

# Synthesis of Sequence-Ordered Copolymers. 3. Glass Transition Temperatures of Sequence-Ordered and -Unordered Copolymers

Kenji Yokota,\* Masanobu Miwa, Tadamichi Hirabayashi, and Yoshihito Inai

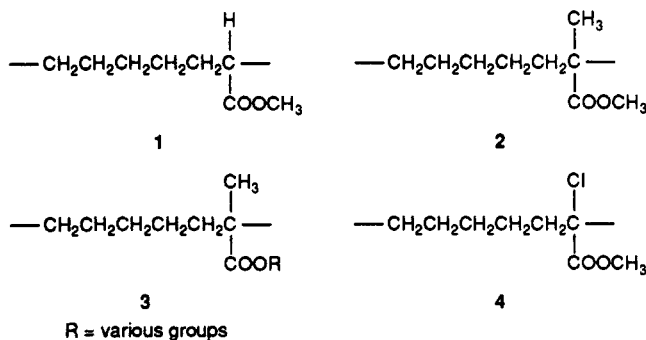
Department of Materials Science & Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

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**ABSTRACT:** Sequence-ordered (periodic) 1:1 and 2:1 ethylene-acrylic copolymers were synthesized. As acrylic monomers, methyl acrylate, methyl methacrylate, and methacrylonitrile were investigated. Sequence-unordered (statistical) copolymers containing various ratios of ethylene and the above acrylic monomers were also synthesized by reducing statistical vinylidene chloride-acrylic copolymers with tri-*n*-butyltin hydride. The glass transition temperatures ( $T_g$ ) of these copolymers were determined by differential scanning calorimetry. The  $T_g$ 's of the sequence-ordered copolymers do not deviate from the  $T_g$ 's of the sequence-unordered copolymers of identical composition in the cases of ethylene-methyl acrylate copolymers and ethylene-methyl methacrylate copolymers but deviate higher in the case of ethylene-methacrylonitrile copolymers.

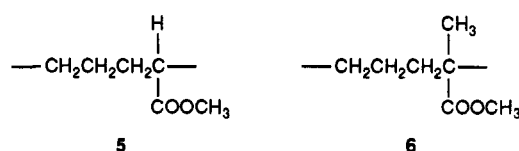
Physical properties of a copolymer are fundamentally determined by its sequence as well as chemical structure and composition. Hirooka et al.<sup>1,2</sup> studied the glass transition temperatures ( $T_g$ ) of alternating and statistical copolymers of an identical (i.e., 1:1) composition. They concluded that the deviation of the  $T_g$  of an alternating copolymer from the  $T_g$  of a statistical 1:1 copolymer depends on the type of  $T_g$ -composition relationship of the statistical copolymer involved. When the  $T_g$ -composition relationship is linear as is in the case of styrene-methyl acrylate copolymers, the alternating and statistical 1:1 copolymers show an identical  $T_g$ . When the  $T_g$ -composition curve is concave or convex for statistical copolymers, the alternating copolymer shows lower or higher  $T_g$  than the statistical 1:1 copolymer, respectively. Styrene-methyl methacrylate and styrene-acrylonitrile copolymers are examples of each.

We<sup>3,4</sup> have synthesized the following periodic (2:1) ethylene-acrylic copolymers 1-4 by hydrogenating alternating butadiene-acrylic copolymers. Some copolymers

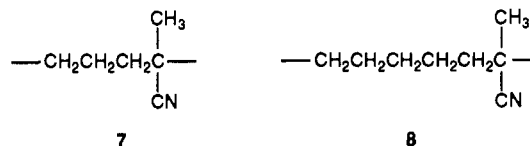


were partially crystalline because of their ordered sequences.

Subsequently we<sup>5,6</sup> have synthesized an alternating (1:1) ethylene-methyl acrylate copolymer 5 by copolymerizing a large excess of ethylene with methyl acrylate in the presence of a Lewis acid and an alternating ethylene-methyl methacrylate copolymer 6 by reducing an alternating vinyl bromide-methyl methacrylate copolymer with tri-*n*-butyltin hydride ( $\text{Bu}_3\text{SnH}$ ).



In the first part of the present paper, we will report the synthesis of sequence-ordered copolymers containing methacrylonitrile units, 7 and 8.



Thus we have the following three types of monomer-paired and two types of sequence-ordered (1:1 and 2:1) copolymers. Monomer unit abbreviations used here are as follows: E = ethylene, MA = methyl acrylate, MMA = methyl methacrylate, and MAN = methacrylonitrile.

P(E-alt-MA), 5    P(E-per-E-per-MA), 1

P(E-alt-MMA), 6    P(E-per-E-per-MMA), 2

P(E-alt-MAN), 7    P(E-per-E-per-MAN), 8

In the second part, we will compare the  $T_g$ 's of the above sequence-ordered (periodic) copolymers with the  $T_g$ 's of the corresponding sequence-unordered (statistical) copolymers. For this purpose, the statistical copolymers containing various ratios of ethylene and acrylic monomer units are synthesized from statistical vinylidene chloride (VDC)-acrylic copolymers by reducing them with  $\text{Bu}_3\text{SnH}$ .

