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

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Introduction. The physical properties of alternating and random copolymers are different.[1,2] Most alternating copolymers containing acrylate or methacrylate units 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".[2−4] Syntheses of poly(styrene-*alt*-methyl acrylate),[3,4] poly(styrene-*alt*-methyl methacrylate (MMA)),[3,4] poly(propylene-*alt*-methyl acrylate),[3,5] poly(ethylene-*alt*-methyl acrylate),[3,4] and poly(vinyl chloride-*alt*-MMA)[4] have been reported. However, the steric bulk of 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.[4,5] We previously synthesized poly(ethylene-*alt*-MMA) by reducing poly(vinyl bromide-*alt*-MMA).[6] Another approach to construct well-defined alternating copolymers might be to 1,4-homopolymerize diene monomers and subsequently hydrogenate the polymers.

This paper reports the anionic polymerization of methyl 2,4-dimethyl-2,4-pentadienoate (MDMPd) and methyl 2-methyl-2,4-hexadienoate (MMHd) by 1,4-addition. Hydrogenation of poly(MDMPd) (**1**) and poly(MMHd) (**2**) produced head-to-tail (H−T) (**3**) and head-to-head (H−H) poly(propylene-*alt*-MMA) (**4**), respectively (Scheme 1). To the best of our knowledge, this is the first synthesis of a completely alternating copolymer between propylene and MMA. 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,[7−10] including H−H poly(methyl acrylate)[7] and poly(styrene),[8] only a few studies on the regioisomeric ordered copolymers have been published.[11,12]

Results and Discussion. MDMPd and MMHd were prepared via Wittig reaction of methacroleine and crotonaldehyde with a phosphoric ylide, $Ph_3P{=}C(CH_3)(COOCH_3)$, respectively,[13,14] according to the procedure of House and Rasmusson.[15]

Hatada et al. have reported that polymerization of MMA by *tert*-butyllithium (*t*-BuLi)−alkylaluminum or bis(2,6-di-*tert*-butylphenoxy)methylaluminum produces stereoregular PMMA with narrow molecular weight distributions in toluene.[16−18] We used similar initiator systems for the polymerization in this work. The polymerization results of MDMPd and MMHd are summarized in Table 1. Both monomers were polymerized in toluene at 0 °C using *t*-BuLi as the initiator in the presence and absence of an organoaluminum reagent. All of the resulting polymers were white and soluble in chloroform, tetrahydrofuran, and *N*,*N*-dimethylformamide. Their structure was determined by IR, ^{1}H, and ^{13}C NMR and elemental analyses.[19] ^{1}H and ^{13}C NMR demonstrated that polymer **1** is composed of only 1,4-addition units. Dorman et al. found that the resonances of carbons 1 and 4 in *cis*-2-hexene were shifted 5.1−5.9 ppm high field of those of *trans*-2-hexene.[20] Similar results were reported for *trans*- and *cis*-3-hexene and 4-octene.[20] However, the proton-decoupled resonance signals of carbons in **1** were all single peaks, and none of the resonances of isomers were observed in the ^{13}C NMR spectrum. 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 demonstrated that all of the polymers **1** consisted of 100% *E*-double bonds. In the absence of an organoaluminum compound, the molecular weight ($M_n = 3.1 \times 10^4$) of polymer **1a** determined by size exclusion chromatography (SEC) is higher than that calculated from the monomer/initiator ratio [M_n(calcd) $= 0.26 \times 10^4$], and the molecular weight distribution is broad ($M_w/M_n = 3.1_4$). The broad molecular weight distribution may be due to attack of the polymer anion at the carbonyl group of the MDMPd monomer. Addition of organoaluminum catalysts produced polymers **1b−d** with relatively narrow molecular weight distributions, although the initiator efficiency (I_{eff}) was still low (runs 2−4). Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD)[21] improves both the polymer yield and initiator efficiency. Organoaluminum aryloxides are bulky but do not reduce the Lewis acidity much.[21] This system produced poly(MDMPd) in 98% yield, with $M_w/M_n = 1.1_3$. This suggests 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.

