Synthesis of Sequence-Ordered Copolymers. 4. Glass Transition and Melting Temperatures of Sequence-Ordered and Unordered Ethylene–Vinyl Alcohol and Ethylene–Vinyl Acetate Copolymers

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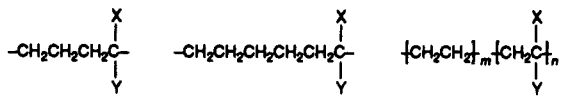
ABSTRACT: The group-transfer polymerization of 1-[(trimethylsilyl)oxy]-1,3-butadiene, initiated by anisaldehyde and catalyzed by zinc bromide, proceeded homogeneously in the presence of diethyl ether at 195 K and gave a high molecular weight polymer. Hydrogenation and subsequent methanolysis of this polymer yielded an alternating ethylene–vinyl alcohol copolymer. Acetylation of this copolymer yielded an alternating ethylene–vinyl acetate copolymer. Glass transition and melting temperatures of these alternating copolymers were determined by differential scanning calorimetry and compared with the glass transition and melting temperatures of statistical copolymers in view of sequence ordering. The statistical copolymers were prepared by a radical-initiated copolymerization of ethylene and vinyl acetate in an autoclave and by the copolymer methanolysis.

In our previous paper,[1] two types of sequence-ordered ethylene–acrylic copolymers, **1** and **2**, were compared with the corresponding sequence-unordered copolymers **3** for their glass transition temperatures (T_g). Acrylic monomer units studied were as follows: **a**, methyl acrylate; **b**, methyl methacrylate; **c**, methacrylonitrile.



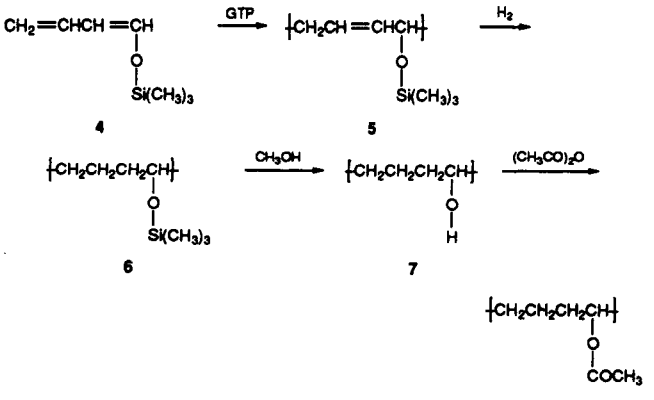
1 **2** **3**

a: X = H and Y = $COOCH_3$
b: X = CH_3 and Y = $COOCH_3$
c: X = CH_3 and Y = CN

The T_g of a sequence-ordered copolymer was almost the same as or slightly higher than the T_g of the corresponding sequence-unordered copolymer of the same composition.

The present paper describes first the synthesis of an alternating ethylene–vinyl alcohol copolymer and an ethylene–vinyl acetate copolymer. The syntheses of corresponding statistical copolymers are also given. Second, the differential scanning calorimetry (DSC) study on these copolymers is described. The T_g and the melting temperatures (T_m) of these copolymers are discussed in view of sequence ordering of copolymers.

The alternating ethylene–vinyl alcohol copolymer (**7**) and the alternating ethylene–vinyl acetate copolymer (**8**) were synthesized by the reaction scheme given below.



The synthesis was started from a cationic group-transfer polymerization (GTP) of a diene monomer, 1-[(trimethylsilyl)oxy]-1,3-butadiene (**4**), followed by polymer reactions. The GTP of **4** and polymer reactions that dealt with relatively low molecular weight polymers were already reported.[2–4] Essentially the same experiments have been presented by Sogah and Harris.[5] Sogah, Hertler, and their co-workers[6,7] also extensively studied the anionic GTP of a number of silylated polyene monomers and the reactions of derived polymers.

Poly[1-[(trimethylsilyl)oxy]-1,3-butadiene] (**5**) was then hydrogenated, methanolyzed, and acetylated to yield **7** and **8**. Syntheses by other polymer reaction orders involving methanolysis, acetylation, and hydrogenation were also studied.

The synthesis of statistical copolymers was based on a radical-initiated copolymerization of ethylene and vinyl acetate and on the copolymer methanolysis.

