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Synthesis of Head-to-Tail and Head-to-Head Poly(propylene-*alt*-methyl methacrylate)s via Anionic Polymerization of Methyl 2,4-Alkadienoates. 2.[1] Synthesis and Thermal Properties

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ABSTRACT: Two methyl 2,4-alkadienoates, i.e., methyl 2,4-dimethyl-2,4-pentadienoate (MDMPd) and methyl 2-methyl-2,4-hexadienoate (MMHd), were polymerized using *t*-BuLi or *t*-BuMgCl as the initiator in toluene. ^1H and ^{13}C NMR and IR analyses demonstrated that complete trans 1,4-addition was achieved in the polymerizations. Addition of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) produced polymers with relatively narrow molecular weight distributions ($M_w/M_n = 1.1-1.2$) at 0 °C. Hydrogenation of poly(MDMPd) and poly(MMHd) with *p*-toluenesulfonylhydrazide produced head-to-tail (H−T) and head-to-head (H−H) poly(propylene-*alt*-methyl methacrylate)s, respectively. The thermal properties of H−H poly(propylene-*alt*-methyl methacrylate) and H−T poly(propylene-*alt*-methyl methacrylate) were different. Differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) measurements indicated that both the H−T and H−H copolymers were amorphous. The glass transition temperature of the H−H copolymer is approximately 30 °C higher than that of the H−T copolymer. According to thermogravimetric (TG) analysis, the H−H copolymer is more thermally stable than the H−T copolymer.

Introduction

The syntheses of alternating copolymers containing ethylene or propylene/polar monomer (acrylate or methacrylate units) have attracted much attention in both fundamental and commercial fields because general physical properties of the alternating and random copolymers are different.[2,3] Most ethylene or propylene/polar monomer alternating copolymers were synthesized by copolymerizing the two monomers in the presence of metal halides or organometallics, which is known as a “Lewis acid-complexed alternating copolymerization”.[3−6] The syntheses of poly(ethylene-*alt*-methyl acrylate)[4,5] and poly(propylene-*alt*-methyl acrylate)[4,6] have already been reported. However, the steric bulk of the α-methyl group in MMA makes it difficult to synthesize poly(ethylene-*alt*-MMA) and poly(propylene-*alt*-MMA) directly by alternating copolymerization of ethylene or propylene with MMA, even in the presence of a Lewis acid.[5,6] We previously synthesized poly(ethylene-*alt*-MMA) by reducing poly(vinyl bromide-*alt*-MMA), which was synthesized by “Lewis acid-complexed alternating copolymerization”.[7] Another method of synthesizing well-defined alternating copolymers is 1,4-homopolymerization of dienes followed by hydrogenation of the remaining double bonds.

This paper describes the anionic polymerizations of methyl 2,4-dimethyl-2,4-pentadienoate (MDMPd) and methyl 2-methyl-2,4-hexadienoate (MMHd) by 1,4-addition and the hydrogenation of poly(MDMPd) (**3**) and poly(MMHd) (**4**) to produce head-to-tail (H−T) (**5**) and head-to-head (H−H) poly(propylene-*alt*-MMA) (**6**), respectively (Scheme 1). To the best of our knowledge, this is the first synthesis of a completely alternating copolymer between propylene and MMA. Substituted monomers with carbon−carbon double bonds can be linked, in principle, in two ways: by formation of H−T linkages or by formation of H−H linkages.[8] The H−H copolymers should have new properties that are different from those of the H−T copolymers. Although Vogl et al. have already reported the synthesis and thermal properties of H−H homopolymers,[9−13] including H−H poly(methyl acrylate)[9] and poly(styrene),[10] only a few studies on the regioisomeric ordered copolymers have been published.[14,15]

Experimental Section

Materials. Triphenylphosphine and sodium hydroxide were purchased from Nacalai Tesque (Kyoto, Japan). Methyl 2-bromopropionate (97%), crotonaldehyde (98%), and methacrolein (85%) were obtained from Tokyo Kasei Co. (Tokyo, Japan) and were purified by distillation. *tert*-Butyllithium (*t*-BuLi, 1.5 M *n*-pentane solution), *tert*-butylmagenesium chloride [*t*-BuMgCl, 1.0 M tetrahydrofuran (THF) solution], and *p*-toluenesulfonylhydrazide

Scheme 1. Head-to-Tail (H−T) and Head-to-Head (H−H) Poly(propylene-*alt*-MMA)s

$$\left(-CH_2-CH(CH_3)-CH_2-C(CH_3)(COOCH_3)-\right)_n \qquad \left(-CH_2-CH(CH_3)-C(CH_3)(COOCH_3)-CH_2-\right)_n$$

Head-to-Tail (H-T) Poly(propylene-*alt*-MMA) (**5**)

Head-to-Head (H-H) Poly(propylene-*alt*-MMA) (**6**)

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Table 1. Anionic Polymerization of Methyl 2,4-Dimethylpentadienoate (MDMPd) Initiated by *t*-BuLi[a] and Subsequent Hydrogenation with *p*-Toluenesulfonylhydrazide (TSH)

										hydrogenation[e]				
run	additive	temp (°C)	time (h)	product	yield (%)	M_n[b] × 10^{-4}	M_w/M_n[b]	I_{eff}[c] (%)	T_g[d] (°C)	product	yield (%)	M_n[b] × 10^{-4}	M_w/M_n[b]	T_g[d] (°C)
1	none	0	72	**3a**	73	3.1	3.1_4	8.3	18	**5a**	72	3.9	2.6_1	16
2	*i*-Bu$_3$Al	0	72	**3b**	13	2.1	1.3_8	2.2	30	**5b**	84	2.1	1.3_9	16
3	*i*-Bu$_3$Al+Sp[f]	0	72	**3c**	40	1.9	1.4_3	7.4	29	**5c**	95	2.2	1.3_3	15
4	MAD[g]	0	72	**3d**	98	5.4	1.1_3	6.4	24	**5d**	89	5.5	1.1_4	18
5	none	−20	168	**3e**	2.2	5.2	5.2_3	0.3	20	**5e**				
6	*i*-Bu$_3$Al	−20	168	**3f**	7.3	3.1	1.6_4	1.7	18	**5f**				
7	MAD[g]	−20	168	**3g**	trace	1.5	1.3_1	–	18	**5g**				
8	none	−78	168	**3h**	0	–	–	–	–	**5h**	–	–	–	–
9	*i*-Bu$_3$Al	−78	168	**3i**	0	–	–	–	–	**5i**	–	–	–	–
10	MAD[g]	−78	168	**3j**	0	–	–	–	–	**5j**	–	–	–	–

[a] $[M]_0 = 1.5$ mol/L in toluene. Feed molar ratio of monomer to *t*-BuLi ($[M]_0/[I]_0$) = 25 (run 1−4) or 50 (run 5−10). [b]Determined by SEC in THF relative to polystyrene. [c]Initiator efficiency, defined as [(MW of monomer) × $[M]_0/[I]_0$ × yield/100]/M_n. [d]Determined by DSC (heating rate: 10 °C /min). [e][repeating unit]$_0$ = 0.08 mol/L in toluene at 110 °C for 260 h, [TSH]$_0$/[repeating unit]$_0$ = 5.0. [f](−)-Sparteine. [g]Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide).

