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# Periodic copolymers

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#### Abstract

The hydrogenated product of an alternating butadiene-(methyl methacrylate) copolymer can be regarded as an "implied" periodic ethylene-ethylene-(methyl methacrylate) copolymer. By different polymer reactions, various periodic copolymers were synthesized from appropriate precursor polymers and copolymers. Such copolymer syntheses have an advantage over the direct copolymerizations to give easily high molecular weight copolymers of common and simple monomer units.

We investigated these periodic copolymers as to their  $T_{g}s$  and  $T_{m}s$  and their material properties, and then discussed the structure-property relationships of periodic copolymers, especially in comparison to the corresponding statistical copolymers. Some periodic copolymers were crystalline materials even when the statistical copolymers were amorphous.

We also discussed the behavior of the periodically arranged functional groups on the copolymer main-chain; dissociation of acid copolymers, intermolecular association of them with a base polymer, and the side-chain crystallization of comb-like copolymers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Structured polymers; Polymer reactions; Polymer properties

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# 1. Introduction

Copolymers are characterized by their chemical structure, composition, molecular weight and sequence. Numerous vinyl copolymers supplied for practical use have been produced via radical mechanisms and have statistical sequences. Their composition and sequence can be expressed in terms of the concentrations of monomer in the feed mixture and the monomer reactivity ratios.

$$m_{\rm A}/m_{\rm B} = ([M_{\rm A}]/[M_{\rm B}]) \cdot \{ (r_{\rm A}[M_{\rm A}] + [M_{\rm B}])/([M_{\rm A}] + r_{\rm B}[M_{\rm B}]) \}$$
(1)

$$P_{AA} = r_A [M_A] / (r_A [M_A] + [M_B])$$
(2a)

$$P_{\rm AB} = 1 - P_{\rm AA} = [M_{\rm B}]/(r_{\rm A}[M_{\rm A}] + [M_{\rm B}])$$
(2b)

$$P_{\rm BB} = r_{\rm B}[M_{\rm B}]/([M_{\rm A}] + r_{\rm B}[M_{\rm B}])$$
(2c)

$$P_{\rm BA} = 1 - P_{\rm BB} = [M_{\rm A}]/([M_{\rm A}] + r_{\rm B}[M_{\rm B}])$$
(2d)

In Eq. (1),  $m_A/m_B$  is the copolymer composition as expressed by the molar ratio of A and B monomer units in the copolymer, and  $[M_A]$  and  $[M_B]$  are the monomer concentrations in the feed mixture. In Eq. 2(a)–2(d),  $P_{IJ}$  (*I* and *J* are either A or B) is the probability that a monomer  $M_J$  adds to a polymer radical  $\sim \sim \sim \sim M_I \cdot to$  form a  $\sim \sim \sim \sim M_I M_J \cdot sequence$ . The probability to find a sequence, e.g. a sequence of *n*ad of  $M_A$  units is given by  $P_{AA}^{(n-1)}P_{AB}$ . The monomer reactivity ratios of monomers A and B are expressed by  $r_A$  and  $r_B$  in these equations.

When the monomer reactivity ratios  $r_A$  and  $r_B$  are both zero, namely the homopropagation rate constants  $k_{AA}$  and  $k_{BB}$  are both zero, the resulting copolymer will be an AB-type alternating copolymer. This type of copolymer can be symbolized and represented as follows:

# -A-B-A-B-A-B-A-B-A-B-A-B-A-B-

#### poly(A-alt-B)

Alternating copolymers are often formed during the copolymerization of strongly electron-donating and electron-accepting monomers. The copolymerization of styrene and maleic anhydride is a wellknown example. In the copolymerization of moderately electron-donating and electron-accepting monomers, alternating copolymers are formed only when an appropriate Lewis acid is added. The spontaneous copolymerization of styrene and methyl methacrylate (MMA) in the presence of ethylaluminum sesquichloride (EASC) is a good example. Without the Lewis acid, the copolymerization of these two monomers gives a statistical copolymer with the monomer reactivity ratios of  $r_{\text{styrene}} = 0.52$  and  $r_{\text{MMA}} = 0.46$ . Two mechanisms that (1) the Lewis acid forms a ternary complex with the two monomers and the complex polymerizes or (2) the Lewis acid forms a binary complex with the electron-accepting propagating radical which selectively reacts with the electron-donating monomer, have been proposed. The electron-donating monomer may be a styrene or diene, the electron-accepting monomer may be an acrylic ester or nitrile, and the effective Lewis acid may be zinc chloride, boron trifluoride, alkylaluminum halides, or the like.

Many reviews on alternating copolymerizations have been published [1]. Different types of alternating copolymerizations have been discussed by Cowie [2, chap. 2] and Bamford [3, chap. 3].