Experimental Section

Reagents. Most reagents were commercially available extra-pure reagents from Nacalai Tesque Inc., Kyoto, Japan, and purified before use by appropriate standard methods.[8] The preparation of 1-[(trimethylsilyl)oxy]-1,3-butadiene monomer (**4**) was already described.[3] The purified monomer was almost of the E-configuration. The zinc bromide catalyst was purified by sublimation.

Polymerization. The heterogeneous GTP of **4** in Table 1 was initiated by anisaldehyde and catalyzed by zinc bromide in toluene. Procedure details were the same as in the previous papers.[2,3] Addition of a small volume of diethyl ether made the GTP homogeneous. Table 2 summarizes this homogeneous GTP. Statistical copolymerization of ethylene and vinyl acetate was initiated by 2,2′-azobis(isobutyronitrile) at 338 K in a 100-mL stainless steel autoclave. After the copolymerization, the excess ethylene was discharged and the copolymer was recovered from the content.

Polymer Reactions. Table 3 shows the catalytic hydrogenation of **5** in a pressure reaction vessel. Table 3 also shows the hydrogenation of related polymer derivatives. A soluble rhodium-complex catalyst, a palladium-active charcoal catalyst, or a platinum oxide catalyst was employed under hydrogen pressure. After a given time of reaction, the organic mixture was separated from the catalyst and concentrated. The hydrogenated product was extracted or precipitated from the concentrate by using an

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Table 1. Heterogeneous Group-Transfer Polymerization[a]

run	[M] (mol dm^{-3})	[M]/[I]	[C]/[I]	temp (K)	time (h)	conv (%)	$M_n \times 10^{-4}$ calcd[c]	$M_n \times 10^{-4}$ found[d]	M_w/M_n
1	1.60	30	1	303	24	84	0.43	0.44	1.53
2	2.46	50	1	303	24	95	0.72	0.72	1.50
3	2.64	100	1	303	5	92	1.42	0.98	2.29
4	3.70	300	3	303	5	88	4.26	1.42	3.10
5	5.80[b]	500	3	303	20	88	7.10	1.84	2.89
6	5.80[b]	1000	3	303	20	95	14.2	1.18	3.24
7	4.92	1000	3	273	96	95	14.2	0.98	2.90
8	5.80[b]	1000	3	253	24	0	14.2		

[a] Monomer M, 1-[(trimethylsilyl)oxy]butadiene; initiator I, anisaldehyde; catalyst C, zinc bromide; solvent, toluene. [b] Bulk. [c] Calculated from [M]/[I]. [d] Determined by GPC.

Table 2. Homogeneous Group-Transfer Polymerization in the Presence of Diethyl Ether[a]

run	[M] (mol dm^{-3})	[M]/[I]	[C]/[I]	temp (K)	time (h)	conv (%)	$M_n \times 10^{-4}$ calcd[c]	$M_n \times 10^{-4}$ found[d]	M_w/M_n
1	5.80	1000	1	303	16	95	14.2	1.04	2.61
2	2.60	300	3	303	5	42	4.26	0.57	1.76
3	5.80	1000	3	273	96	95	14.2	2.01	1.71
4	2.60	300	3	273	17	61	4.26	1.08	1.83
5	2.60	300	3	253	18	65	4.26	1.66	1.76
6	3.70	300	3	195	9	74	4.26	3.18	2.36
7	1.08	300	3	195	12	90	4.26	4.55	1.24

[a] Monomer M, 1-[(trimethylsilyl)oxy]butadiene; initiator I, anisaldehyde; catalyst C, zinc bromide; solvent, toluene. Zinc bromide was used as 30 wt % in diethyl ether. [b] Bulk. [c] Calculated from [M]/[I]. [d] Determined by GPC.

Table 3. Hydrogenation of Poly[1-[(trimethylsilyl)oxy]butadiene] (5) and Its Derivatives

run	polymer[a]	catalyst[b] (%)	solvent	H_2 (MPa)	temp (K)	time (h)	hydrogenation (%)
1	5	Rh (20)	$CHCl_3$	0.7	323	20	100
2	5-OH	Rh (20)	CH_3OH	0.8	373	130	100
3	5-OAc	Rh (20)	$CHCl_3$	0.7	323	63	100
4	5	Pd (30)	C_6H_{12}	9.5	383	96	0
5	5-OH	Pd (30)	CH_3OH	8.0	383	48	54
6	5-OH	Pd[c] (30)	CH_3OH	0.6	338	20	98
7	5	Pt (10)	C_6H_{12}	0.8	373	80	0
8	5-OH	Pt (20)	CH_3OH	0.8	373	20	98
9	5-OH	Pt (15)	CH_3OH	8.0	373	154	100
10	5-OAc	Pt (6)	$CHCl_3$	0.7	323	62	21