(95%) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and used without further purification. 4-*tert*-Butylpirocatecol (99%) was obtained from Wako Pure Chemicals Co. (Osaka, Japan). Triisobutylaluminum (*i*-Bu$_3$Al, 1.0 M toluene solution, Wako Pure Chemicals Co., Osaka, Japan), methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD, 0.4 M toluene solution, Tokyo Kasei Co., Tokyo, Japan), and L-(−)-sparteine (Nacalai Tesque, Kyoto, Japan) were used for polymerizations as additives. Poly(MMA) was prepared by radical polymerization of MMA in toluene, and poly(propylene) (isotactic, M_w=250,000) was purchased from Aldrich Chemical Co., Inc. Toluene was distilled from sodium/benzophenone, and chloroform and dichloromethane were distilled from calcium hydride. Methanol used was purified by distillation.

Measurements. FT-IR spectra were recorded of KBr disks using a JASCO FT/IR-430 spectrometer. ^{1}H and ^{13}C NMR spectra were measured at 27 °C using a JEOL JNM-GX400 spectrometer (400 MHz for ^{1}H NMR). All chemical shifts were expressed as δ downfield from tetramethylsilane (TMS). The number average molecular weights (M_n) and the polydispersity indexes (M_w/M_n) of polymers were estimated by size exclusion chromatography (SEC) calibrated with polystyrene standards using system of Tosoh HLC 803D with a Tosoh RI-8020 detector and Tosoh G2000-(bead size, 5 μm; pore size, 60 Å), G3000-(bead size, 5 μm; pore size, 100 Å), G4000-(bead size, 5 μm; pore size, 200 Å), and G5000-HXL(bead size, 9 μm; pore size, 500 Å) columns (eluent, THF; flow rate, 1.0 mL/min; temperature, 40 °C). Differential scanning calorimetry (DSC) was measured on a DSC 210 unit with a Seiko SSC/5200H TA Station unit from −70 to 200 °C at a heating rate of 10 °C/min. A 4−6 mg sample was taken in an aluminum pan with a lid. The glass transition temperature (T_g) was determined at the inflection point of the corresponding heat capacity jump of the DSC trace. A Seiko TG/DTA 6200 was used for TGA/DTG measurement. The measurement of the sample (ca. 5 mg) was carried out from 20 to 650 °C at a heating rate of 10 °C/min under a nitrogen atmosphere flowing at 100 mL/min. Wide-angle X-ray diffraction (WAXD) patterns were recorded on a Rigaku RINT 2000 X-ray diffraction meter using nickel-filtered Cu Kα radiation (λ=0.15405 nm). The scanning rate was 0.3 °C/min over a range of 2θ = 5−35 °C. All measurements were taken using a generator voltage of 30 kV and 40 mA.

Preparation of MDMPd. In a three-necked flask, triphenylphosphine (235.6 g, 0.90 mol) was dissolved in 850 mL of benzene. Methyl 2-bromopropionate (150.0 g, 0.90 mol) was added at 27 °C. The solution was placed in a water bath at 70 °C for 5 h. As the reaction proceeded, a white powder precipitated. The reaction mixture was cooled to 27 °C and kept for 12 h. The precipitate was collected by filtration and dried to give phosphonium salt **1** (210.9 g, yield 55%, mp 144−147 °C). The phosphonium salt **1** 210.9 g (0.49 mol) was dissolved in 1.9 L of distillated water, and the aqueous solution was neutralized with 10% aq. NaOH to give a white precipitate. After 1 h, it was collected by filtration, washed with distillated water, and dried under reduced pressure. The ylide **2** (106.3 g, 0.31 mol) obtained was dissolved in dichloromethane (400 mL). Methacrolein (28.0 g, 0.40 mol) was added to the solution at 27 °C. The mixture was heated at 45 °C for 12 h. After the reaction, ca. 130 mL of dichloromethane was removed by evaporation. Petroleum ether was added to precipitate triphenylphosphine oxide. The precipitate was removed by filtration, and the filtrate was distilled twice to give MDMPd (27.0 g, yield 63%, bp 65.0−66.0 °C/11 mmHg). ^{1}H NMR (CDCl$_3$, δ, ppm): 1.94 (s, CH$_2$=C−CH_3), 2.02 (s, −CH=C−CH_3), 3.76 (s, −O−CH_3), 5.07 and 5.22 (s, CH_2=CCH$_3$−), 7.11 (s, −CH=C). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 13.9 (CH$_2$=C−CH$_3$), 22.8 (=C−CH$_3$), 51.9 (−O−CH$_3$), 119.7 (CH$_2$=CCH$_3$), 127.5 (−CH=C−), 140.7 (CH$_2$=C−CH$_3$), 140.9 (=CH−), 169.2 (−COOCH$_3$).