For copolymers in which three or more monomer units are regularly arranged, the following sequence-ordered copolymers are possible and are termed as periodic copolymers:

#### -A-B-C-A-B-C-A-B-C-A-B-C-A-B-C-

#### -A-A-B-A-A-B-A-A-B-A-A-B-A-A-B-

# -A-B-C-D-A-B-C-D-A-B-C-D-A-B-C-D-

In the same manner with the representation for an alternating copolymer as given above, they are represented as follows according to the recommendation by IUPAC Macromolecular Nomenclature Commission [4].

poly(**A**-*per*-**B**-*per*-**C**) poly(**A**-*per*-**A**-*per*-**B**) poly(**A**-*per*-**B**-*per*-**C**-*per*-**D**)

For an example, the ABC-type periodic copolymer **1** synthesized by Saegusa and his coworkers [5], is represented by a source-based nomenclature as poly[(ethylene phenylphosphite)-*per*-(methyl acrylate)-*per*-(carbon dioxide)].



In a broad sense, the term periodic copolymer includes alternating copolymers which are a specific case of periodic copolymers. However, we will often use below both the terms alternating copolymer and periodic copolymer in a limited sense.

# 2. Synthesis of periodic copolymers

This section will describe the synthesis of sequence-ordered copolymers by polymer reactions.

The synthesis of various AB-type sequence-ordered copolymers, i.e. alternating copolymers, from donor-acceptor monomer pairs have often been reported in the literature as briefly mentioned in Section 1. However not all monomer pairs give alternating copolymers and so we cannot synthesize an alternating copolymer from any pair of monomers at will. We cannot generally synthesize periodic copolymers in which three or more monomer units are sequence-ordered by means of the direct copolymerization of relevant common monomers. The periodic copolymer **1** shown above is a rare example that contains uncommon and special monomer units [5].

This author has synthesized various alternating and periodic copolymers by different polymer reactions. Most of these copolymers are made of common and simple monomers and have high molecular weights. Therefore, when studying material properties, we can discuss the structure–property relationships of periodic copolymers on the basis of the chemical structure of the monomer units. We can also compare the periodic copolymers to the statistical copolymers with respect to their material properties. Because of their sequence-ordered structures, some periodic copolymers are partially crystalline materials even when the statistical copolymers are amorphous. The functional groups in periodic copolymers appear regularly on the main-chain and will exhibit behavior that differs from the functional groups in statistical copolymers. Discussions regarding copolymer properties based on ordered sequence will be given later in Section 3.

# 2.1. Synthesis of periodic copolymers by copolymerization and by polymer reactions

In contrast to the successful synthesis of various alternating copolymers, the synthesis of periodic copolymers by any direct copolymerization of relevant monomers seems very difficult. Hsieh [6] claimed that the ring-opening copolymerization of ethylene oxide, phthalic anhydride and an excess of tetrahydrofuran catalyzed by triisobutylaluminum yielded poly[(ethylene oxide)-*per*-(phthalic anhydride)-*per*-(phthalic anhydride).

# -[-CH<sub>2</sub>CH<sub>2</sub>O-COC<sub>6</sub>H<sub>4</sub>COO-(CH<sub>2</sub>)<sub>4</sub>O-]<sub>n</sub>-2

However, his identification of the periodic sequence depended only on the elemental analysis of the product. It showed 1:1:1 composition of the three-monomer units for a copolymer obtained in an experiment, which fed a very large excess of tetrahydrofuran. However, more evidence was needed to actually prove the periodic sequence.

Saegusa and his coworkers [5] copolymerized ethylene phenylphosphite, methyl acrylate, and carbon dioxide and obtained the periodic copolymer **1**. They hydrolyzed this copolymer and isolated the following three products in a 1:1:1 ratio. This result provides some evidence for the periodic sequence.

$$\begin{array}{c} O \\ \parallel \\ \underline{1} \rightarrow \text{HOCH}_2\text{CH}_2\text{OH} + \text{NaO-P-CH}_2\text{CH}_2\text{COONa} + \text{CH}_3\text{OH} \\ \mid \\ \text{C6H}_5 \end{array}$$

They also reported [7,8] the synthesis of some analogous ABC and  $A_2B$ -type periodic copolymers as an extension of their new type of polymerization via a zwitter ion mechanism [9].