## Experimental Section

**Reagents.** Reagents were commercially available extrapure reagents from Nacalai Tesque Inc., Kyoto, Japan, and purified by appropriate standard methods.<sup>7</sup> MA, MMA, and MAN monomers were washed with sodium hydroxide, sodium hydrogen sulfite, and sodium chloride solutions, dried over calcium hydride, and distilled under reduced nitrogen pressure. Butadiene and VDC monomers were obtained as in pressure cans and condensed into reaction vessels when copolymerized. Ethylaluminum chlorides obtained from Ethyl Corporation were distilled and used as toluene solutions (4 mol L<sup>-1</sup>). Extrapure  $\text{Bu}_3\text{SnH}$  was used as received.

Table I  
Alternating Copolymerization of Vinyl Bromide (VB) and Methacrylonitrile (MAN)<sup>a</sup>

run	monomer feed					alkylaluminum halide soln <sup>b</sup>	copolymer							
	VB		MAN		MAN, mol %		copolymn		yield		MAN, <sup>c</sup> mol %	$M_n^d \times 10^{-4}$		
	mL	mmol	mL	mmol			temp, °C	time, h	mg	% <sup>e</sup>				
1	6.0	85.1	1.6	18.9	81.8	EASC	5.0	20.3	0	2	97	4	42.7	0.7
2	9.0	128	1.2	14.3	89.9	EASC	4.0	15.9	0	10	185	11	36.5	
3 <sup>f</sup>	10.0	142	1.2	14.3	90.8	EADC	4.0	16.0	-78-0	40	trace			
4	10.0	142	1.2	14.3	90.8	EADC	4.0	16.0	0	24	405	16	48.2	2.0
5	19.0	270	4.0	47.8	84.9	EADC	13.0	51.2	-78	20	137	2	38.0	
6	14.3	203	2.0	23.9	89.5	EADC	7.0	27.7	-20	20	411	10	49.9	1.8
7	16.0	227	2.1	25.1	90.0	EADC	7.0	27.7	0	24	607	14	47.6	1.3
8	18.5	262	2.4	28.7	90.1	EADC	7.0	27.7	0	24	1080	22	48.7	1.5

<sup>a</sup> A radical initiator (benzoyl peroxide for run 1 and AIBN for runs 2 and 4–8, 50–200 mg) and toluene (3–10 mL) were added. <sup>b</sup> Ethylaluminum sesquichloride (EASC) or ethylaluminum dichloride (EADC) were used as 4 mol L<sup>-1</sup> toluene solutions. <sup>c</sup> Copolymer composition was determined by its <sup>1</sup>H NMR peak intensity. <sup>d</sup> Number-averaged molecular weight was determined by GPC with reference to polystyrene standards. <sup>e</sup> Yield percent was based on MAN in the feed. <sup>f</sup> No radical initiator was added.

**Copolymerization and Polymer Reaction.** The alternating copolymerization of vinyl bromide (VB) and MAN and the reduction of the resultant copolymer with Bu<sub>3</sub>SnH were carried out with reference to the procedure for the synthesis of 6.<sup>6</sup> A mixture of VB, MAN, an ethylaluminum chloride (ethylaluminum sesquichloride (EASC) or ethylaluminum dichloride (EADC)) solution, a radical initiator, and toluene solvent were placed in a nitrogen-purged test tube and kept in a constant-temperature bath for a given time. Then the mixture was poured into a large volume of methanol containing 1% hydrochloric acid and a trace of hydroquinone. The collected copolymer was reprecipitated three times from chloroform solution into methanol and dried in vacuo. This copolymer was reduced to obtain 7 by refluxing with Bu<sub>3</sub>SnH and 2,2'-azobisisobutyronitrile (AIBN) in tetrahydrofuran (THF).<sup>8</sup>

The alternating copolymerization of butadiene and MAN was carried out by the same procedure as described in our previous papers.<sup>3,4</sup> Hydrogenation of the resultant copolymer was carried out by three reagents: *p*-toluenesulfonyl hydrazide<sup>9</sup> in toluene, high-pressure hydrogen with platinum black catalyst, and high-pressure hydrogen with the Wilkinson catalyst, [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>3</sub>RhCl.

Statistical copolymerizations of VDC-MA, VDC-MMA, and VDC-MAN were carried out by warming the monomer mixtures of various feed compositions with AIBN. A small volume of an appropriate solvent was added for homogenous copolymerization. The resultant copolymers were reduced again with Bu<sub>3</sub>SnH in THF to convert them into statistical ethylene copolymers.

**Measurements.** <sup>1</sup>H (200-MHz) and <sup>13</sup>C (50-MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Varian XL-200 spectrometer. The pulse sequence are as follows: for <sup>1</sup>H, 7-μs pulse width, 3-s acquisition time, and 10-s interval; for <sup>13</sup>C, 18-μs pulse width, 0.8-s acquisition time, and 1-s interval. A Hitachi H-90 spectrometer was also used for 90-MHz <sup>1</sup>H NMR. Most of spectra were determined for 5–10 w/v % polymer solutions at 25 °C with tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra were recorded on a Jasco IR Report 100 spectrometer for polymer films or KBr discs. Gel permeation chromatography (GPC) of copolymers was determined on a Tosoh HLC 803D with GMX-, G1000-, G2000-, and G4000-HXL columns in series. The eluent was THF and its flow rate was 1 mL min<sup>-1</sup> at 40 °C. The retention time was taken as a measure of the copolymer molecular weight with reference to polystyrene standards. The T<sub>g</sub> values of copolymers were determined by differential scanning calorimetry (DSC) on a Seiko I TA Station with a DSC 210 unit. A sample (2–6 mg) was taken in an aluminum pan with lid and the heating and cooling rate was 10 °C min<sup>-1</sup>.