[a] Polymer abbreviations are as follows: 5, poly[1-[(trimethylsilyl)oxy]butadiene]; 5-OH, poly(1-hydroxybutadiene); 5-OAc, poly(1-acetoxybutadiene). A polymer sample (1–2 g) in a solvent (20–40 mL) was hydrogenated. [b] Catalyst abbreviations are as follows: Rh, chlorotris(triphenylphosphine)rhodium; Pd, palladium on active charcoal; Pt, Adams' platinum oxide. The numbers are the catalyst charged, Rh in mol % and Pd or Pt in wt % of polymer. [c] The Pd catalyst was activated 2 h at 393 K under a hydrogen atmosphere.

appropriate solvent. Detail of the most successful hydrogenation of 5 (run 1) was as follows: 5 (1.33 g, 9.30 mmol) in benzene (20 mL) was hydrogenated by hydrogen (0.7 MPa) in the presence of chlorotris(triphenylphosphine)rhodium (1.53 mg, 1.70 mmol) and triphenylphosphine (0.43 g, 1.70 mmol) at 323 K for 50 h. The crude product was repeatedly reprecipitated by chloroform–ethanol and dried in vacuum.

Methanolysis (desilylation) was studied mostly on 5. Methanolysis of 6 proceeded similarly. The polymer solution in excess methanol was stirred at room temperature or at reflux as shown in Table 4. In some cases, an additional reagent was added for complete methanolysis. After the reaction, the mixture was concentrated and the product was precipitated from the concentrate by adding ether. The purified product was obtained by reprecipitating repeatedly and drying in vacuum. Methanolysis of statistical ethylene–vinyl acetate copolymers was conducted by 3 equiv of sodium methoxide in a methanol–benzene mixture at room temperature.

Table 4. Methanolysis of 5

run	methanolyzing reagent	temp (K)	time (h)	polymer yield (%)	degree of methanolysis (%)
1	CH_3OH	room	50	57	96
2	CH_3OH	338	100	83	98
3	CH_3OH + 0.1% HCl	338	24	gelation	
4	CH_3OH + 0.1% HCl[a]	room	24	64	100
5	CH_3OH + 110% TBAF[b]	room	22	gelation	
6	CH_3OH + 10% TBAF[b]	338	52	82	100

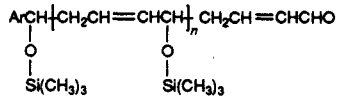
[a] Neutralized with $KHCO_3$ before the workup. [b] Tetra-*n*-butylammonium fluoride.

Acetylation was carried out by stirring a mixture of 7 (0.5 g, 7 mmol), acetic anhydride (12 mL, 127 mmol), and pyridine (30 mL) for 72 h at room temperature. Then methanol (100 mL) was added while ice-cooling to decompose the excess reagent. The mixture was concentrated and the acetylated product was recovered by precipitating with ether.

Measurements. ^{1}H nuclear magnetic resonance (NMR) spectra at 200-MHz were recorded on a Varian XL-200 spectrometer for 5–10 w/v % polymer solutioins in $CDCl_3$ or dimethyl-d_6 sulfoxide (DMSO) at 298 K. Tetramethylsilane (TMS), hexamethyldisiloxane (HMDS), or chloroform was an internal standard. ^{1}H-decoupled ^{13}C NMR spectra at 50 MHz were also studied to confirm the assignments of ^{1}H spectra. The pulse sequences were the same as in the previous paper.[1] Infrared (IR) spectra were recorded on a Jasco IR Report 100 spectrometer. Gel permeation chromatography (GPC) was determined on a Tosoh HLC 803D with GMX-, G1000-, G2000-, and G4000-HXL columns. Tetrahydrofuran was the eluent and its flow rate was 1 mL min^{-1} at 313 K. The retention volume was taken as a measure of the polymer molecular weight calibrating by polystyrene standards. The molecular weight was further corrected by the *Q*-factor method.[9] The corrected molecular weights by this method were almost identical to the molecular weights by an osmotic method.[10] Differential scanning calorimetry (DSC) was determined on a Seiko I TA Station with a DSC 210 unit from 223 to 423 K at a heating rate of 10 K min^{-1}. A copolymer sample (2–6 mg) was taken in an aluminum pan with a lid. DSC traces were recorded by normalizing to 10-mg sample weights. T_m was taken at the top of a peak and T_g at the middle point of an inflection.