A successful way to synthesize an ABC-type periodic copolymer from three monomers might involve

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a combination of highly selective reactions among three propagating active ends and three monomers. The active A end must react selectively with B monomer and must not react with monomers C and A. Then the active B end must react with monomer C and the active C end must react with monomer A.

~~~~ <b>A-C*,</b> ~~~~ <b>A-A</b> *)	(not	~~~ <b>A-B</b> *	$\rightarrow$	~~~~ <b>A</b> * + <b>B</b>
~~~~ <b>B-A*,</b> ~~~~ <b>B-B*</b> )	(not	~~~~ <b>B-C</b> *	$\rightarrow$	~~~ <b>B</b> * + C
~~~~ <b>C-B*,</b> ~~~~ <b>C-C*</b> )	(not	~~~~C-A*	$\rightarrow$	~~~~ <b>C</b> * + <b>A</b>

Then we have a periodic copolymer, -A-B-C-A-B-C-A-B-C-.

Any concurrent reaction of an active end with wrong monomers in place of the right monomer would give rise to an imperfectly periodic copolymer.

Even if a series of selective propagation reactions could be found for a combination of monomers, the copolymerization process might not yield high molecular weight copolymers. That is because such a copolymerization would occur only for special monomers under special conditions and these might lead to unfavorable side-reactions and thus give rise to low molecular weight products. In fact, the periodic copolymer **1** shown above has been reported [5] to have a molecular weight of only 3000 and was a low melting powdery material. From the standpoint of material science, a polymer should be of high molecular weight so as to show its intrinsic material properties and to be useful for practical applications.

Another synthetic approach to periodic copolymers may utilize various polymer reactions. By a copolymerization of common monomers, a precursor alternating copolymer can be synthesized and then, by a polymer reaction, this precursor copolymer can be transformed into a modified copolymer. This modified alternating copolymer can be regarded as a new alternating or periodic copolymer by an appropriate definition of constitutional repeating units. If the precursor copolymer has a high molecular weight, then the derived alternating or periodic copolymer will also be a high molecular weight product. This approach to periodic copolymers by polymer reactions has an advantage over direct copolymer-ization in that it can give high molecular weight materials readily.

The synthesis of various alternating copolymers by polymer reactions have often been reported in the literature. For example, Suzuki [10] hydrogenated poly(2-phenyl-1,3-butadiene) to give poly(ethylene-*alt*-styrene) **3**. Ethylene and styrene would not directly give an alternating copolymer by any standard polymerization process. Kamachi [11] hydrogenated poly(methyl 4-ethoxy-2,4-pentadienoate) to obtain poly[(ethyl vinyl ether)-*alt*-(methyl acrylate)] **4**. Chien [12] synthesized syndiotactic poly(ethylene-*alt*-propylene) **5** by hydrogenating *cis*-1,4-poly(1,3-pentadiene).



However, the direct synthesis of these "implied" [13] alternating copolymers by the copolymerization of related monomers is generally not possible.

# 2.2. Synthesis and identification of periodic ethylene-ethylene-(methyl methacrylate) copolymers

A good example for the synthesis of periodic copolymers by polymer reactions may be the hydrogenation of alternating butadiene–MMA copolymers by Yokota and his coworkers [14,15]. By the same polymer reaction, various  $A_2B$ -type periodic ethylene–ethylene–acrylic copolymers have been synthesized as products according to Eq. (3).