## Results and Discussion

**Synthesis of Sequence-Ordered Methacrylonitrile Copolymers.** P(E-*alt*-MAN) (7) and P(E-*per*-E-*per*-MAN) (8) were successfully synthesized via the same reaction route for P(E-*alt*-MMA) (6)<sup>6</sup> and P(E-*per*-E-*per*-MMA) (2).<sup>3</sup>

The experiments of alternating copolymerization of VB and MAN are summarized in Table I. The product copolymers were white solids and soluble in chloroform, acetone, THF, dimethyl sulfoxide, and *N,N*-dimethylformamide. Table I shows a copolymer of 1:1 composition can be obtained under the following copolymerization conditions: a large excess (90 mol %) VB monomer feed, use of EADC (not EASC) in combination with a radical initiator, and a temperature between 0 and -20 °C. The copolymer structure was identified by its IR and <sup>1</sup>H and <sup>13</sup>C NMR spectra.

The 1:1 VB-MAN copolymer obtained under the above copolymerization conditions was reduced with Bu<sub>3</sub>SnH and AIBN in THF at reflux. An example is as follows. A mixture of VB-MAN copolymer (500 mg), Bu<sub>3</sub>SnH (3.5 mL, 3.8 equiv to VB unit), AIBN (200 mg), and THF (18 mL) was heated at 70 °C. After 72 h of a homogeneous reaction, THF was removed under vacuum and the residue was poured into methanol. The precipitated product was collected, repeatedly reprecipitated with chloroform-methanol, and dried in vacuo. The reduced copolymer 7 was obtained in 90% yield. Figure 1a,b shows the <sup>1</sup>H NMR spectra of the copolymers before and after the reduction. A complete replacement of bromine by hydrogen is clearly seen. The <sup>13</sup>C NMR spectrum for 7 in Figure 1c was assigned as shown with reference to a DEPT<sup>10</sup> spectrum. The fact that only five <sup>13</sup>C NMR peaks are observed in spite of six carbons in one repeating structure is evidence for the alternating structure of 7 (and hence of the precursor VB-MAN copolymer). Molecular weights of copolymers did not change appreciably during the Bu<sub>3</sub>SnH reduction. A precursor copolymer with a number-average molecular weight ( $M_n$ ), as estimated by GPC, of  $1.2 \times 10^4$  gave 7 with an  $M_n$  of  $1.1 \times 10^4$ . These  $M_n$ 's correspond to the degree of polymerization of 56 and 53, respectively, when corrected for the repeating structure by the *Q*-factor method.<sup>11</sup>

Alternating butadiene-MAN copolymer was obtained from butadiene (8.1 g, 150 mmol) and MAN (12.6 mL, 150 mmol) with the EASC solution (7.5 mL, 30 mmol) and vanadium oxytrichloride (3 mmol). The mixture was gently stirred at 0 °C for 44 h and then poured into a large volume of methanol containing 1% hydrochloric acid. After three reprecipitations with chloroform-methanol and drying in vacuo, the alternating copolymer (11 g, 60% conversion) was obtained. Its  $M_n$  determined by GPC was  $1.35 \times 10^5$ . This copolymer was subjected to hydrogenation to obtain 8 by using three reagents. Among them, the homogeneous catalytic hydrogenation with the Wilkinson's catalyst gave the best result. When heated with

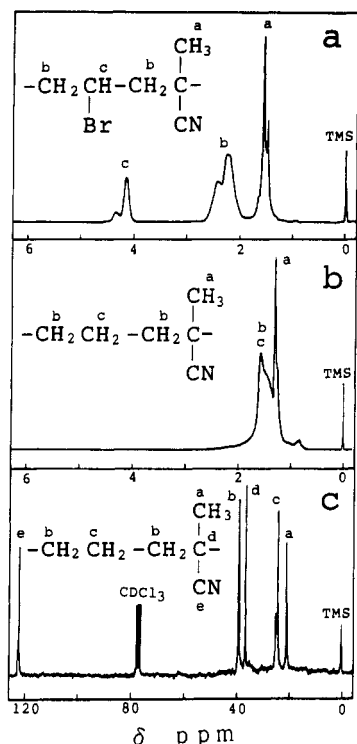


Figure 1. (a)  $^1\text{H}$  NMR spectrum of P(VB-alt-MAN); (b)  $^1\text{H}$  and (c)  $^{13}\text{C}$  NMR spectra of P(E-alt-MAN) (7).