Anionic Polymerization of MDMPd. In a typical anionic polymerization of MDMPd, MDMPd (1.12 g, 8.0 mmol), toluene (1.0 mL), and a toluene solution of MAD (0.4 M, 1.2 mL, 0.48 mmol) were placed in a Schlenk tube equipped with a rubber septum under N$_2$. A solution of *t*-BuLi in *n*-pentane (0.16 M, 2.0 mL, 0.32 mmol) was added at −78 °C. After the tube was kept in a bath at 0 °C for 72 h, the reaction mixture was poured into methanol (500 mL) containing a trace amount of aq. HCl (5%). A white powder (1.10 g) was isolated by filtration following precipitation from chloroform into methanol (yield 98%, run 4 in Table 1). ^{1}H NMR (CDCl$_3$, δ, ppm): 1.16 (=CH−C−CH_3), 1.38 (=C−CH_3), 2.06−2.13 and 2.50−2.53 (−CH_2−), 3.59 (−O−CH_3), 5.09 (=CH−). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 18.0 (=CH−C−CH$_3$), 22.9 (=C−CH$_3$), 46.7 (−CH$_2$−), 51.7 (=CH−C−CH$_3$), 51.8 (−O−CH$_3$), 133.4 (−CH$_2$−C−CH$_3$), 135.0 (=CH−), 177.1 (−COOCH$_3$). IR (KBr disk,

Table 2. Anionic Polymerization of Methyl 2-Methyl-2,4-hexadienoates (MMHd)[a] and Subsequent Hydrogenation with *p*-Toluenesulfonylhydrazide (TSH)

											hydrogenation[e]				
run	initiator	additive	temp (°C)	time (h)	product	yield (%)	M_n[b] × 10^{-4}	M_w/M_n[b]	I_{eff}[c] (%)	T_g[d] (°C)	product	yield (%)	M_n[b] × 10^{-4}	M_w/M_n[b]	T_g[d] (°C)
1	*t*-BuLi	none	0	168	**4a**	0	–	–	–	–	**6a**	–	–	–	–
2	*t*-BuLi	*i*-Bu_3Al	0	168	**4b**	78	10.6	1.6_4	5.2	27	**6b**	97	7.3	1.8_4	45
3	*t*-BuLi	*i*-Bu_3Al+Sp[f]	0	168	**4c**	80	4.1	1.4_0	13.7	36	**6c**	83	6.0	1.4_6	46
4	*t*-BuLi	MAD[g]	0	168	**4d**	60	2.4	1.2_2	8.8	30	**6d**	77	2.9	1.2_1	44
5	*t*-BuLi	MAD[g]	0	96	**4e**	34	2.1	1.2_1	5.6	35	**6e**	67	2.7	1.2_1	44
6	*t*-BuLi	none	−20	168	**4f**	0	–	–	–	–	**6f**	–	–	–	–
7	*t*-BuLi	*i*-Bu_3Al	−20	168	**4g**	22	5.9	1.6_4	2.5	27	**6g**	–	–	–	–
8	*t*-BuLi	MAD[g]	−20	168	**4h**	0	–	–	–	–	**6h**	–	–	–	–
9	*t*-BuMgCl	none	0	168	**4i**	25	0.63	2.5_8	27.7	−12	**6i**				
10	*t*-BuMgCl	*i*-Bu_3Al	0	168	**4j**	56	3.0	1.4_9	13.2	30	**6j**	95	3.0	1.4_7	38
11	*t*-BuMgCl	MAD[g]	0	168	**4k**	43	2.7	1.6_0	11.2	34	**6k**	91	3.7	1.4_5	46

[a] $[M]_0 = 1.5$ mol/L in toluene at 0 °C. Feed molar ratio of monomer to initiator ($[M]_0/[I]_0$) = 50 (runs 1−3 and runs 6−11) and 25 (runs 4 and 5). [b]Determined by SEC in THF relative to polystyrene. [c]Initiator efficiency, defined as [(MW of monomer) × $[M]_0/[I]_0$ × yield/100]/M_n. [d]Determined by DSC (heating rate: 10 °C/min). [e][repeating unit]$_0$ = 0.08 mol/L in toluene at 110 °C for 260 h, $[TSH]_0$/[repeating unit]$_0$ = 5.0. [f](−)-Sparteine. [g]Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide).

cm^{-1}): 2948 (ν_{C-H}), 1733 [$\nu_{C=O}$(ester)], 1651 ($\nu_{C=C}$), 1455 (δ_{C-H}), 1200 and 1103 [ν_{C-O-C}(ester)], 848 ($\delta_{C=C-H}$). Anal. Calcd for $(C_8H_{12}O_2)_n$: C, 68.55; H, 8.63; O, 22.83. Found: C, 68.42; H, 8.70; O, 22.88.

Hydrogenation of Poly(MDMPd). A solution of poly(MDMPd) (**3d**) (0.60 g, 4.3 unit mmol) and *p*-toluenesulfonylhydrazide (3.91 g, 21 mmol) in toluene (54 mL) was stirred at 110 °C for 260 h under N_2. The solvent was evaporated, and the polymeric material was purified by reprecipitation from chloroform into methanol, and dried in vacuo to yield white powder **5d** (89%). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.55, 0.64, and 0.79 (−CH−CH_3), 1.02−1.06 (−C−CH_3), 1.12−1.33 (−CH_2−), 1.52 (−C*H*−), 3.52−3.57 (−O−CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 19.0−23.8 (−CH−*C*H_3 and −C−*C*H_3), 26.2 and 26.8 (−CH−), 44.4−45.7 (−CH_2− and −C−), 49.0−51.3 (−O−*C*H_3), 177.9−178.9 (−*C*OOCH_3). IR (KBr disk, cm^{-1}): 2951 (ν_{C-H}), 1733 ($\nu_{C=O}$), 1457 (δ_{C-H}), 1207 and 1149 (ν_{C-O-C}). Anal. Calcd for $(C_8H_{14}O_2)_n$: C, 67.58; H, 9.92; O, 22.50. Found: C, 67.47; H, 10.12; O, 22.41.

Preparation of MMHd. Preparation of MMHd was carried out by the same procedure as that for MDMPd. Phosphoric ylide **2** (83.2 g, 0.24 mol) was dissolved in 200 mL of dichloromethane. Crotonaldehyde (16.2 g, 0.23 mol) was added. The solution was kept at 45 °C for 4 h and 70 mL of dichloromethane was evaporated to condense. Petroleum ether was poured into the solution to precipitate triphenylphosphine oxide. The filtrate was distilled twice to give MMHd (26.7 g, yield 82%, bp 71.0−72.5 °C/10 mmHg). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.87 (d, $J = 6.3$ Hz, CH_3−CH=), 1.92 (s, −CH=C−CH_3), 3.74 (s, −O−CH_3), 6.06−6.13 (m, CH_3−C*H*=), 6.37 (dd, $J = 11.2$, 14.8 Hz, C*H*=CH−), 7.16 (d, $J = 11.2$ Hz, −C*H*=C−). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 12.5 (*C*H_3−CH=), 18.9 (*C*H_3−C=), 51.7 (−O−*C*H_3), 124.6 (CH_3−CH=*C*H−), 127.4 (−CH=*C*−), 137.8 (CH_3−*C*H=), 138.7 (−*C*H=C−), 169.1 (−*C*OOCH_3).