MMHd also polymerized regioselectively by 1,4-trans addition, although the initiator efficiency was low.[22] The trans 1,4-structure was confirmed by the fact that the ^{1}H NMR coupling constant of $CH{=}CH{-}C$ ($J_{CH=CH}$) was 15.6 Hz in $CDCl_3$.[23] In the absence of an aluminum catalyst, no polymer was obtained (run 5). Neither MDMPd nor MMHd polymerized at −78 °C.

Polymers **1** and **2** were hydrogenated with diimide generated by thermal decomposition of *p*-toluenesulfonylhydrazide (TSH),[24] to generate H−T copolymer **3** and H−H copolymer **4**, respectively, in good yields (Table 1).[25] Polymers **3** and **4** have no IR absorptions due to carbon−carbon double bonds. The ^{1}H NMR resonances of the C=C double bonds are also completely absent, and the spectrum is consistent with a copolymer containing equimolecular amounts of propylene and MMA units. The molecular weights of the hydrogenated polymer (M_n and M_w/M_n of **1d** were 5.4×10^4 and 1.1_3) indicated that dehydrogenation proceeds without main chain scission (those of **3d** produced by hydrogenation of **1d** were 5.5×10^4 and 1.1_4). The chemical shifts in the ^{13}C NMR spectra of the alternating copolymers **3** and **4** reflected their different stereochemistries. However, we have not assigned the resonances yet. We will

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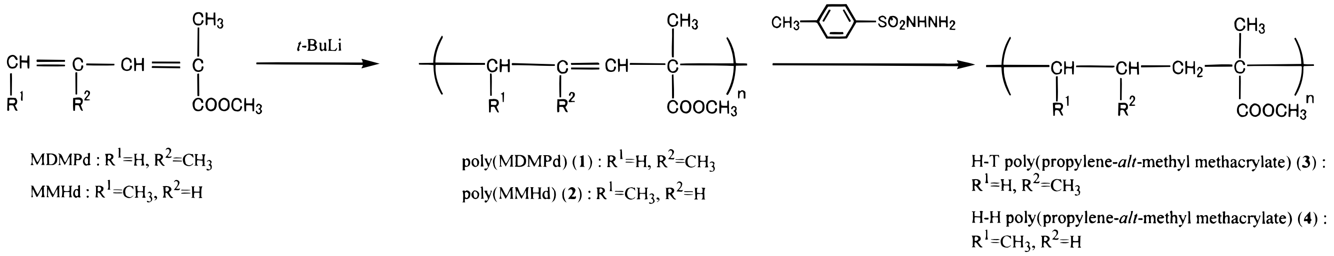
Table 1. Anionic Polymerization of Methyl 2,4-Alkadienoates Initiated by *t*-BuLi[a] and Subsequent Hydrogenation with *p*-Toluenesulfonylhydrazide (TSH)

										hydrogenation[f]		
run	monomer	additive	$[M]_0/[I]_0$[b]	time (h)	product	yield (%)	M_n[c] × 10^{-4}	M_w/M_n[c]	I_{eff}[d] (%)	T_g[e] (°C)	product	yield (%)	T_g[e] (°C)
1	MDMPd	none	25	72	**1a**	73	3.1	3.1_4	8.3	18	**3a**	72	16
2	MDMPd	*i*-Bu_3Al	25	72	**1b**	13	2.1	1.3_8	2.2	30	**3b**	84	16
3	MDMPd	*i*-Bu_3Al + Sp[g]	25	72	**1c**	40	1.9	1.4_3	7.4	29	**3c**	95	15
4	MDMPd	MAD[b]	25	72	**1d**	98	5.4	1.1_3	6.4	24	**3d**	89	18
5	MMHd	none	50	168	**2a**	trace					**4a**		
6	MMHd	*i*-Bu_3Al	50	168	**2b**	78	10.6	1.6_4	5.2	27	**4b**	97	35
7	MMHd	*i*-Bu_3Al + Sp[g]	50	168	**2c**	80	4.1	1.4_0	13.7	36	**4c**	83	46
8	MMHd	MAD[h]	25	168	**2d**	60	2.4	1.2_2	8.8	30	**4d**	77	44

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

Scheme 1



report more extensive work on the stereochemistry of these polymers by detailed NMR spectroscopy in the future.