Results and Discussion

Synthesis of Alternating Ethylene–Vinyl Alcohol and Ethylene–Vinyl Acetate Copolymers. The GTP of 4 can be initiated by an aromatic aldehyde and catalyzed by a Lewis acid in a hydrocarbon solvent at 303 K. Under these polymerization conditions, a heterogeneous GTP occurred on the solid catalyst via a living mechanism. Each propagation step of the GTP involves a transfer of the trimethylsilyl group from the incoming monomer to the active end. Then, in general, poly[1-[(trimethylsilyl)oxy]-1,3-butadiene] (5) has one aromatic group and one formyl group as its terminal groups and its molecular weight can be controlled by the monomer-to-initiator ratio in the feed.[2,3]



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In Table 1, runs 1 and 2 that were carried out under low monomer-to-initiator ratios (30 and 50) gave polymers of calculated molecular weights 4×10^3 and 7×10^3. But we should deal with polymers of high enough molecular weight to discuss physical properties (T_g and T_m are of our interest) intrinsic to its chemical structure. When, however, the polymerization was carried out under high

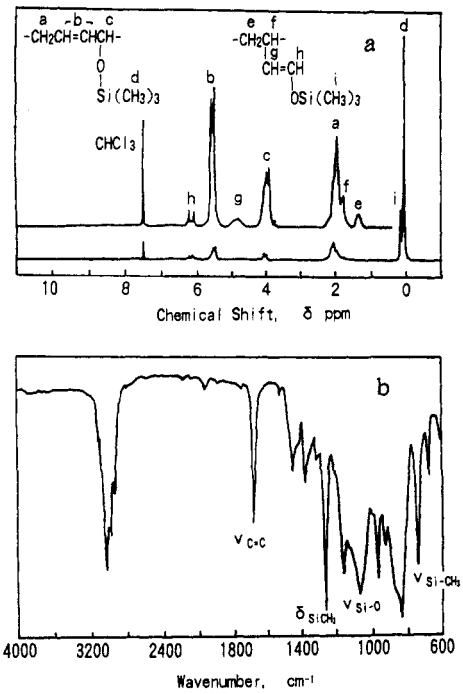


Figure 1. (a) ^{1}H NMR and (b) IR spectra of poly[1-[(trimethylsilyl)oxy]-1,3-butadiene] (5).

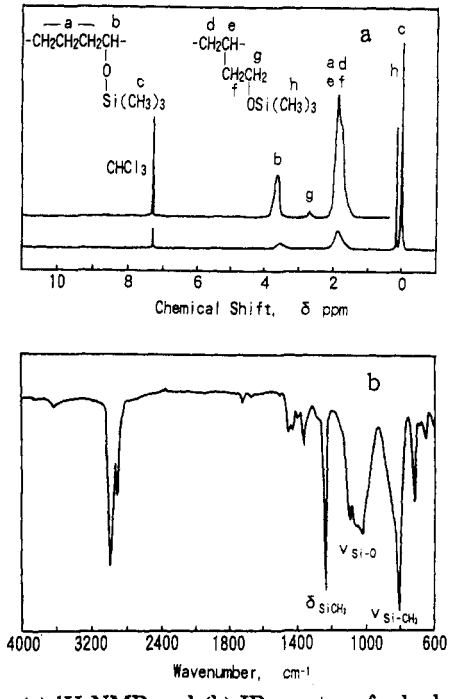


Figure 2. (a) ^{1}H NMR and (b) IR spectra of a hydrogenated poly[1-[(trimethylsilyl)oxy]-1,3-butadiene], 6.

monomer-to-initiator ratios (100–1000) as in runs 3–6, the product polymers showed much lower molecular weights than the calculated ones. Their molecular weight distributions as expressed by M_w/M_n were broad. The polymerization at 273 K in run 7 did not improve the molecular weight and proceeded with retardation. At 253 K as in run 8, the polymerization virtually stopped. The heterogeneous GTP seems to accompany undesirable side reactions that interfere with the living polymerization of 4 and the synthesis of high molecular weight polymers.