Anionic Polymerization of MMHd. MMHd was polymerized in a manner similar to that for MDMPd (yield 80%, run 3 in Table 2). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.88 (=CH−CH−CH_3), 1.11 (=CH−C−CH_3), 2.64 (=CH−C*H*−CH_3), 3.62 (−O−CH_3), 5.26 (=C*H*−CH−), 5.64 (=C*H*−C−). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 15.1 (=CH−CH−*C*H_3), 17.8 (=CH−C−*C*H_3), 43.9 (=CH−*C*H−CH_3), 51.7 (−O−*C*H_3), 51.8 (=CH−*C*−CH_3), 131.1 and 131.4 (=*C*H−CH−), 133.6 (=*C*H−C−), 175.7 (−*C*OOCH_3). IR (KBr disk, cm^{-1}): 2973 (ν_{C-H}), 1733 [$\nu_{C=O}$(ester)], 1653 ($\nu_{C=C}$), 1457 (δ_{C-H}), 1241 and 1120 [ν_{C-O-C}(ester)], 978 ($\delta_{H-C=C-H}$). Anal. Calcd for $(C_8H_{12}O_2)_n$: C, 68.55; H, 8.63; O, 22.83. Found: C, 68.58; H, 8.73; O, 22.69.

Hydrogenation of Poly(MMHd). Poly(MMHd) (**4d**) was hydrogenated by a procedure similar to that for poly(MDMPd) (yield 77%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.50−0.71 (−CH−CH_3), 0.86−0.90 (−C−CH_3), 1.04−1.16 (−CH_2−CH−), 1.33−1.42 (−CH_2−C−), 1.60 (−C*H*−), 3.52−3.57 (−O−CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 13.4 (−CH−*C*H_3), 15.0 and 15.9 (−C−*C*H_3), 25.8 (−*C*H_2−CH−), 28.2 (−*C*H_2−C−), 36.1 and 36.9 (−*C*−), 40.2−41.5 (−*C*H−), 50.1 and 51.1 (−O−*C*H_3), 177.3 and 177.5 (−*C*OOCH_3). IR (KBr disk, cm^{-1}): 2951 (ν_{C-H}), 1733 ($\nu_{C=O}$), 1457 (δ_{C-H}), 1207 and 1149 (ν_{C-O-C}). Anal. Calcd for $(C_8H_{14}O_2)_n$: C, 67.58; H, 9.92; O, 22.50. Found: C, 67.35; H, 10.08; O, 22.57.

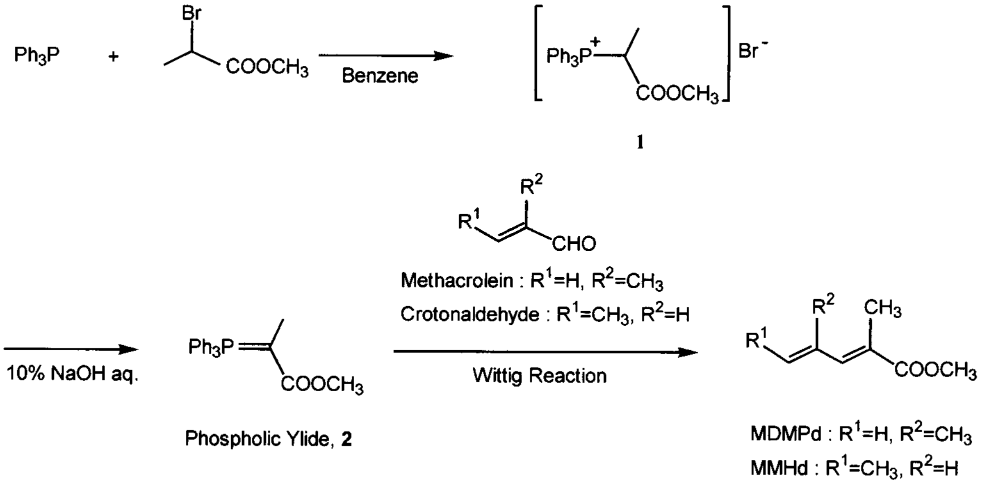
Preparation of Films of H−T and H−H Poly(propylene-*alt*-MMA)s. Films of H−T and H−H copolymers were prepared by casting from chloroform solution. The alternating copolymer (200 mg) was dissolved in 5 mL of distilled chloroform at room temperature. The solution was poured into a Teflon dish (50 mm diameter) with a flat bottom, and the solvent was allowed to evaporate under atmospheric pressure at room temperature for 2 days. After drying further in vacuo at 60 °C for 3 days, the films were stored over P_2O_5 in a desiccator.

Results and Discussion

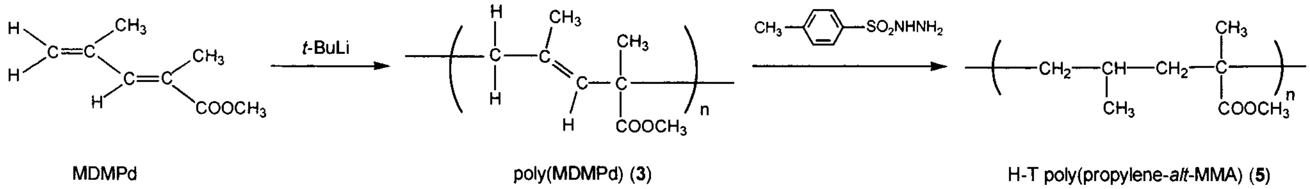
Monomer Synthesis. As shown in Scheme 2, MDMPd and MMHd were prepared via Wittig reactions of methacroleine and crotonaldehyde, respectively, with a phosphoric ylide **2**, Ph_3P=C(CH_3)($COOCH_3$), according to the procedure of House and Rasmusson.[16] ^{1}H and ^{13}C NMR revealed that MDMPd and MMHd prepared in this study have 100% *E*- and *E*,*E*-structure, respectively.