Differential scanning calorimetry (DSC) demonstrated that polymers **1**−**4** are amorphous with prominent glass transitions (T_g) in Table 1 and no melting endotherm (T_m) in the range −60 to 200 °C. The T_g of polymer **1** which had the T_g at 18−30 °C is lower than that of polymer **2** (27−36 °C). As expected, the T_g of hydrogenated polymer **3** (H−T) at 15−18 °C is lower than that of the parent polymer **1**. In contrast, the T_g of H−H type copolymer **4** at 35−46 °C is 8−14 °C higher than those of parent polymer **2**. Interestingly, the T_g's of **4** are about 30 °C higher than those of **3**. These results agree well with the 30 °C higher T_g's of H−H poly(methyl acrylate) relative to the corresponding H−T polymers.[7] This is presumably due to more restricted molecular motion in the H−H type copolymer due to steric hindrance between the ester and methyl substituents.[7,11]

The thermal degradation behavior of the H−T and H−H alternating copolymers was investigated under nitrogen atmosphere by thermogravimetric (TG) analysis. Figure 1 shows the TG curves of isotactic poly(propylene) (M_n = 250 000), atactic poly(MMA) (M_n = 104 000, $M_w/M_n = 1.8_5$), H−T copolymer **3d**, and H−H copolymer **4d**. H−H copolymer **4d** is the most thermally stable of the four polymers. The 10% weight loss temperature of copolymer **4d** is 367 °C, and that of **3d** is 350 °C. The difference in the thermal decomposition behavior of these polymers is more clear from the derivative thermogravimetric (DTG) curve. The decomposition rate maximum temperature of **3d** is 399 °C, and that of **4d** is 27 °C higher. Similarly, the decomposition rate maximum of **4c** (426 °C) in the DTG curve is higher than that of **3c** (392 °C). Alternating polymers **3c** and **4c** were obtained by *t*-BuLi/*i*-Bu_3Al + Sp initiator, while **3d** and **4d** were obtained from *t*-BuLi/MAD initiator system. From the ^1H NMR split pattern of methoxy protons (3.52−3.62 ppm), the stereoregularities of **3c** and **4c** were considered to be different from those of **3d** and **4d**, respectively. M_n of **3c** (2.2 × 10^4) was lower than that of **4c** (6.0 × 10^4), whereas M_n of **3d** (5.5 × 10^4) was higher than that of **4d** (2.9 × 10^4). These results confirm that the thermal stability of poly(propylene-*alt*-MMA) is mostly influenced by its chemical structure (sequence), and the H−H structures are not the weakest bonds. This is consistent with thermal stability of H−H polystyrene[8] and H−H poly(methyl acrylate-*alt*-MMA).[11]

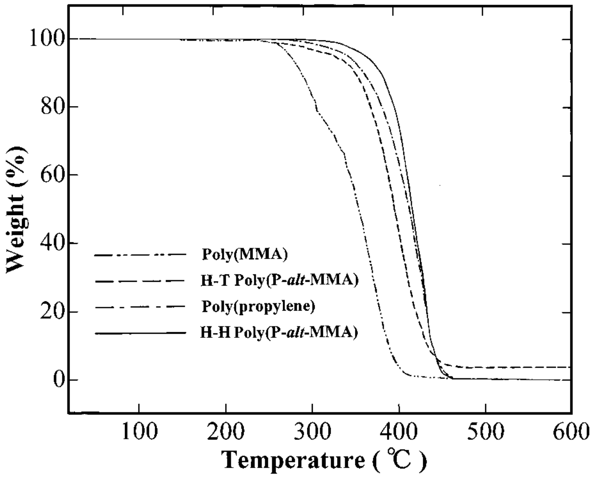


Figure 1. Thermogravimetric (TG) curves of polymers under N_2 atmosphere: (− ·· −) poly(MMA); (- - -) H−T copolymer **3d**; (− · −) poly(propylene); (—) H−H copolymer **4d**.