Recently, we[11] have found that, by adding a small volume of diethyl ether to the polymerization mixture, the zinc bromide catalyst becomes soluble and a homogeneous GTP of 4 proceeds even at low temperature. Table 2 shows some results of homogeneous experiments. Especially in run 7, the polymerization proceeded even at 195 K and gave a polymer of the calculated molecular weight at a low monomer concentration (1.0 mol dm^{-3}), and the molecular weight distribution index M_w/M_n was as low as 1.26. Then a polymer of a molecular weight of 4×10^4 was available. The low polymerization temperature and the low monomer concentration suppressed the unfavorable side reactions that might lead to termination. The other runs in Table 2 gave better results than those in Table 1 but were still unsatisfactory as an ideal living GTP. A detailed mechanism study on the side reactions as well as the GTP itself will be published elsewhere in the future.

Catalytic hydrogenation of 5 to 6 was successful by medium-pressure hydrogen in the presence of soluble chlorotris(triphenylphosphine)rhodium as shown by run 1 of Table 3. The other polymer derivatives were also hydrogenated by using this catalyst. The insoluble platinum and palladium catalysts were inactive for 5 but active for the other polymers. Complete hydrogenation of 5 by using the soluble Rh catalyst is obvious when the NMR and IR spectra of 5 in Figure 1 are compared with the spectra of 6 in Figure 2. Absorption peaks due to the carbon–carbon double bond in 5 are gone after the hydrogenation. During the hydrogenation, the molecular weight of 5 did not change appreciably as confirmed by GPC.

Table 4 shows the methanolysis experiments of 5. It was best accomplished in run 6 where a solution of 5 in methanol was first refluxed for 40 h and then had 10 mol % tetra-*n*-butylammonium fluoride added to it. The solution was stirred for 12 h more at room temperature for complete methanolysis. Without the fluoride (runs 1 and 2), a small percent of the (trimethylsilyl)oxy group remained unreacted. Addition of 0.1 mol % hydrochloric acid in place of the fluoride (runs 3 and 4) also led to complete methanolysis but was often accompanied by gelation during the workup. Methanolysis with 110 mol % fluoride in methanol at room temperature (run 5) also resulted in gelation. Methanolysis of 6 to 7 was successful by the procedure of run 6 without a change in the degree of polymerization.

The alternating ethylene–vinyl alcohol copolymer 7 is a tough and semicrystalline material, soluble in dimethyl sulfoxide, tetrahydrofuran, and hot methanol and insoluble in diethyl ether, chloroform, and water. An X-ray diffraction experiment (Cu Kα) showed a crystalline peak at $2\theta = 21°$. The crystalline-to-amorphous peak area ratio gave an extent of crystallization of 42%. The ^{1}H NMR and IR spectra in Figure 3 demonstrate the hydroxylated copolymer structure.

Acetylation of 7 by acetic anhydride in pyridine gave a pale yellow rubbery material. The alternating ethylene–vinyl acetate copolymer 8 was thus obtained. Figure 4 shows strong acetoxy ^{1}H NMR and IR absorptions and demonstrates the copolymer structure. It is soluble in chloroform, benzene, and tetrahydrofuran and insoluble in methanol. Acetic chloride in place of acetic anhydride was unsuccessful because of contamination by pyridine hydrochloride and undesirable side reactions (dehydration and gelation).

The following orders of polymer reaction, i.e., methanolysis–hydrogenation–acetylation or methanolysis–acetylation–hydrogenation also gave the identical product 8. However, the above-described order, i.e., hydrogenation–methanolysis–acetylation, seems most advantageous in view of the solubilities of polymer intermediates.

Synthesis of Statistical Copolymers. Statistical copolymers were synthesized by copolymerizing ethylene

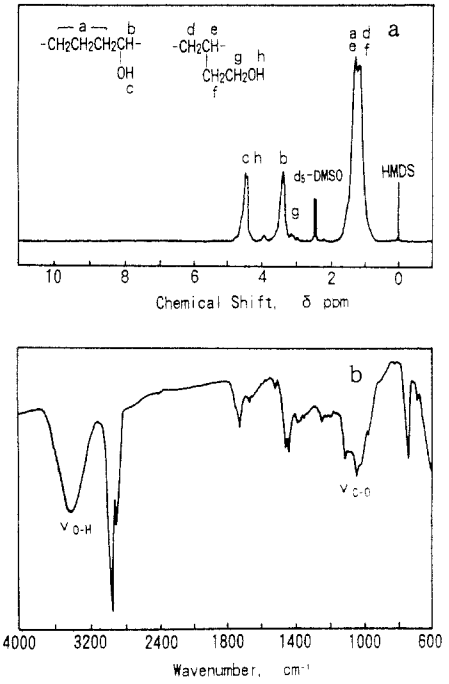


Figure 3. (a) ^{1}H NMR and (b) IR spectra of an alternating ethylene–vinyl alcohol copolymer, 7.