Anionic Polymerization of MDMPd and Subsequent Hydrogenation of Poly(MDMPd) (3). To yield H−T alternating copolymer **5**, MDMPd must polymerize with 100% 1,4-polydiene regioselectively. Hatada et al. have reported that polymerization of MMA by *t*-BuLi/alkylaluminum or bis(2,6-di-*tert*-butylphenoxy)methylaluminum produces stereoregular PMMA with narrow molecular weight distributions in toluene.[17−19] We used similar initiator systems in this work. For MDMPd, coordination of a Lewis acid to the carbonyl group

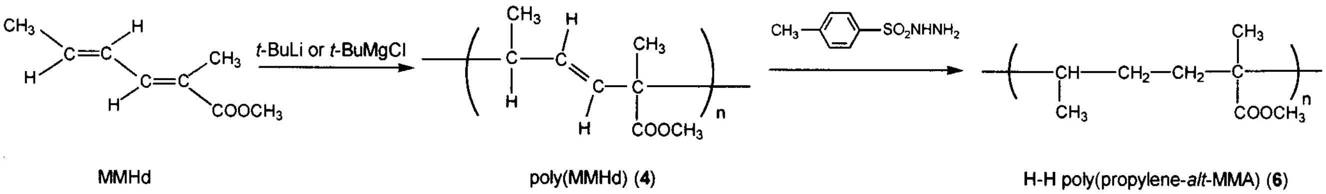
Scheme 2. Syntheses of MDMPd and MMHd



Scheme 3. Polymerization of Methyl 2,4-Dimethyl-2,4-pentadienoate (MDMPd) and Subsequent Hydrogenation



Scheme 4. Polymerization of Methyl 2-Methyl-2,4-hexadienoate (MMHd) and Subsequent Hydrogenation



presumably promoted the 1,4-addition and simultaneously prevented the attack at the ester carbonyl group. The results of the MDMPd polymerization are summarized in Table 1. MDMPd was polymerized in toluene using *t*-BuLi as the initiator in both the presence and absence of *i*-Bu_3Al or MAD. All of the resulting polymers were white and soluble in toluene, chloroform, tetrahydrofuran, and *N*,*N*-dimethylformamide. Their structure was determined by IR, ^1H and ^{13}C NMR, and elemental analyses. In the ^{13}C NMR spectra, the assignments were accomplished by attached proton test (APT) measurements. ^1H and ^{13}C NMR demonstrated that polymer **3** was composed of only 1,4-addition units without 1,2- and 3,4-addition. Dorman et al. found that the responses of carbons 1 and 4 in *cis*-2-hexene were shifted 5.1−5.9 ppm upfield relative to *trans*-2-hexene.[20] Similar results were reported for *trans*- and *cis*-3-hexene and 4-octene.[20] The proton-decoupled resonance signals of carbons in **3** were all singlets and none of the resonances ascribed to other isomers were observed in the ^{13}C NMR spectrum (Figure 1a). The difference nuclear Overhauser effect (NOE) analysis (irradiated $=CH$ at 5.09 ppm) showed a negative signal (1.7%) for $-CH_2-$ at 2.06−2.13 and 2.50−2.53 ppm. These results demonstrate that all of the polymers **3** consisted of 100% *E*-double bonds.

In the absence of an organoaluminum compound (runs 1 and 5), the molecular weights of polymer **3a** ($M_n = 3.1 \times 10^4$) and **3e** ($M_n = 5.2 \times 10^4$) determined by SEC were higher than those calculated from the monomer/initiator ratio [M_n(calcd) $= 0.35 \times 10^4$ for **3a** and 0.70×10^4 for **3e**], and the molecular weight distribution was broad ($M_w/M_n = 3.1_4$ for **3a** and 5.2_3 for **3e**). The broad molecular weight distribution may be due to attack of the polymer anion at the carbonyl group of MDMPd. Addition of an organoaluminum catalyst, i.e., *i*-Bu_3Al or MAD,[21] produced polymers **3b**−**d** and **3f**−**g** with relatively narrow molecular weight distributions, although the initiator efficiency (I_{eff}) was still low (runs 2−4 and 6−7). In the case of polymerization at 0 °C, addition of MAD improves both the polymer yield and the M_w/M_n index. Organoaluminum aryloxides are bulky but do not reduce the Lewis acidity much.[21] This system produced poly(MDMPd) in 98% yield with $M_w/M_n = 1.1_3$ (run 4). The results suggest that coordination of MAD or *i*-Bu_3Al to the monomer not only activates the monomer but also prevents termination by attack of the growing polymer at the ester group of the monomer. Coordination of *i*-Bu_3Al or MAD to the carbonyl group in MDMPd was confirmed by ^{13}C NMR analysis of MDMPd/*i*-Bu_3Al or MAD (1:1, mol/mol) mixture in toluene-d_6. Addition of the Lewis acids make shift the carbon signals of MDMPd to lower field. The carbonyl (168.5 ppm) and δ-carbon (119.7 ppm) resonances appeared at 172.7 and 122.6 ppm in the presence of *i*-Bu_3Al and at 169.2 and 120.7 ppm in the presence of MAD. In the case of MDMPd/MAD, there was little difference in the pres-

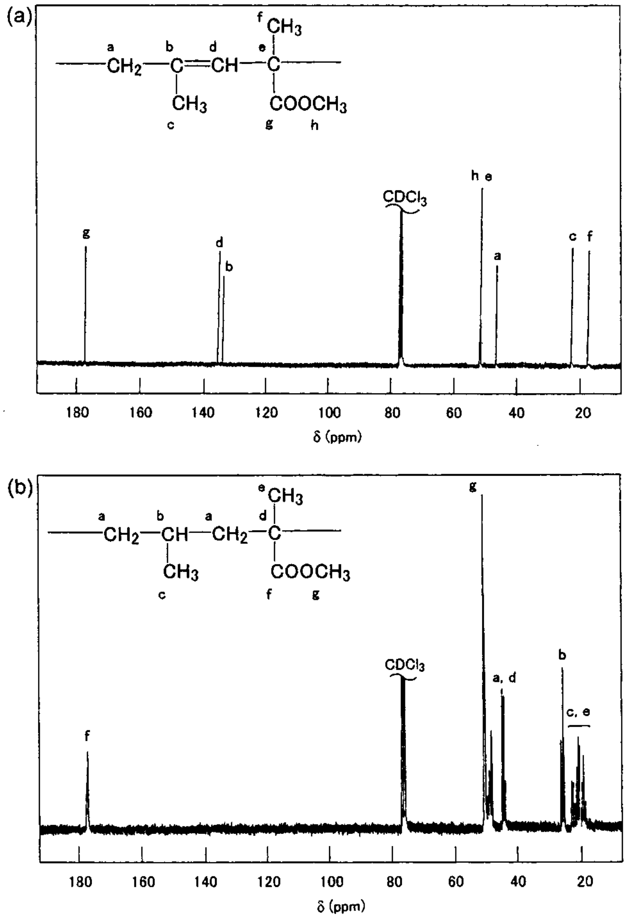


Figure 1. ^{13}C NMR spectra of (a) poly(MDMPd) (**3d**) and (b) H−T poly(propylene-*alt*-MMA) (**5d**) in $CDCl_3$ (run 4 in Table 1).