*p*-toluenesulfonyl hydrazide, the copolymer showed 100% disappearance of the  $\text{C}=\text{C}$  double bond in  $^1\text{H}$  NMR but was accompanied by a significant addition of *p*-toluenesulfinic acid to the double bond. Catalytic hydrogenation over platinum black (200 wt % of the copolymer) under  $8\text{ kg cm}^{-2}$  hydrogen pressure at room temperature in THF was very slow and gave only 25% hydrogenation even after 10 days. This is a marked contrast to the case of the alternating butadiene-MMA copolymer in our previous paper,<sup>3</sup> where the hydrogenation was completed in 4 days under the same conditions. Successful hydrogenation with Wilkinson's catalyst was carried out as follows. The alternating copolymer (5.0 g, 41 mmol), Wilkinson's catalyst (1.9 g, 2.1 mmol), and triphenylphosphine (2.8 g, 10.7 mmol) were dissolved in chloroform (50 mL) in a pressure reaction vessel. The vessel was charged with hydrogen at  $6\text{ kg cm}^{-2}$  and kept at  $60^\circ\text{C}$  with gentle stirring. After 1 week of homogeneous reaction, the hydrogen pressure was released and the hydrogenated product was precipitated by adding methanol. Then it was repeatedly reprecipitated with chloroform-methanol and dried in vacuo. Thus the periodic copolymer 8 was obtained (4.3 g, 86%) and its completely hydrogenated structure was identified by IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in Figure 2. Its periodic structure was best confirmed by the  $^{13}\text{C}$  NMR spectrum in Figure 2c, which shows only six peaks in spite of eight carbons in one repeating structure.  $M_n$  was again  $1.35 \times 10^5$ .

**Synthesis of Statistical Copolymers.** Three statistical copolymers, P(E-stat-MA), P(E-stat-MMA), and P(E-stat-MAN), of various compositions were synthesized from the corresponding statistical VDC-acrylic copolymers, i.e., P(VDC-stat-MA), P(VDC-stat-MMA), and P(VDC-stat-MAN), respectively. Here X and Y are the substituents in the acrylic units involved. Copolymerizations of VDC-MA, VDC-MMA, and VDC-MAN were carried out at a relatively low temperature ( $30^\circ\text{C}$ ) so as to obtain precursor copolymers of high molecular weight as possible and, in some cases, allowed to proceed to medium conversions for the purpose of obtaining enough

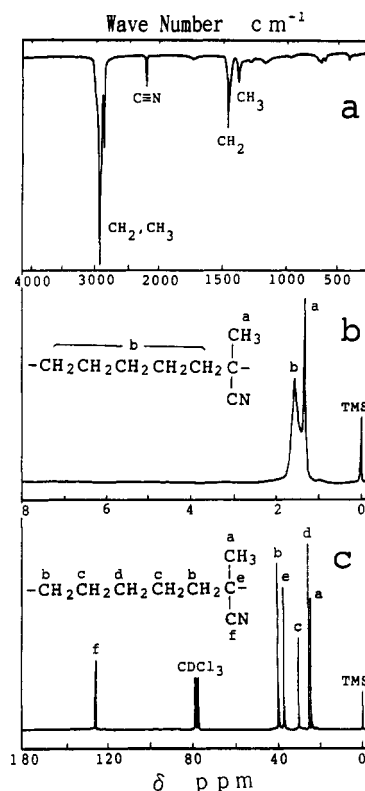
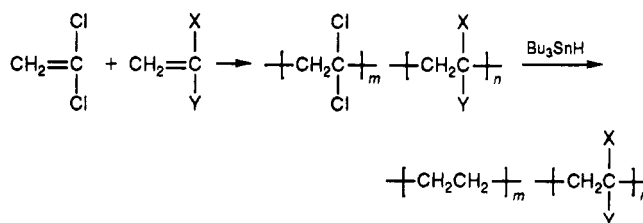


Figure 2. (a) IR and (b)  $^1\text{H}$  and (c)  $^{13}\text{C}$  NMR spectra of P(E-per-E-per-MAN) (8).



quantity of copolymers. Tables II, III, and IV show the monomer feed compositions, copolymerization times, conversions, copolymer compositions, and  $M_n$ 's for VDC-MA, VDC-MMA, and VDC-MAN copolymerizations, respectively. Thus copolymers with a wide range of compositions were obtained. Their  $M_n$ 's are  $10^5$  for VDC-MA and VDC-MMA copolymers but  $10^4$  for VDC-MAN copolymers.

These three VDC-acrylic copolymers were reduced with  $\text{Bu}_3\text{SnH}$ , usually under the same conditions as for P(VB-

Table II  
Synthesis and Reduction of Statistical Vinylidene Chloride (VDC)-Methyl Acrylate (MA) Copolymers

run	feed MA mol %	copolymeri- zation <sup>a</sup> time, h	conv, <sup>b</sup> %	P(VDC-stat-MA)		P(E-stat-MA)	
				MA, <sup>c</sup> mol %	$M_n \times 10^{-5}$	reductn, %	$M_n \times 10^{-5}$
1	8.9	5	1	7.4	1.01	100	
2	20.2	5	2	19.5	3.03	100	1.07
3	27.4	5	2	25.8	1.23	100	0.78
4	33.6	24	32	35.0	1.84	100	1.37
5	41.4	5	4	38.0	3.49	100	2.61
6	62.5	5	4	50.2	1.94	100	1.06
7	46.9	20	28	53.0	1.77	100	0.69
8	58.5	5	11	54.2	3.54	100	3.09
9	67.3	5	5	59.3	4.70	100	3.04
10	77.9	3.5	7	72.9	7.57	100	3.77
11	83.3	5	2	76.7	3.90	100	3.04

<sup>a</sup> Total monomer 5–18 mL; toluene 4 mL; AIBN 50 mg; at  $30^\circ\text{C}$ .  
<sup>b</sup> Based on MA fed. <sup>c</sup> Determined by  $^1\text{H}$  NMR peak areas.