```
CH_2 = CH - CH = CH_2 + CH_2 = CXY
```

The alternating copolymerization of butadiene and an acrylic monomer in the presence of a Lewis acid was extensively studied by Furukawa, Kobayashi, and their coworkers [16]. They found that the addition of a transition metal compound greatly improves the yield of soluble products. The acrylic monomer may include acrylic esters, nitriles, and amides. According to Furukawa's procedure, the copolymerization of butadiene and MMA is carried out first in the presence of EASC to give poly(-butadiene-*alt*-MMA) **6**. Hydrogenation then furnished an  $A_2B$  type periodic copolymer with two ethylene units and one MMA unit copolymer, i.e. poly(ethylene-*per*-ethylene-*per*-MMA) **7**.



The molecular weight of this periodic copolymer 7, which we have synthesized ranges from  $5 \times 10^4$  to  $5 \times 10^5$ . We did not examine the effect of copolymerization conditions on copolymer molecular weight, but it seems to be dependent on the monomer feed ratio, the amount of EASC, the conversion of

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Fig. 1. Identification of periodic sequence of poly[ethylene-*per*-ethylene-*per*-(methyl methacrylate)] **7** by proton-decoupled <sup>13</sup>C NMR (25 MHz).

copolymerization, and the amount of solvent. A kinetic study of this type of alternating copolymerization was reported also by Furukawa [16,17]. From experience, high concentrations of both monomers and the Lewis acid and a long polymerization time gives rise to a high molecular weight copolymer. The hydrogenation of **6** was easily carried out in tetrahydrofuran with gaseous hydrogen over a catalyst. The catalyst can be platinum black or palladium on active charcoal. The application of low or medium hydrogen pressures was preferable. Another convenient hydrogenating reagent was *p*-toluenesulfonyl hydrazide [18] in refluxing toluene. Both the hydrogenating methods gave the identical product copolymer. Gel permeation chromatography (GPC) showed essentially the same molecular weights for **6** and **7**.

It is important to identify the periodic sequence of the product copolymer 7. The alternating sequence of the precursor copolymer 6 was already well proved by Furukawa and coworkers. In view of the simpleness of the polymer reaction (hydrogenation) applied in this case, the periodic sequence of 7 seems evident. Some evidence for the periodic sequence is given by the <sup>13</sup>C NMR spectrum in Fig. 1. In one constitutional repeating unit of this periodic copolymer, there are nine carbon atoms, but because of the symmetry around the quaternary carbon atom (<sup>C</sup>C) there are seven kinds of carbon atoms, labelled a to g.

In fact, we observe in Fig. 1 only seven NMR peaks and cannot find any other peaks. This is strong evidence for the periodic sequence and high sequential purity of the copolymer **7**.

Poly(ethylene-*per*-ethylene-*per*-MMA) 7 is a soft and extendable material and is soluble in benzene, chloroform, and tetrahydrofuran. It is partially crystalline as determined by differential scanning calorimetry (DSC) and X-ray diffraction experiments, and shows its glass transition temperature ( $T_g$ ) and polymer melt temperature ( $T_m$ ) at 45 and 90°C, respectively as determined by DSC. Crystallization control of 7 will be described later in Section 3.4.

# 2.3. Synthesis of other periodic ethylene–ethylene–acrylic copolymers

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The MMA monomer in the above synthesis could be substituted for other acrylic monomers. The acrylic monomers studied were methyl acrylate [19], methyl  $\alpha$ -chloroacrylate [19], acrylonitrile [19], methacrylonitrile [20], methacrylamide [21], *N*-methylmethacrylamide [21], and *N*,*N*-dimethylacrylamide [21]. Ethyl, isopropyl, benzyl, and phenyl methacrylate monomers were also copolymerized [19]. Alternating copolymerization of these acrylic monomers with butadiene in the presence of EASC and the hydrogenation of the unsaturated alternating copolymers according to Eq. (3) proceeded smoothly to give the following periodic ethylene–ethylene–acrylic copolymers, **8**–15.



R= C2H5, CH(CH3)2, C6H5, or CH2C6H5

However, the hydrogenated product **10** of the alternating butadiene–acrylonitrile copolymer could not be isolated as a soluble material. It was identified by <sup>1</sup>H NMR only as a poorly dissolved product in  $d_{6}$ -dimethylsulfoxide. Poly[ethylene-*per*-ethylene-*per*-(methyl acrylate)] **8** contained a few per cent of methyl acrylate homosequence which was difficult to control. The copolymerization of acrylic amide derivatives having reactive NH moieties had to be conducted at lower temperatures because of reactions with the ethylaluminum compounds.