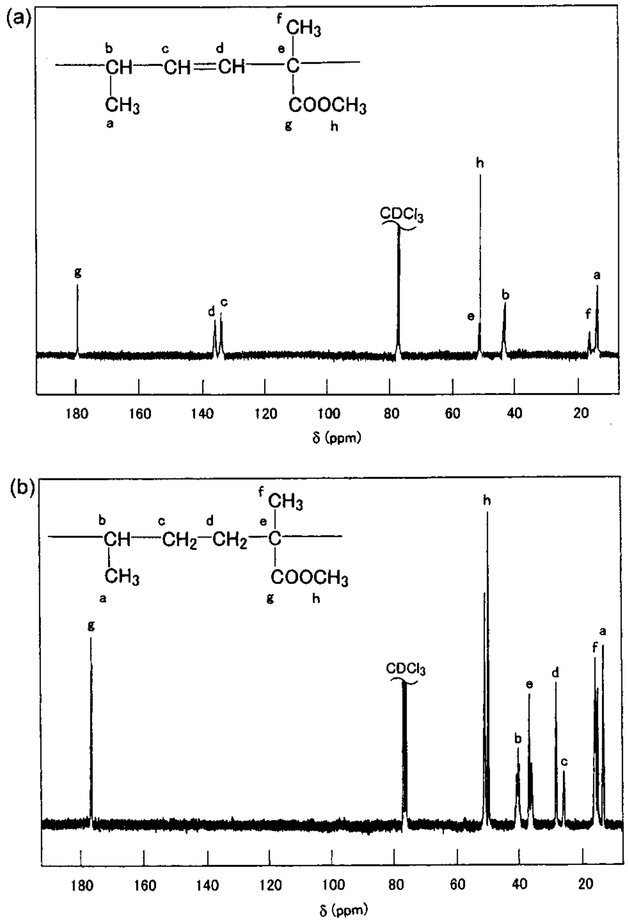


Figure 2. ^{13}C NMR spectra of (a) poly(MMHd) (**4d**) and (b) H−H poly(propylene-*alt*-MMA) (**6d**) in $CDCl_3$ (run 4 in Table 2).

ence and absence of MAD, although the peaks were broadened remarkably indicating that the ester carbonyl in MDMPd was coordinated to MAD.

The polymerizations were carried out at 0, −20, and −78 °C. While the yields were higher at 0 °C, lowering the polymerization temperature to −20 °C not only decreased the yields but broadened the M_w/M_n (runs 5−7); further lowering to −78 °C resulted in no polymerization (runs 8−10). These results are ascribed to slower initiation by *t*-BuLi at −20 and −78 °C compared with that at 0 °C.

Polymer **3** was hydrogenated with diimide generated by thermal decomposition of *p*-toluenesulfonylhydrazide[22] to generate H−T copolymer **5** in good yield. The results are also collected in Table 1. Polymer **5** has no IR absorptions due to carbon−carbon double bonds. The ^1H NMR resonances of the C=C double bonds disappeared completely and the spectrum was consistent with a copolymer containing equimolecular amounts of propylene and MMA units. In SEC measurements, M_n and M_w/M_n of **3d** were 5.4×10^4 and 1.1_3, and those of **5d** produced by hydrogenation of **3d** were 5.5×10^4 and 1.1_4. This indicates that hydrogenation proceeds without main chain scission. Each peak in the ^{13}C NMR spectra of the alternating copolymers **5d** split minutely, reflecting their different stereochemistries (Figure 1b).

Anionic Polymerization of MMHd and Subsequent Hydrogenation of Poly(MMHd) (4). MMHd also polymerized regioselectively by 1,4-trans addition, although the initiator efficiency was low (Table 2). The trans 1,4-structure was confirmed by the fact that the ^1H NMR coupling constant of $CH{=}CH{-}C$ ($J_{CH=CH}$) was 15.6 Hz in $CDCl_3$.[23] The olefinic carbon resonances are sensitive to the configuration of the adjacent sp^2 carbon as well as the configuration of the next nearest double bond. Polymer **4d** exhibits two resonances (peaks c and d) in the olefinic region of the ^{13}C NMR spectrum (Figure 2a). While peak d is a singlet, peak c is split into two resonances (131.1 and 131.4 ppm). However, the chemical shifts difference was 0.3 ppm, which seem to be due to different stereochemistries in the main chain. MMHd hardly polymerize at −20 °C (runs 6−8) and did not in the least polymerize at −78 °C even in the presence of MAD. MAD plays two roles in the polymerization: stabilization of the propagating anions and activation of the monomer.[24] The stabilized anion apparently does not attack the activated monomer at low temperatures.

The polymerization was also initiated by *t*-BuMgCl to give poly(MMHd) even in the absence of Lewis acid. However, NMR analyses demonstrated that the polymerization without an additive contained both 1,4- and 3,4-addition units. In the ^1H NMR spectrum, peaks at 1.79 and 6.53 ppm are due to protons in 3,4-addition unit [$-CH{=}C(CH_3)(COOCH_3)$ and $-CH{=}C(CH_3)(COOCH_3)$, respectively]. The content of 3,4-addition units was approximately 35% on the basis of the peak intensity ratio of these peaks and the corresponding peaks of the 1,4-addition unit (at 1.11 and 5.64 ppm). In the presence of the additive, 1,4-addition occurred selectively but the M_w/M_n index and polymer yield were not improved compared to those using the *t*-BuLi initiator system. This was due to the low reactivity of *t*-BuMgCl versus *t*-BuLi with MMHd.