Table III  
Synthesis and Reduction of Statistical Vinylidene Chloride (VDC)-Methyl Methacrylate (MMA) Copolymers

run	feed MMA, mol %	copolymerization <sup>a</sup>		P(VDC- <i>stat</i> -MMA)		P(E- <i>stat</i> -MMA)		
		time, h	conv, <sup>b</sup> %	MMA, <sup>c</sup> mol %	$M_n \times 10^{-5}$	method <sup>d</sup>	%	$M_n \times 10^{-5}$
1	15.0	19	20	37.0	1.27	C	100	0.41
2	16.6	27	21	36.6	1.04	B	100	0.33
3	21.4	28	27	48.8	1.13	C	100	0.34
4	29.9	20	29	55.7	1.35	B	100	0.29
5	33.3	20	31	62.3	1.17	A	100	0.041
5'						B	100	0.26
6	37.4	20	28	65.5	1.10	B	100	0.22
7	50.0	20	20	69.3	1.41	B	100	0.21
8	60.0	20	21	87.8	4.08	C	100	0.47
9	74.9	20	20	90.0	2.33	A	100	0.034
9'						C	100	0.34

<sup>a</sup> Total monomer 5–11 mL; toluene 2–4 mL; AIBN 50 mg; at 30 °C. <sup>b</sup> Based on MMA fed. <sup>c</sup> Determined by <sup>1</sup>H NMR peak areas. <sup>d</sup> A, at +65 °C for 120 h; B, at 0 °C for 70 h under UV irradiation; C, double reduction at –65 °C for 100 h each and then at –20 °C for 72 h under UV irradiation.

Table IV  
Synthesis and Reduction of Statistical Vinylidene Chloride (VDC)-Methacrylonitrile (MAN) Copolymers

run	feed MAN, mol %	copolymerization <sup>a</sup>		P(VDC- <i>stat</i> -MAN)		P(E- <i>stat</i> -MAN)	
		time, h	conv, <sup>b</sup> %	MAN, <sup>c</sup> mol %	$M_n \times 10^{-5}$	reductn, %	$M_n \times 10^{-4}$
1	12.5	347	6	28.7	0.46	100	0.99
2	14.7	327	6	30.7	0.39	100	1.80
3	24.0	25 <sup>d</sup>	29	38.7	0.18	98	0.97
4	22.2	352	18	49.5	0.24	98	0.87
5	19.9	379	16	50.4	0.21	97	0.64
6	29.9	490	15	52.2	0.17	94	0.87
7	26.3	64 <sup>e</sup>	12	55.6	0.18	93	0.63
8	29.0	330	13	56.1	0.16	93	0.73
9	26.3	335	10	57.0	0.20	93	0.61

<sup>a</sup> Total monomer 5–12 mL; acetone 1.5–6 mL; AIBN 50 mg; at 30 °C. <sup>b</sup> Based on MAN fed. <sup>c</sup> Determined by <sup>1</sup>H NMR peak areas. <sup>d</sup> At 50 °C. <sup>e</sup> At 40 °C.

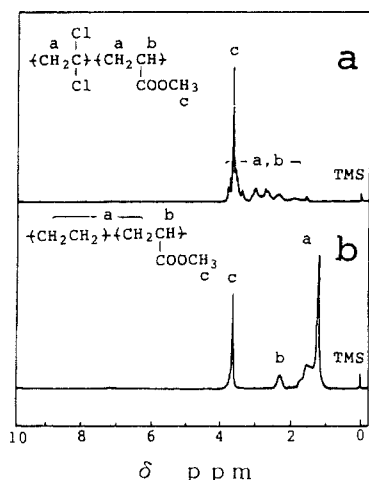


Figure 3. <sup>1</sup>H NMR spectra (a) before and (b) after the reduction of the P(VDC-*stat*-MA); Table II, run 4.

*alt*-MAN) described above. Tables II–IV also show the results of the reduction experiments. The successful reduction for each copolymer was confirmed by its IR and <sup>1</sup>H and <sup>13</sup>C NMR spectra. Figure 3 shows <sup>1</sup>H NMR spectra for the VDC-MA copolymers as an example before and after the reduction experiment. Before the reduction, the main-chain CH<sub>2</sub> absorptions appear in a wide range from 1.5 to 4.0 ppm as shown in Figure 3a, according to the various sequences of VDC and MA units. The CH<sub>2</sub> group in the middle of a long VDC sequence would show an absorption at around 4 ppm as in VDC homopolymer and