In addition, poly[ethylene-*per*-ethylene-*per*-(acrylic acid)] **19**, poly[ethylene-*per*-ethylene-*per*-(methacrylic acid)] **20**, and poly[ethylene-*alt*-(methacrylic acid)] **21** were synthesized by hydrolyzing their methyl ester copolymers **8**, **7**, and **22** with potassium hydroxide in a dioxane-methanol-water solution [22,23].



When converting an ester copolymer to an acid copolymer, it was essential for complete hydrolysis to change the solvent composition according to the extent of reaction to keep the reaction mixture as homogeneous as possible.

The properties of periodic copolymers synthesized in this section will be discussed in Section 3.1.

#### 2.4. Synthesis of an alternating ethylene–(Methyl methacrylate) copolymer

The synthesis of a periodic copolymer having two ethylene units and one MMA unit, 7, has been described in Section 2.2. The synthesis of an alternating copolymer with one ethylene unit and one MMA unit copolymer, namely poly(ethylene-*alt*-MMA) **22**, will be described in this section.

This alternating copolymer was first synthesized [24] by reducing an alternating (vinyl bromide)-MMA copolymer with tri-*n*-butyltin hydride but the resulting copolymer contained a small amounts of lactone structure and irregular sequences.

A much better synthesis [25,26] is the following process via a precursor polymer, poly(methyl 2-methyl-2,4-pentadienoate) **23**. In Eq. (5), the monomeric methyl 2-methyl-2,4-pentadienoate **24** should

be polymerized exclusively in 2,5-fashion.



The 2,5-polymerization of **24** and ethyl 2-methyl-2,4-pentadienoate by a group transfer initiator (a combination of methyl trimethylsilyl dimethylketene acetal and tetra-*n*-butylammonium *m*-chlorobenzoate) was previously reported by Hertler and coworkers [27]. The author and Hirabayashi [25,26] studied the polymerization of **24** by using radical, Ziegler–Natta type, and anionic initiators as well as group transfer initiators. Table 1 shows that *n*-butyl lithium and *tert*-butyl lithium-triisobutyl aluminum initiators as well as the group transfer initiator gave exclusively *trans*-2,5-polymerized **23** having very high molecular

(5)

Table 1Polymerization of methyl 2-methyl-2,4-pentadienoate 24

Polymerization <sup>a</sup>	Polymer							
Initiator <sup>b</sup>	Temperature (°C)	[M]/[I]	Yield (%)	$M_{\rm n} \times 10^{6\rm c}$	$M_{\rm w}/M_{\rm n}^{\rm c}$	Microstructure <sup>d</sup>		
						2,5-	2,3-	4,5-
AIBN	60	100	21	2.3	1.36	77	9	14
BPO-Et <sub>3</sub> Al	0	67	2	3.3	1.43	74	11	15
VOCl <sub>3</sub> -Et <sub>3</sub> Al	0	30	5	7.8	1.44	93	3	4
PhMgBr	0	30	66	3.3	2.24	96	2	2
n-BuLi	- 78	30	89	22.0	2.09	100	0	0
<i>n</i> -BuLi <sup>e</sup>	- 78	6.6	84	16.2	2.55	100	0	0
<i>n</i> -BuLi <sup>f</sup>	- 78	6.6	86	9.3	2.05	100	0	0
Tert-BuLi-isoBu3Al <sup>g</sup>	- 78	102	94	10.6	1.10	100	0	0
SKA-Bu <sub>4</sub> NCB	25	46	72	12.7	1.72	100	0	0

<sup>a</sup> Polymerization experiments were carried out for 3-278 h at  $[M] = 1-6 \text{ mol } l^{-1}$  in toluene or other hydrocarbon solvents in sealed tubes unless otherwise noted.

<sup>b</sup> Initiators are abbreviated as: AIBN,  $\alpha$ ,  $\alpha'$ -azobisisobutyronitrile; BPO, benzoyl peroxide; Et<sub>3</sub>Al, triethylaluminum; PhMgBr, phenylmagnesium bromide; *n*-BuLi, *n*-butyl lithium; *tert*-BuLi, *tert*-butyllithium; isoBu<sub>3</sub>Al, triisobutylaluminum; SKA, methy trimethylsilyl dimethylketene acetal; Bu<sub>4</sub>NCB, tetra-*n*-butylammonium *m*-chlorobenzoate.

<sup>c</sup> Determined by GPC with reference to polystyrene standards. A 100 m would give  $M_{\rm nl} = 1.26 \times 10^4$ .

<sup>d</sup> Determined by <sup>1</sup>H NMR. 2,5-Constitutional repeating units were exclusively *trans*-configuration.

<sup>e</sup> In tetrahydrofuran.

<sup>f</sup> In diethoxyethane.

<sup>g</sup> This polymerization experiment was performed under a high vacuum apparatus.

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weights. It should be emphasized that the *tert*-butyl lithium-triisobutyl aluminum initiator gives a polymer of uniform molecular weight. Thus, after its hydrogenation, the synthesis of a copolymer uniform both in sequence and in molecular weight was successfully accomplished.

Hydrogenation of 23 to 22 could be easily conducted by the same method as in the synthesis of 7 from 6. The very high sequential purity was proved again by the  $^{13}$ C NMR spectrum shown in Fig. 2. The spectrum shows only six NMR peaks and does not show any other additional peaks which would have been attributed to irregular sequences if present.

Poly(ethylene-*alt*-MMA) **22** is amorphous when precipitated and freeze-dried. However when a film is allowed to stand for a long time at room temperature, it gradually crystallizes to some degree as will be described in Section 3.4. It is a soluble, soft and elastomeric material.