As described above, well-defined H−T and H−H poly(propylene-*alt*-MMA)s were synthesized via anionic polymerization of methyl 2,4-alkadienoates. Further studies on the living polymerization and the properties of the resulting polymers are in progress.

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(19) In a typical anionic polymerization of MDMPd, MDMPd (1.12 g, 8.0 mmol), toluene (1.0 mL), and 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 $\mathrm{N_2}$. A solution of *t*-BuLi in *n*-pentane (0.16 M, 2.0 mL, 0.32 mmol) was added at −78 °C. After 72 h at 0 °C, the reaction mixture was poured into methanol (500 mL) containing a trace amount of aqueous HCl (5%). A white powder (1.10 g) was isolated by filtration following precipitation from $\mathrm{CHCl_3}$ solution into methanol (yield 98%, run 4 in Table 1). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ, ppm): 1.16 $(=\mathrm{CH-C-C}H_3)$, 1.38 $(=\mathrm{C-C}H_3)$, 2.06−2.13 and 2.50−2.53 $(-\mathrm{C}H_2-)$, 3.59 $(-\mathrm{O-C}H_3)$, 5.09 $(=\mathrm{C}H-)$. ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, δ, ppm): 18.0 $(=\mathrm{CH-C-}C\mathrm{H_3})$, 22.9 $(=\mathrm{C-}C\mathrm{H_3})$, 46.7 $(-\mathrm{CH_2}-)$, 51.7 $(=\mathrm{CH-}C\mathrm{-CH_3})$, 51.8 $(-\mathrm{O-}C\mathrm{H_3})$, 133.4 $(-\mathrm{CH_2-}C\mathrm{-CH_3})$, 135.0 $(=C\mathrm{H}-)$, 177.1 $(-C\mathrm{OOCH_3})$. IR (KBr disk, cm^{-1}): 2948 ($\nu_{\mathrm{C-H}}$), 1733 [$\nu_{\mathrm{C=O}}$(ester)], 1651 ($\nu_{\mathrm{C=C}}$), 1455 ($\delta_{\mathrm{C-H}}$), 1200 and 1103 [$\nu_{\mathrm{C-O-C}}$(ester)], 848 ($\delta_{\mathrm{C=C-H}}$). Anal. Calcd for $(\mathrm{C_8H_{12}O_2})_n$: C, 68.55; H, 8.63; O, 22.83. Found: C, 68.42; H, 8.70; O, 22.88.

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(22) MMHd was polymerized in a manner similar to MDMPd in ref 19, yield, 80% (run 7 in Table 1). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ, ppm): 0.88 $(=\mathrm{CH-CH-C}H_3)$, 1.11 $(=\mathrm{CH-C-C}H_3)$, 2.64 $(=\mathrm{CH-C}H\mathrm{-CH_3})$, 3.62 $(-\mathrm{O-C}H_3)$, 5.26 $(=\mathrm{C}H\mathrm{-CH}-)$, 5.64 $(=\mathrm{C}H\mathrm{-C}-)$. ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, δ, ppm): 15.1 $(=\mathrm{CH-CH-}C\mathrm{H_3})$, 17.8 $(=\mathrm{CH-C-}C\mathrm{H_3})$, 43.9 $(=\mathrm{CH-}C\mathrm{H-CH_3})$, 51.7 $(-\mathrm{O-}C\mathrm{H_3})$, 51.8 $(=\mathrm{CH-}C\mathrm{-CH_3})$, 131.4 $(=C\mathrm{H-CH}-)$, 133.6 $(=C\mathrm{H-C}-)$, 175.7 $(-C\mathrm{OOCH_3})$. IR (KBr disk, cm^{-1}): 2973 ($\nu_{\mathrm{C-H}}$), 1733 [$\nu_{\mathrm{C=O}}$(ester)], 1653 ($\nu_{\mathrm{C=C}}$), 1457 ($\delta_{\mathrm{C-H}}$), 1241 and 1120 [$\nu_{\mathrm{C-O-C}}$(ester)], 978 ($\delta_{\mathrm{H-C=C-H}}$). Anal. Calcd for $(\mathrm{C_8H_{12}O_2})_n$: C, 68.55; H, 8.63; O, 22.83. Found: C, 68.58; H, 8.73; O, 22.69.