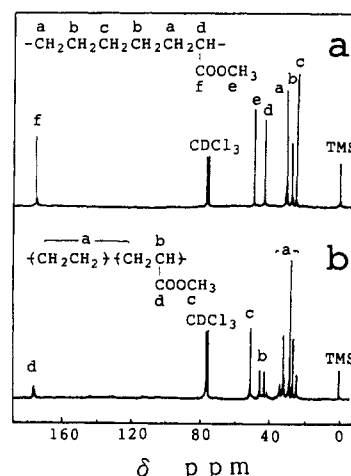
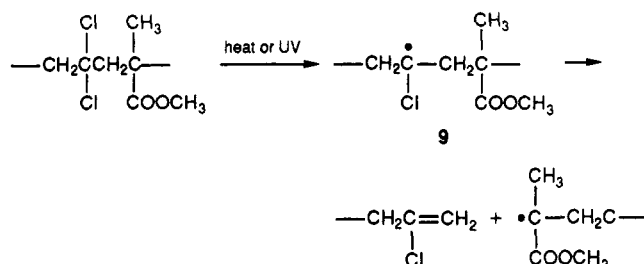


Figure 4. <sup>13</sup>C NMR spectra of (a) P(E-*per*-E-*per*-MA) (1) and (b) P(E-*stat*-MA); Table II, run 4.

the CH<sub>2</sub> group in a long MA sequence at 1.5 ppm as in MA homopolymer. The CH<sub>2</sub> groups in various VDC-MA sequences would show absorptions between these two extremes. After the reduction, the Cl atoms, which gave rise to the large difference in the chemical shift of CH<sub>2</sub> groups, are removed and substituted for hydrogens. The increased CH<sub>2</sub> absorptions now appear in a narrow range from 1.1 to 1.9 ppm as shown in Figure 3b. The extents of reduction can be determined from the relative peak intensities of CH<sub>2</sub> and COOCH<sub>3</sub> absorptions and are given in the Table II. Figure 4 compares the <sup>13</sup>C NMR spectra of a reduced copolymer (run 4) and of 1. Simpler CH<sub>2</sub> and C=O spectra for 1 should be noticed. Also before and after the reduction of VDC-MMA and VDC-MAN copolymers, similar spectral changes due to the reduction were also observed.

Changes in copolymer molecular weight occurred during the reduction to some extent for VDC-MA and VDC-MAN copolymers. P(E-*stat*-MA) and P(E-*stat*-MAN) samples, however, still show  $M_n$ 's of 10<sup>5</sup> and 10<sup>4</sup>, respectively. On the other hand, a serious decrease in  $M_n$  was observed for VDC-MMA copolymers as shown in Table III, run 5 or 9, where the reduction was carried out at 65 °C, as for VDC-MA and VDC-MAN copolymers. In these runs, no product could be recovered by precipitating with methanol, but it could be recovered only by using column chromatography. The  $M_n$ 's of the recovered products were about 1/100 of that of the precursor copolymers. A separate experiment in which a solution of P(VDC-*stat*-MMA) in THF (without Bu<sub>3</sub>SnH and AIBN) was refluxed for the

same amount of time showed the same order of decrease in  $M_n$ . Another experiment in which the same solution was irradiated by an ultraviolet lamp at 0 °C also showed an  $M_n$  decrease. These results suggest that a significant scission reaction of the main chain occurs for VDC-MMA copolymers when heated at 65 °C or irradiated by ultraviolet light at 0 °C. The  $^1\text{H}$  NMR spectrum of the product in run 5 showed two olefinic peaks at 5.0–5.3 ppm that resemble that of 2-chloropropene.<sup>12</sup> The scission reaction may occur according to the following scheme:



The radical intermediate 9 may undergo a scission at its main chain or a reduction by abstracting a hydrogen atom from  $\text{Bu}_3\text{SnH}$ . The crowded substituents around the VDC-MMA sequence in VDC-MMA copolymer are likely to lead to the scission reaction. The less crowded VDC-MA and VDC-MAN copolymers lead mostly to the reduction reaction.

To suppress the scission reaction of VDC-MMA copolymers, the reduction was conducted at lower temperatures and copolymers of  $M_n \sim 10^4$  were obtained in runs 5' and 9'. Reduction at 0 and -20 °C was successful to give P(E-stat-MMA). Incidentally, only one Cl atom was removed at -65 °C to give a vinyl chloride-MMA copolymer.

**Glass Transition Temperatures of the Sequence-Ordered and -Unordered Copolymers.** Now the expected samples of the sequence-ordered (periodic) and sequence-unordered (statistical) ethylene-acrylic copolymers are available. Acrylic units are MA, MMA, and MAN. On these samples, DSC experiments were carried out in a temperature range from -50 to 100 °C. Reproducible and definite  $T_g$  points were observed when heating, but they were ambiguous when cooling.  $T_g$  values were taken as the inflection points of the heating traces, averaged for three repeated experiments and shown in Table V. All samples did not show melting peaks. A quenching experiment on the partially crystalline 2 to obtain an amorphous sample was reported elsewhere.<sup>13</sup> The  $T_g$  values of polyethylene and acrylic homopolymers were taken from a compilation in *Polymer Handbook*.<sup>14</sup> For the  $T_g$  of polyethylene, many conflicting data are given and may be classified into three groups, around -125, -80, and -40 °C. We will use hereafter a  $T_g$  value of -81 °C according to Tobolsky<sup>15</sup> who estimated it by using the Fox equation<sup>16</sup> from the data on an amorphous polypropylene and an ethylene-propylene copolymer. Illers<sup>17</sup> also gave an approximate value of -77 °C through the study on ethylene copolymers with vinyl acetate, vinyl propionate, and propylene.