Fig. 2. Identification of alternating structure of poly[ethylene-alt-(methyl methacrylate)] 22 by proton decoupled <sup>13</sup>C NMR.

# 2.5. Synthesis of alternating ethylene-(methyl acrylate) copolymer and related olefin copolymers

The alternating copolymerization of styrene and methyl acrylate easily occurs in the presence of a Lewis acid. Various Lewis acids which bring about the alternating copolymerization have been used. Among them, alkylaluminum halides, especially EASC, may be most widely used in view of their spontaneous initiation at room temperature, easy work-up after copolymerization, high yield and high sequential purity of the product copolymer [28]. The alternating copolymerization occurs for a wide range of molar ratios of styrene and methyl acrylate in the feed. If the monomer feed ratio of styrene-to-(methyl acrylate) is not unity, the copolymerization virtually stops when an alternating 1:1 styrene– (methyl acrylate) copolymer is quantitatively formed.

The copolymerization of ethylene with methyl acrylate, however, in the presence of boron trifluoride gave alternating copolymer **25** only under the extreme conditions where a large excess of ethylene monomer (13-fold of methyl acrylate) was employed [29].

Even under such a condition, the alternating sequence of **25** seems imperfect. In the literature [29], the fact that the methyl acrylate content in the product copolymer converged to 50% when the feed ratio of ethylene-to-(methyl acrylate) became large was taken as evidence for an alternating structure.

Fujiwara and this author [30] also carried out this copolymerization by using EASC under high pressure ethylene in an autoclave in a toluene solution at  $-78^{\circ}$ C and obtained a 1:1 copolymer. The <sup>13</sup>C NMR spectrum of this product copolymer showed, besides the five necessary peaks, additional weak peaks which could be ascribed to irregular sequences. Such inferior alternating copolymerization of ethylene and methyl acrylate in comparison to that of styrene and methyl acrylate is apparently due to the poor donating character of the ethylene monomer. The alternating 1:1 copolymer **25** was best obtained at low yields with a feed of > 98% ethylene in the presence of EASC.

The 1:1 propylene– (methyl acrylate) copolymer **26** was obtained in medium yields at a feed of 94% propylene and 6% methyl acrylate [31]. Excess propylene monomer was again needed in this copolymerization but not as large an excess as in ethylene copolymerizations. Irregular sequences were still found for this propylene copolymer but less than for the ethylene copolymers.

In the presence of boron trifluoride as the complexing reagent, Logothetis [29] obtained a 1:1 ethylene-methyl acrylate copolymer using a high ethylene monomer feed ratio. He also obtained a 1:1 propylene-methyl acrylate copolymer at a feed of equimolar amounts of propylene and methyl acrylate. Both our results and Logothesis results show that the electron-donating capability of the methyl substituent in the propylene monomer seems to improve the alternating copolymerizability of the olefin monomer.

Propylene also gave an alternating copolymer 27 with methyl  $\alpha$ -chloroacrylate in the presence of EASC, but the addition of vanadyl chloride to the copolymerization mixture and the removal of tetrahydrofuran-insoluble poly(methyl  $\alpha$ -chloroacrylate) from the crude product were both necessary [31].

Attempted alternating copolymerizations of ethylene and MMA under various conditions, however, were unsuccessful even with a very large excesses of ethylene in the feed [30]. The MMA contents in the product copolymers were always greater than 50%. Methyl substitution at the  $\alpha$ -position of the acrylate monomer apparently hindered its copolymerization. When we [24] replaced ethylene with vinyl bromide, we obtained a 1:1 vinyl bromide-MMA copolymer by the copolymerization of 95% vinyl bromide and 5% MMA in the presence of EASC and benzoyl peroxide between -20 and 0°C. The introduction of the electron-donating bromine substituent onto the ethylene monomer improved the alternating copolymerizability as expected. Reduction of this 1:1 (vinyl bromide)– MMA copolymer. Irradiation with a tungsten lamp and the addition of a radical initiator were utilized for the low temperature reduction. This copolymer was essentially an alternating ethylene–MMA copolymer **22** but contained 2% of a lactone unit which was formed by an intramolecular substitution reaction between the vinyl bromide unit and the MMA unit in the copolymer chain. An improved synthesis of **22** via poly(methyl 2-methyl-2,4-pentadienoate) **23** has already been described in Section 2.4.