No polymer was obtained from MMHd in the absence of Lewis acid at 0 °C for 168 h (Table 2, run 1), while anionic polymerization of MDMPd at 0 °C for 72 h gave polymer in 73% yield (Table 1, run 1). It seems that the polymerization rate of MMHd is lower than that of MDMPd. In anionic polymerizations of MDMPd and MMHd, the electron density and steric hindrance at the δ carbon influence their polymerization rates. The ^{13}C NMR chemical shifts of the δ carbon in MDMPd and MMHd reflect their electron density and appear at 119.7 and 137.8 ppm, respectively. This indicates that steric repulsion of methyl group at the δ carbon of MMHd suppresses its reactivity.

Polymer **4** was soluble in toluene, chloroform, tetrahydrofuran, and *N*,*N*-dimethylformamide and had a T_g at 27−36 °C except for **4i** (Table 2). Polymer **4i** had a T_g at −12 °C due to the structural irregularity with both 1,4- and 3,4-addition units.

Polymers **4** were hydrogenated by same method as that for polymer **3** to give H−H copolymer **6** (Table 2). The yields were 67−97%, and the SEC traces were not broadened relative to the parent polymers **4**. After hydrogenation for 260 h, the IR and ^{1}H NMR absorptions due to carbon−carbon double bonds disappeared completely. Preparation of H−H copolymer was confirmed by IR, NMR, and elemental analyses (see Experimental Section). The IR spectra including the fingerprint region (1500−600 cm^{-1}) of the H−H copolymers **6** were similar to those of H−T copolymer **5**. The ^{13}C NMR spectrum of a H−H copolymer **6** is shown in Figure 2b. Some peaks are split reflecting the stereoregurarity. For H−H copolymer **6**, there should be four stereoisomers, i.e., erythro-diisotactic, erythro-disyndiotactic, threo-diisotactic, and threo-disyndiotactic, were expected in considering the influence of longer range order of methyl and methyl ester substituents (ϵ-tacticity). In fact, peaks e, f, g, and h are split to two peaks clearly indicating the existence of both erythro and threo stereoisomers. Peak b in the spectrum is split into four peaks, which probably corresponds to the four steroisomers. However, we have not assigned the resonances yet. We will report more extensive work on the stereochemistry of these polymers by detailed NMR spectroscopy in the future.

Glass Transition Temperature of H−T 5 and H−H 6 Alternating Copolymers. H−T **5** and H−H **6** alternating copolymers are similar in overall composition but different in addition-form structure. DSC demonstrated that alternating copolymers **5** and **6** are amorphous with prominent glass transitions (T_g) summarized in Tables 1 and 2, and no melting endotherms (T_m) in the range of −60 to 200 °C. X-ray diffraction investigation of flat films of samples **5d** and **6b** prepared by solvent casting from chloroform also showed only a very broad band from 5 to 35 °(2θ). Polymer **3** has a T_g at 18−30 °C (Table 1), which is lower than that of polymer **4** (27−36 °C except for **4i**, Table 2). As expected, the T_g of hydrogenated polymer **5** (H−T) at 15−18 °C is lower than that of the parent polymer **3**. In contrast, the T_g of H−H type copolymer **6** at 38−46 °C is 8−18 °C higher than that of parent polymer **4**. The T_g's of **6** are about 30 °C higher than those of **5**. Figure 3 shows the DSC traces of H−T **5d** and H−H **6b** copolymers in the glass transition region. The T_g of **5d** was 18 °C and **6b** was 45 °C. The position of the substituents in the H−H structure relative to the H−T structures produces two opposite effects: (1) increased flexibility of backbone segments caused by tail-to-tail (T−T) linkages ($-CH_2-CH_2-$ sequence) and (2) stiffened backbone segments caused by the H−H linkages [$-CH(CH_3)-C(COOCH_3)(CH_3)-$]. In the case of poly(propylene-*alt*-MMA), the latter affected the molecular motion of the main chain much more than the former. Similarly, the T_g's of H−H

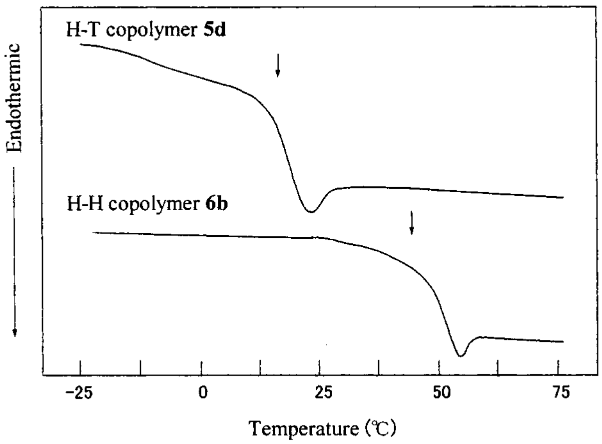


Figure 3. DSC curves of H−T (**5d**) (run 4 in Table 1) and H−H poly(propylene-*alt*-MMA) (**6b**) (run 2 in Table 2). Heating rate, 10 °C/min.