In Figure 5, parts a, b, and c, the  $T_g$  values of copolymers as well as homopolymers are plotted against copolymer compositions for E-MA, E-MMA, and E-MAN pairs, respectively. Statistical copolymers and homopolymers are represented by open circles and periodic copolymers are shown by filled circles. Regression analysis on the data of statistical copolymers together with homopolymers was carried out to obtain the curve  $T_g = A + BX + CX^2$ , where  $X$  denotes mole percent of the acrylic unit in the

Table V  
Glass Transition Temperatures of Ethylene-Acrylic Copolymers<sup>a</sup>

E-MA copolymer		E-MMA copolymer		E-MAN copolymer	
MA, mol %	$T_g$ , °C	MMA, mol %	$T_g$ , °C	MAN, mol %	$T_g$ , °C
Periodic Copolymer <sup>b</sup>					
5 50	-22	6 50	19	7 50	60
1 33.3	-34	2 33.3	-6	8 33.3	22
Statistical Copolymer <sup>c</sup>					
0	-81	0	-81	0	-81
19.5	-35.3	36.6	-4.2	28.7	-2.2
25.8	-35.3	37.0	1.5	30.7	-0.3
35.3	-35.4	48.8	13.4	38.7	26.2
38.0	-29.2	55.7	31.9	49.5	24.4
50.2	-21.4	62.3	36.5	50.4	39.8
53.0	-18.4	65.5	45.0	52.2	52.8
54.2	-15.1	69.3	63.9	55.6	59.5
59.3	-10.3	87.8	81.8	57.0	63.6
72.9	-12.3	90.0	92.7	57.1	59.0
76.7	-3.0				
100	8	100	105	100	120

<sup>a</sup> Monomer units are abbreviated as follows: E = ethylene, MA = methyl acrylate, MMA = methyl methacrylate, and MAN = methacrylonitrile. <sup>b</sup> The copolymer with 50 mol % of acrylic unit means an alternating ethylene-acrylic copolymer, and the copolymer with 33.3 mol % of acrylic unit means a periodic ethylene-ethylene-acrylic copolymer. <sup>c</sup> To plot Figure 5,  $T_g$ 's for statistical copolymers were given to one decimal place as averaged in spite of their accuracy. The  $T_g$  of each homopolymer was taken from the *Polymer Handbook*<sup>14</sup> and determined also on our own samples. The  $T_g$  for polyethylene is taken as -81 °C. See text for discussion.

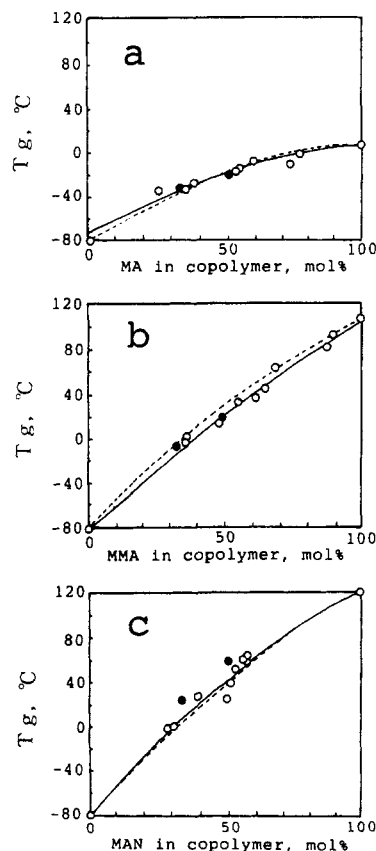


Figure 5.  $T_g$ -composition relationships for (a) E-MA, (b) E-MMA, and (c) E-MAN copolymers. Open circles denote statistical copolymers and homopolymers. Filled circles denote periodic copolymers.

copolymer. The evaluated parameters  $A$ ,  $B$ , and  $C$  are given in Table VI and the calculated curves by using these parameters are drawn by solid lines in Figure 5. Table VI also gives  $T_g(\text{calcd})$ ,  $T_g(\text{obsd})$ ,  $T_g(\text{obsd}) - T_g(\text{calcd})$ , and

Table VI  
Regression Analysis on the Glass Transition  
Temperature-Composition Relationships for Statistical  
Ethylene-Acrylic Copolymers<sup>a</sup>

	copolymer		
	E-MA	E-MMA	E-MAN
regression curve param <sup>b</sup>			
A	-72.70	-80.08	-81.00
B	1.391	2.173	2.972
C	-0.006	-0.003	-0.010
std dev in ordinate, °C	6.41	5.18	7.83
significant deviation at 90% confidence level, °C	>10.55	>8.52	>12.88
$T_g(\text{calcd})$ , °C			
1:1	-18.8	20.5	43.7
2:1	-33.3	-11.3	7.4
$T_g(\text{obsd})$ , °C			
1:1	-22	19	60
2:1	-34	-6.0	22
$T_g(\text{obsd}) - T_g(\text{calcd})$ , °C			
1:1	-3.2	-1.5	16.3
2:1	-0.7	5.3	14.6