By the polymer reaction via vinyl bromide copolymers, poly(ethylene-*alt*-acrylonitirile) **28** and poly(ethylene-*alt*-methacrylonitrile) **29** were also synthesized [20]. When reducing the bromide copolymers, unexpected structures did not form in the copolymers.



The above examples show, in spite of many successful alternating copolymerizations of conjugated olefins like styrenes and dienes with acrylic monomers in the presence of Lewis acids, the copolymerizations of unconjugated olefins do not always occur smoothly and usually require a large excess of olefins to obtain 1:1 copolymers. The 1:1 copolymers have essentially alternating sequences, yet they do contain some irregular sequences. The copolymerization of unconjugated olefins has another shortcoming in that it often does not give high molecular weight copolymers (usually under  $10^4$ ).

Other unconjugated monomers that have been studied include allyl chloride and allyl trimethylsilyl ether. By appropriate polymer reactions of their alternating copolymers, copolymers 30-35 were synthesized [32].

-[-CH2CH-CH	H2CH-]n- →	-[-CH2CH-CH	[2CH-]n[-C	H2CH-CH	[2CH-]n	-
CH2	COOC <sub>2H5</sub>	CH2	COOC <sub>2H5</sub>	CH2	CN	
I						
<b>C</b> 1		ococ	НЗ	Cl		
30		31		32		
<u></u>		<u>01</u>				

-[-CH2CH-CH2CH-]n- →	· -[-CH2CH-CH2CH-]n- $\rightarrow$	-[-CH2CH-CH2CH-]n
СН2 СN   ОSi(СН3)3	CH2 CN   OH	CH2 CN   OCOCH3
<u>33</u>	<u>34</u>	35

The alternating styrene– (methyl acrylate) copolymer **36** was transformed into an alternating styrene– (allyl alcohol) copolymer **37** by reduction with lithium aluminum hydride. The copolymer **37** was further reacted with acetic anhydride to give alternating styrene– (allyl acetate) copolymer **38**.



The allyl alcohol copolymer **37** was also transformed into poly(styrene-*alt*-propylene) **40** via an allyl iodide copolymer **39**. This is a donor–donor type alternating copolymer [33].

<u>37</u>	→	-[-CH2CH-CH   C6H5	[2CH-]n-   CH2   I	→	-[-CH2CH-CH   C6H5	2CH-]n-   CH3
		<u>39</u>			<u>40</u>	

In this section, the syntheses of alternating copolymers of various unconjugated olefins were described. The  $T_{gs}$  of these alternating copolymers will be discussed in Section 3.3.

2.6. Synthesis of alternating ethylene-(vinyl alcohol) and ethylene-(vinyl acetate) copolymers

Alternating ethylene– (vinyl alcohol) and ethylene– (vinyl acetate) copolymers, 43 and 44, were synthesized by the author and his coworkers [34] according to Eq. (7), where the diene monomer 41

polymerizes in a 1,4-fashion.



The starting material was 1-trimethylsilyloxy-1,3-butadiene 41. This monomer of trans-configuration,



could be easily prepared from crotonaldehyde, trimethylsilyl chloride, and triethylamine [35]. Polymerization of **41** was conducted by using an aldol-type group transfer polymerization initiator. In most experiments, *p*-anisaldehyde was the initiator and zinc bromide was the catalyst [36,37]. Sublimated anhydrous zinc bromide was used as a solid or as a solution in diethyl ether. When the solid zinc bromide was used, a heterogeneous polymerization occurred on the catalyst surface near room temperature. When the zinc bromide solution was used as the catalyst, the polymerization occurred homogeneously at temperatures between 0 and  $-78^{\circ}$ C. The polymerization of **41** at lower temperatures gave rise to higher molecular weight polymers. Typical results are shown in Table 2. A polymer **42** of the highest molecular weight of  $4.5 \times 10^4$  was obtained under homogeneous conditions. In accordance with the aldol type group transfer mechanism, one terminal group of **42** was a *p*-anisyl group and the other was a formyl group. Because group transfer polymerization has a living nature, the resulting polymer molecular weight distribution was indicated by its lowest  $M_w/M_n$ , 1.24.

Hydrogenation, methanolysis, and acetylation of 42 easily gave 44 and 45. The following sequence of reactions, namely methanolysis-hydrogenation-acetylation or methanolysis-acetylation-hydrogenation also gave the identical product 45, but the first mentioned sequence seemed most advantageous in view of the solubilities of the polymer intermediates. Hydrogenation of 42 to 43 in chloroform solution was successful by medium-pressure hydrogen in the presence of a soluble catalyst, chlorotris(triphe-nylphosphine)rhodium. Insoluble platinum and palladium catalysts were inactive for 42 but active for its desilylated or acetylated polymer. Methanolysis of 42 or 43 was best accomplished when their solutions

Table 2

Polymerization of 1-trimethylsilyloxy-1,3-butadiene 41 (initiator, *p*-anisaldehyde; catalyst, zinc bromide; solvent, toluene; polymerization time, 5–96 h; conversion, 88–95%)

Run <sup>a</sup>	Polymerization			Polymer				
	$[M] \pmod{l^{-1}}$	[M]/[I]	Temperature (°C)	$M_{\rm n} \times 10^{-4}  ({\rm calcd})^{\rm b}$	$M_{\rm n} \times 10^{-4}  ({\rm found})^{\rm c}$	$M_{\rm w}/M_{\rm n}^{\rm c}$		