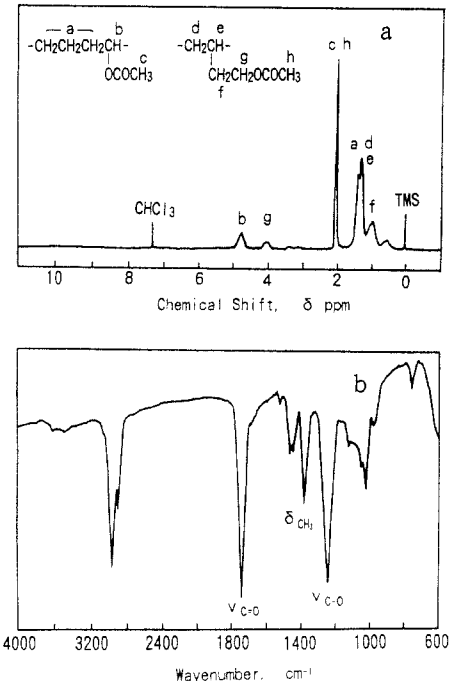


Figure 4. (a) ^{1}H NMR and (b) IR spectra of an alternating ethylene–vinyl acetate copolymer, 8.

and vinyl acetate with azobis(isobutyronitrile) in an autoclave. A copolymer sample of high ethylene content was supplied by Tosoh Corp. Copolymer compositions were calculated from their ^{1}H NMR absorption peak intensities. Thus the statistical copolymers of 18–25 mol % ethylene contents were prepared as shown in Table 5. Statistical ethylene–vinyl alcohol copolymers were prepared by methanolyzing the vinyl acetate copolymers with sodium methoxide in a methanol–benzene mixture. According to the ethylene content in the copolymer, the methanol-to-benzene ratio was controlled for smooth methanolysis.

Branching in Copolymers. Primarily the GTP of 4, a diene monomer, occurs through its 1,4-trans-addition.[2,3] But a detailed examination of ^{1}H and ^{13}C NMR and IR

Table 5. Synthesis of Ethylene–Vinyl Acetate Copolymer[a]

run	E^b (MPa)	VAc[c] (g)	solv[d]	time (h)	yield (g)	$M_n \times 10^{-4}$	E^e (mol %)	branch[f]
1[g]						4.17	85.0	8.1
2	9	4.3	benzene	12	0.6	1.23	61.1	9.2
3	6	9.0	t-BuOH	3	3.5	3.47	46.0	12.0
4	6	13.7	t-BuOH	3	8.9	5.39	34.7	10.7
5	4	22.6	t-BuOH	3	10.5	5.88	26.3	11.1
6	4	25.7	benzene	4	8.5	3.55	18.2	7.1

[a] Copolymerized in a 100-mL autoclave with azobis(isobutyronitrile) (50 mg). [b] Ethylene pressure charged, MPa. [c] Vinyl acetate weight charged, g. [d] 10-mL solvent was used. [e] Ethylene content in copolymer. [f] Branches per 1000 main-chain carbon atoms. [g] Supplied by Tosoh Corp.

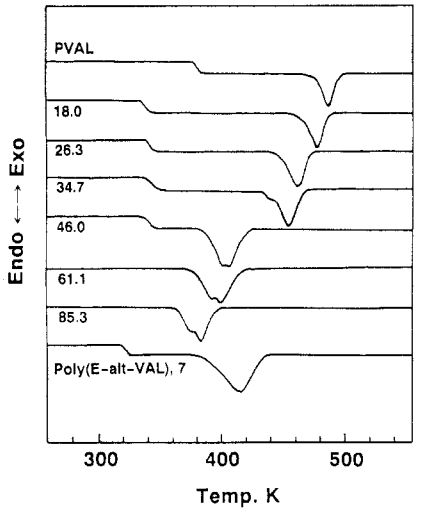
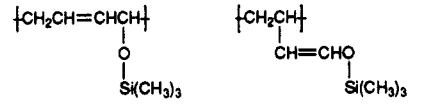


Figure 5. DSC traces of ethylene–vinyl alcohol copolymers as precipitated. The top trace is of poly(vinyl alcohol), the bottom is of the alternating ethylene–vinyl alcohol copolymer, 7, and the others are of statistical poly(ethylene–vinyl alcohol) copolymers. The numbers refer to the ethylene content in mol % in the statistical copolymers.

spectra revealed that 3,4-addition also occurs. Weak absorption peaks that should be assigned to the 3,4-addition unit 9 are observed in Figure 1a. The amount of 3,4-addition units estimated by the ^{1}H NMR peak areas was about 15% at 195 K and slightly increased with the polymerization temperature.