<sup>a</sup> Monomer units are abbreviated as follows: E = ethylene, MA = methyl acrylate, MMA = methyl methacrylate, and MAN = methacrylonitrile. <sup>b</sup> Regression curve is given by  $T_g = A + BX + CX^2$ , here X denotes mole percent of acrylic unit in the copolymer. <sup>c</sup>  $T_g(\text{obsd})$  and  $T_g(\text{calcd})$  denote the  $T_g$  observed and the  $T_g$  calculated, respectively, for 1:1 and 2:1 periodic copolymers.  $T_g(\text{calcd})$  was calculated by using the above regression curve.

the deviation parameters.  $T_g(\text{calcd})$  denotes the calculated  $T_g$  by using the above parameters (or read on the calculated curves) for 1:1 (50 mol %) and 2:1 (33.3 mol %) statistical copolymers.  $T_g(\text{obsd})$  are experimental values already given in Table V for the two types of periodic copolymers. Therefore  $T_g(\text{obsd}) - T_g(\text{calcd})$  values represent how the periodic copolymers differ in  $T_g$  from the statistical copolymers of the same composition.

In Figure 5a, i.e., for the case of E-MA copolymers, both the periodic copolymers 5 and 1 show their  $T_g$ 's on the regression curve for statistical copolymers. In other words,  $T_g(\text{obsd}) - T_g(\text{calcd})$  in Table VI for both the periodic E-MA copolymers are insignificantly small in view of the standard deviation of the regression analysis. The same situation can be found in Figure 5b and Table VI for the case of E-MMA copolymers. For the case of E-MAN copolymers in Figure 5c, however, both the periodic copolymers 7 and 8 show about 15 °C higher  $T_g$ 's than the statistical copolymers of identical compositions. These deviations seem rather large. Statistically studying Table VI,  $T_g(\text{obsd}) - T_g(\text{calcd})$  for both the periodic copolymers are significantly larger than the experimental errors in view of the standard deviation of regression analysis at a confidence level of 90%.

The regression curves in Figures 5, which show  $T_g$ -composition relationships of the three statistical copolymers, are all gently convex. According to Hirooka et al.'s finding as described in the introductory section, the  $T_g$  of a periodic copolymer should deviate above the curve when it is convex. This situation is found only in the case of E-MAN copolymers. In the case of E-MA and E-MMA copolymers, the  $T_g$ 's of periodic copolymers do not show any significant deviation from the regression curve. A reasonable explanation for such results is not available now. We should study further various other copolymers to accumulate data but could give here the  $T_g$  sequence data for three copolymers, in which two types of sequence-ordered copolymers are involved.

A number of equations that predict the  $T_g$  of statistical copolymers have been proposed. The Fox additive equation<sup>16</sup> is simple but often gives unsatisfactory results. The

Gordon-Taylor equation<sup>18</sup> considers the specific volumes of relevant homopolymers and needs the data on their thermal expansion coefficients. The Gibbs-DiMarzio theory<sup>19</sup> is based on the stiffness energy of the copolymer chain. The stiffness energy is assumed to be given by the number of rotatable bonds in the monomer unit concerned. Subsequently, this assumption has come to the Johnston<sup>20</sup> and the Barton<sup>21</sup> equations, both of which predict the  $T_g$  in terms of the monomer unit sequences (diad sequences) in the copolymer. We use below the Johnston equation.

The Johnston equation is given by

$$\frac{1}{T_{gp}} = \frac{W_A P_{AA}}{T_{gAA}} + \frac{W_A P_{AB} + W_B P_{BA}}{T_{gAB}} + \frac{W_B P_{BB}}{T_{gBB}}$$

in which  $T_{gp}$  denotes the  $T_g$  of a copolymer in question containing weight fraction  $W_A$  and  $W_B$  of two monomer units A and B.  $T_{gAA}$ ,  $T_{gBB}$ , and  $T_{gAB}$  denote the  $T_g$  contribution of the AA, BB, and AB diads in the copolymer and can be substituted by  $T_g$  of A homopolymer, B homopolymer, and alternating A-B copolymer, respectively.  $P_{AA}$ ,  $P_{BB}$ ,  $P_{AB}$ , and  $P_{BA}$  denote the probabilities of finding AA, BB, AB, and BA diads in the copolymer chain, respectively, and can be calculated by using the monomer feed compositions and monomer reactivity ratios. The latter are naturally of the copolymerizations with VDC.

$$r_1 = 0.96 \quad r_2 = 0.58 \quad M_1 = \text{VDC} \quad M_2 = \text{MA} \quad \bullet$$

(present study)

$$r_1 = 0.34 \quad r_2 = 2.50 \quad M_1 = \text{VDC} \quad M_2 = \text{MMA} \quad (\text{lit.}^{22})$$

$$r_1 = 0.40 \quad r_2 = 2.50 \quad M_1 = \text{VDC} \quad M_2 = \text{MAN} \quad (\text{lit.}^{23})$$

Literature values of  $r_1$  and  $r_2$  were used in the calculation of diads for VDC-MMA and VDC-MAN copolymerizations because the copolymers were not isolated at low enough conversions. (As a matter of fact, the differences in copolymer composition between found and calculated values were small. The product of  $r_1$  and  $r_2$  is about unity in each case and therefore we are dealing here with "random" copolymers.) By substitution of the diad probabilities and the relevant  $T_g$  values of homopolymers and of alternating copolymers, 5, 6, or 7, into the Johnston equation, broken curves are plotted in Figure 5 and found in good accordance with experimental results.

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