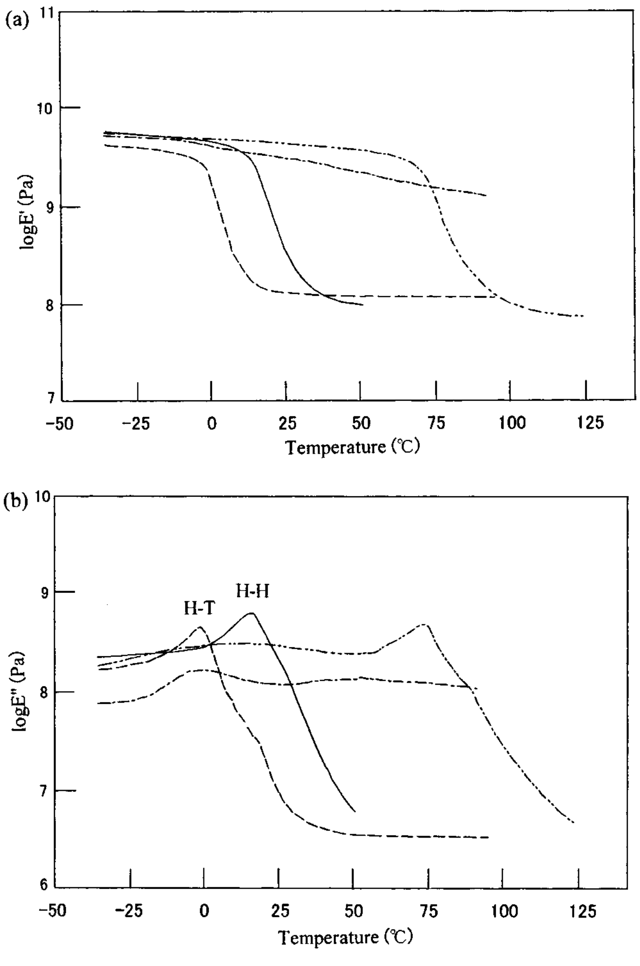


Figure 4. Temperature dependence of (a) dynamic storage modulus (*E*′) and (b) loss modulus (*E*″) for polymer films: (-• •-) poly(MMA); (- - -) H−T copolymer **5d** (run 4 in Table 1); (— - —) poly(propylene); (—) H−H copolymer **6b** (run 2 in Table 2).

Table 3. Thermal Degradation Behaviors of H−T (5) and H−H (6) Poly(propylene-*alt*-MMA)s[a]

polymer	$M_n{}^b$ x 10^{-4}	$M_w/M_n{}^b$	10% weight loss temperature[a] (°C)	maximum degradation rate temperature[a] (°C)
5a	3.9	2.61	350	403
5c	2.2	1.33	325	392
5d	5.5	1.14	350	399
6c	6.0	1.46	382	426
6d	2.9	1.21	367	426
poly(MMA)	10.4	1.85	284	367
PP	–[c]	–[c]	359	428

[a] By TG measurement; heating rate, 10 °C/min; under nitrogen atmosphere. [b]Determined by SEC in THF relative to polystyrene. [c]Insoluble in THF.

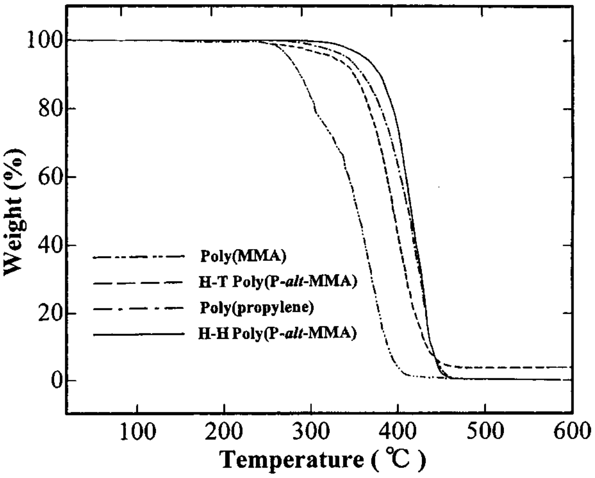


Figure 5. Thermogravimetric (TG) curves of polymers under N_2 atmosphere: (-••-) poly(MMA); (- - -) H−T copolymer **5d** (run 4 in Table 1); (—•—) poly(propylene); (—) H−H copolymer **6d** (run 4 in Table 2).

poly(methyl acrylate)s are 30 °C higher than the corresponding H−T polymers.[9]

The dynamic mechanical properties of **5d** and **6b** films were also investigated to clarify the different T_g's in the DSC measurement. Figure 4 shows the temperature dependence of dynamic storage modulus (E') and loss modulus (E'') of cast films of the copolymers and of poly(MMA) and poly(propylene). E' values at −25 °C of **5d** and **6b** were 3.98 × 10^9 and 5.43 × 10^9 MPa, which are comparable to those of poly(propylene) (5.12 × 10^9 MPa) and PMMA (5.30 × 10^9 MPa). The E' value of **5d** and **6b** started to decrease at −17 and 1 °C, respectively. A main mechanical dispersion (E'') reflecting the T_g appeared at 15 °C for **5d** and 26 °C for **6b**. DMA analyses also revealed that H−H linkage of **6** has more restricted molecular motion.

Thermal Degradation. The thermal degradation behavior of the H−T and H−H alternating copolymers were investigated under nitrogen atmosphere by thermogravimetric analysis (TGA). Figure 5 shows the TGA curves of poly(propylene), poly(MMA), H−T copolymer **5d**, and H−H copolymer **6d**. H−H copolymer **6d** is the most thermally stable of the four polymers. The results are summarized in Table 3. The 10% weight loss temperature of copolymer **6d** is 367 °C, and that of **5d** is 350 °C. The difference in the thermal decomposition behavior of these polymers is much clearer from the derivative thermogravimetric (DTG) curve. The decomposition rate maximum temperature of **5d** is 399 °C, and that of **6d** is 27 °C higher. Similarly, the decomposition rate maximum of **6c** (426 °C) in the DTG curve is higher than that of **5c** (392 °C). Alternating copolymers **5c** and **6c** were obtained using *t*-BuLi/*i*-Bu_3Al+Sp initiator, while **5d** and **6d** were obtained from *t*-BuLi/MAD. On the basis of the ^1H NMR splitting pattern of the methoxy protons (3.52−3.62 ppm), the stereoregularities of **5c** and **6c** are different from those of **5d** and **6d**, respectively. The M_n of **5c** (2.2 × 10^4) was lower than that of **6c** (6.0 × 10^4), whereas the M_n of **5d** (5.5 × 10^4) was higher than that of **6d** (2.9 × 10^4). These results confirm that the thermal stability of poly(propylene-*alt*-MMA) is influenced mostly by its chemical structure (head-to-tail or head-to-head linkage), and the H−H structures in the copolymer are not the weakest bonds. This is consistent with thermal stability of H−H polystyrene[10] and H−H poly(methyl acrylate-*alt*-MMA).[12]

Conclusion

H−T and H−H poly(propylene-*alt*-MMA)s were synthesized via anionic polymerization of methyl 2,4-alkadienoates. MDMPd and MMHd were polymerized by 1,4-addition. The polymer yield, initiator efficiency, and molecular weight distribution were improved by coordination of alkyl aluminum or aluminum aryloxide to the ester carbonyl group of the monomer. Further studies on the stereoregularities of the resulting alternating copolymers are in progress. This paper clarifies that anionic polymerization of methyl 2,4-alkadienoates and subsequent hydrogenation are useful to synthesizing well-defined ethylene or propylene/polar monomer alternating copolymer.

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