Branching also occurred in the synthesis of statistical copolymers. The number of branches in the copolymers was determined by their CH_3 ^{1}H NMR intensities according to a literature method[12] and given in Table 5.

DSC Study of Copolymers. Figure 5 shows the DSC traces of the above-synthesized alternating and statistical ethylene–vinyl alcohol copolymers. They were determined for samples as precipitated. A trace for a poly(vinyl alcohol) (PVAL) sample is also shown. Melting endotherms are observed between 360 and 500 K and at a lower temperature with increasing ethylene content. Glass transition inflections are hardly observed for the two copolymers of high ethylene content. The crystallization should predominantly be due to the hydrogen bondings between the copolymer molecules. To discuss the structure–T_g relationship of a copolymer independently of the crystalline region as in our previous paper,[13] amorphous

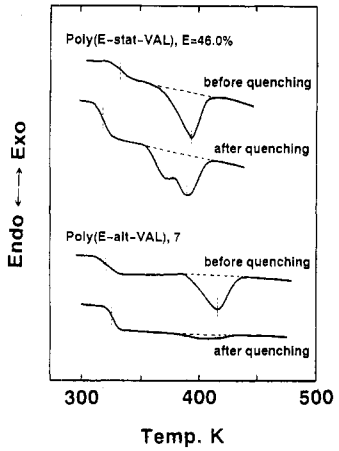


Figure 6. DSC traces of a statistical ethylene–vinyl alcohol copolymer and the alternating ethylene–vinyl alcohol copolymer 7, before and after quenching.

Table 6. DSC Study on Ethylene–Vinyl Alcohol and Ethylene–Vinyl Acetate Copolymers

		ethylene–vinyl alcohol copolymer			ethylene–vinyl acetate copolymer		
run[a]	ethylene mol % in copolymer	T_g[b] (K)	T_m[c] (K)	ΔH_m[d] (mJ mg^{-1})	T_g[e] (K)	T_m[e] (K)	ΔH_m[f] (mJ mg^{-1})
	100[g]	192	386		192	386	
1	85.3	310	365	249	210	309	5
2	61.1	312	397	180	249		
3	46.0	315	399	76	269		
4	34.7	323	457	91	284		
5	26.3	328	458	104	286		
6	18.2	326	470	98	295		
	0[h]	332	500	98	305		
	50[i]	325	413	80	233		

[a] Identical with in Table 5. [b] After quenching. [c] After annealing. [d] Per vinyl alcohol unit in the copolymer. [e] As precipitated. [f] Per copolymer. [g] Taken from a literature.[14] [h] A poly(vinyl acetate) sample was prepared in this paper (M_n = 3.72 × 10^4) and hydrolyzed. [i] The alternating copolymers 7 and 8.

samples were considered desirable. Therefore, a quenching experiment in which melted samples were thrown into liquid nitrogen was carried out. Figure 6 shows the DSC traces before and after this quenching of a statistical copolymer and the alternating copolymer 7. The alternating copolymer 7 showed a trace with a melting peak before the quenching and an almost flat trace after the quenching. Its T_g rose slightly from 319 to 325 K by quenching. On the other hand, the statistical copolymer that has an almost identical composition with the alternating copolymer showed a one-peak melting trace before quenching and a two-peak melting trace after quenching. At the same time, the T_g inflection became clearer after quenching. Thus the effect of quenching seems most prominent in the crystallizing process. The alternating copolymer in which all the vinyl alcohol units are separated from one another by one ethylene unit has a tendency to be amorphous by quenching, whereas the statistical copolymer in which several vinyl alcohol units are consecutively connected to each other as in poly(vinyl alcohol) easily crystallizes.