(23) The coupling constant (15.6 Hz) of olefin proton $(\mathrm{CH=C}H\mathrm{-C})$ in **2** was in the range 12−18 Hz of many model compounds containing a trans carbon−carbon double bond (Bothner-By, A. A.; Naar-Colin, C. *J. Am. Chem. Soc.* **1961**, *83*, 231). For poly(ethyl 2-methylpentadienoate) having trans geometry, the coupling constant $(\mathrm{CH=C}H\mathrm{-C})$ was reported to be 16.1 Hz (Hertler, W. R.; Rajanbabu, T. V.; Ovenall, D. W.; Reddy, G. S.; Sogah, D. Y. *J. Am. Chem. Soc.* **1988**, *110*, 5841). In this paper, the trans configuration of polymer **2** was supported by the IR absorption at 978 cm^{-1} ($\delta_{\mathrm{H-C=C-H}}$).

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(25) A solution of poly(MDMPd) (**1d**) (0.60 g, 4.3 unit mmol) and TSH (3.91 g, 21 mmol) in toluene (54 mL) was stirred at 110 °C for 260 h under $\mathrm{N_2}$. The solvent was evaporated, and the polymeric material was purified by reprecipitation from chloroform into methanol and dried in vacuo to yield a white powder **3d** (89%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ, ppm): 0.55, 0.64, and 0.79 $(-\mathrm{CH-C}H_3)$, 1.02−1.06 $(-\mathrm{C-C}H_3)$, 1.12−1.33 $(-\mathrm{CH_2}-)$, 1.52 $(-\mathrm{C}H-)$, 3.52−3.57 $(-\mathrm{O-C}H_3)$. ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, δ, ppm): 19.0−23.8 ($-\mathrm{CH-}C\mathrm{H_3}$ and $-\mathrm{C-}C\mathrm{H_3}$), 26.2 and 26.8 $(-\mathrm{CH}-)$, 44.4−45.7 ($-\mathrm{CH_2}-$ and $-\mathrm{C}-$), 49.0−51.3 $(-\mathrm{O-}C\mathrm{H_3})$, 177.9−178.9 $(-C\mathrm{OOCH_3})$. IR (KBr disk, cm^{-1}): 2951 ($\nu_{\mathrm{C-H}}$), 1733 ($\nu_{\mathrm{C=O}}$), 1457 ($\delta_{\mathrm{C-H}}$), 1207 and 1149 ($\nu_{\mathrm{C-O-C}}$). Poly(MMHd) (**2d**) was hydrogenated in a similar manner, yield 77%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ, ppm): 0.50−0.71 $(-\mathrm{CH-C}H_3)$, 0.86−0.90 $(-\mathrm{C-C}H_3)$, 1.04−1.16 $(-\mathrm{C}H_2\mathrm{-CH}-)$, 1.33−1.42 $(-\mathrm{C}H_2\mathrm{-C}-)$, 1.60 $(-\mathrm{C}H-)$, 3.52−3.57 $(-\mathrm{O-C}H_3)$. ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, δ, ppm): 13.4 $(-\mathrm{CH-}C\mathrm{H_3})$, 15.0 and 15.9 $(-\mathrm{C-}C\mathrm{H_3})$, 25.8 $(-C\mathrm{H_2-CH}-)$, 28.2 $(-C\mathrm{H_2-C}-)$, 36.1 and 36.9 $(-C-)$, 40.2−41.5 $(-C\mathrm{H}-)$, 50.1 and 51.1 $(-\mathrm{O-}C\mathrm{H_3})$, 177.3−177.5 $(-C\mathrm{OOCH_3})$. IR (KBr disk, cm^{-1}): 2951 ($\nu_{\mathrm{C-H}}$), 1733 ($\nu_{\mathrm{C=O}}$), 1457 ($\delta_{\mathrm{C-H}}$), 1207 and 1149 ($\nu_{\mathrm{C-O-C}}$).

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