1	1.60	30	30	0.43	0.44	1.53		
2	2.64	100	30	1.42	0.98	2.29		
3	5.80	500	30	7.10	1.84	2.89		
4	5.80	1000	30	14.2	1.18	3.24		
5	4.92	1000	0	14.2	0.98	2.90		
6	5.80	1000	- 20	14.2	d	d		
7	2.60	300	30	4.26	0.57	1.76		
8	2.60	1000	0	14.2	2.01	1.71		
9	5.80	300	0	4.26	1.08	1.83		
10	2.60	300	- 20	4.26	1.66	1.76		
11	3.70	300	-78	4.26	3.18	2.36		
12	1.08	300	- 78	4.26	4.55	1.24		

<sup>a</sup> Run 1–6 were heterogeneous polymerization by using solid zinc bromide catalyst, and Runs 7–12 were homogeneous polymerization by using zinc bromide catalyst as a solution in diethyl ether.

<sup>b</sup> Calculated from [M]/[I] in feed.

<sup>c</sup> Determined by GPC with reference to standard polystyrenes.

<sup>d</sup> No polymer was obtained after 24 h.

in methanol were first refluxed for 40 h and then had 10 mol% tetra-*n*-butylammonium fluoride added to them. The solution was stirred for more than 12 h at room temperature for complete methanolysis. Without the fluoride, a small percent of trimethylsilyloxy groups remained unreacted. Acetylation of **44** to **45** was successful by keeping the solution at room temperature with an excess of acetic anhydride in pyridine. The completion of each of the polymer reactions was confirmed by various spectroscopic methods.

The group transfer polymerization of **41** essentially occurred in a *trans*-1,4-fashion. However when the polymer structure **42** was studied in detail by IR and NMR spectroscopy and chemical reactions, it was determined that the polymer contained about 14% of the 3,4-polymerized structure [38].



This structure gave additional formyl groups on methanolysis of **42**. Polymerization at lower temperatures decreased the content of 3,4-polymerized structure only by a small extent.

Poly[ethylene-*alt*-(vinyl alcohol)] **44** is a partially crystalline, tough material. A reprecipitated and dried sample showed in an X-ray diffraction experiment crystalline peaks corresponding to 42% of crystallinity. It was soluble in dimethylsulfoxide, tetrahydrofuran, hot methanol, and insoluble in diethyl ether. Its  $T_g$  and  $T_m$  were measured as 52 and 173°C, respectively. Poly[ethylene-*alt*-(vinyl acetate)] **45** is a pale yellow rubbery material and is soluble in chloroform, benzene, tetrahydrofuran and insoluble in

methanol. It is amorphous and shows a  $T_g$  at  $-40^{\circ}$ C. The  $T_g$  and  $T_m$  of 44 and 45 are discussed in Section 3.2 in comparison to those for statistical copolymers.

The same alternating copolymer 44 was synthesized by Chung [39] and Ramakrishnan [40] through the ring-opening polymerization of (5-cyclooctenyl)diethylborane, followed by hydroboration and oxidation. Their copolymers contained many irregular sequences because of the two possible orientations for the addition reaction during the hydroboration. They reported a much higher decomposition temperature (400°C) than for poly(vinyl alcohol) (253°C). They also reported a  $T_g$  and  $T_m$  for their copolymers as 49 and 114°C, respectively.

#### 2.7. Stereochemistry of periodic copolymers

This author has studied [41] the stereochemistry of alternating copolymers of styrenes and acrylic monomers by using <sup>1</sup>H NMR. The stereochemistry of this type of copolymer is conveniently expressed in terms of coisotacticity which is the probability that the phenyl-substituted carbon in a styrene unit and the ester-or nitrile-substituted carbon in the succeeding (or preceding) acrylic unit take the same configuration. Table 3 compares the coisotacticities of alternating copolymers with those for various copolymers. Table 3 shows that the coisotacticity of an alternating copolymer has a rough tendency to approach 0.5 (i.e. atactic propagation) even when the coisotacticity of a free-radical initiated statistical copolymer appreciably deviates from 0.5. The statistical copolymerization of styrene and methyl  $\alpha$ -chloroacrylate gave a coisotacticity of 0.69. The coisotacticity for the statistical copolymerization of styrene and methyl acrylate was 0.80 but for the alternating copolymerization it was 0.53. The statistical and alternating copolymerization of styrene and MMA both gave coisotacticities of about 0.5.

Alternating copolymerization according to Eq. (3) in Sections 2.2 and 2.3 gave alternating butadiene– acrylic copolymers. All the carbon–carbon double bonds of the butadiene units in these copolymers were of a *trans*-configuration as confirmed by their <sup>1</sup>H NMR and IR spectra [14–17,19]. As to the configuration of acrylic units in these copolymers, however, no information has been obtained from various spectroscopic data. The alternating butadiene–MMA copolymer **6** and its hydrogenated,

Copolymer<sup>a</sup> