is mediated by an anionic species.

Conclusions

The findings in this work are summarized as follows:

1. In the absence of O_2, complex **1** simply inhibits radical polymerization with AIBN in THF−pyridine.

2. Interaction of CHMI, **1**, and O_2 generates an initiating species probably through single-electron transfer from the **1**−O_2 complex to CHMI, and the propagating species has anionic character with relatively low nucleophilicity.

3. The resulting polymers appear to possess a telechelic structure with −OH or −OOH groups at the chain terminals introduced probably through termination with O_2.

4. The (*R*,*R*)- or (*S*,*S*)-*trans*-configuration of the main chain is generated in excess by the influence of the cobalt(III) species with a bulky, chiral ligand that originates from **1** and acts as a countercation for the anionic growing species.

The proposed anionic mechanism of the present system involving is in a stark contrast to that in the living radical polymerization system of acrylates[11] or catalytic chain-transfer systems[12] using cobalt(II) porphyrin in the absence of O_2. Formation of ionic initiating species through electron transfer has been reported for the pairs of strongly electron-rich and -poor olefins involving no metallic species.[13] The initiation system found here may expand the scope of such type of polymerization because one might possibly be able to control the tendency of electron transfer by tuning the complex structure including the internal and external ligands and the kind of metal and also by choosing an additive that replaces O_2 so that the system can be applicable to a wider range of monomers.

Acknowledgment. Mr. T. Nishikawa (NAIST) is acknowledged for his valuable experimental assistances. We thank Ms. Y. Nishikawa (NAIST) for mass spectrometric analyses. We are indebted to Prof. T. Yamada (Keio University) and Prof. A. Kajiwara (Nara University of Education) for helpful discussions. This work was supported in part by Grant-in-Aid for Priority Area Research No. 13128203 “Construction of Dynamic Redox Systems Based on Nano-Space Control“ from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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MA025857Q