"As-precipitated" samples often showed melting peaks with a shoulder or of two peaks. When these samples were annealed at 30 K above their T_g for 30 min, they turned out to show simple one-peak traces. Therefore, Table 6 collects the T_g values after quenching and the T_m values after annealing for all copolymer samples. It shows that the T_m for a statistical copolymer becomes higher when its ethylene content decreases (namely, when its vinyl alcohol content increases). The heats of melting

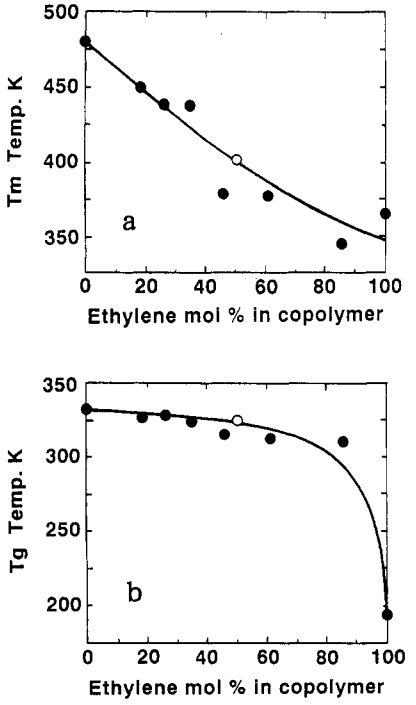


Figure 7. (a) T_m and (b) T_g against the composition of ethylene–vinyl alcohol copolymers. O refer to the alternating copolymer 7, and ● refer to the statistical copolymers.

ΔH_m were estimated from the melting peak areas. Crystallization of two copolymer samples with higher ethylene content (runs 1 and 2) seems, at least partly, due to aggregation of their polyethylene segments. The ΔH_m for other copolymers (runs 3–6) and for poly(vinyl alcohol), as expressed in mJ mg^{-1} of the vinyl alcohol unit, are about 80–100 mJ mg^{-1}. The fact that the ΔH_m of 7 is also 80 mJ mg^{-1} suggests that the hydrogen bonding between the vinyl alcohol units occurs to the same extent for both the alternating and statistical copolymers. In Figure 7a, T_m values are plotted against the copolymer compositions in ethylene mol %. The plottings for statistical copolymers give a rough correlation curve, and the T_m of the alternating copolymer 7 falls on the curve. Figure 7b shows that the T_g of 7 is also the same as the T_g of a statistical copolymer of identical composition. The sequence ordering in ethylene–vinyl alcohol copolymers does not affect either the T_m or the T_g of the copolymer but does affect the ease of crystallization as revealed by the quenching experiment. Matsumoto et al.[15] studied the crystalline structure of statistical copolymers of various compositions. They determined T_m by polarizing microscopy and T_g by dilatometry at a very slow heating rate (0.2–0.4 K min^{-1}). Their T_m and T_g values are about 20 K higher than ours, but their T_m- and T_g-composition curves are parallel to our curves in Figure 7.

Recently, Chung[16] and Ramakrishnan[17] also synthesized the alternating ethylene–vinyl alcohol copolymer 7 through the ring-opening polymerization of (5-cyclooctenyl)diethylborane, followed by hydroboration and oxidation. Their alternating copolymer contained many unordered sequences because of the two possible orientations at the hydroboration but showed a much higher decomposition-initiating temperature (673 K) than poly(vinyl alcohol) (526 K). They also reported T_g and T_m values for their copolymer as 322 and 387 K, respectively. This T_g is almost the same as our T_g in Table 6, and the T_m is 26 K lower than ours.

The ethylene–vinyl acetate copolymers as precipitated were noncrystalline except the sample of the highest

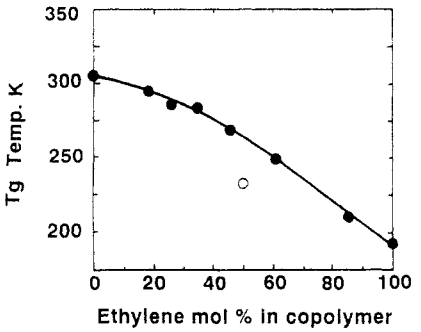


Figure 8. T_g against the composition of ethylene–vinyl acetate copolymers. O refer to the alternating copolymer 8, and ● refer to the statistical copolymers.

ethylene content (run 1; the heat of melting ΔH_m for this sample was very small). They showed T_g between 210 and 300 K as given in Table 6. Their plottings against the copolymer compositions give a good correlation curve in Figure 8. This correlation curve is essentially the same as that reported by Illers.[18] The T_g of the alternating copolymer 8 appears at 30 K lower from the correlation curve for the statistical copolymers. A sequence-ordering effect on T_g is apparent in this case. The strong intermolecular forces due to hydrogen bonding in the vinyl alcohol copolymers covered the effect of sequence ordering in Figure 7, and the weak intermolecular forces in the vinyl acetate copolymers uncovered it in Figure 8. There is a possibility that the branching in 7 and 8 as well as in ethylene copolymers might also complicate the circumstances.

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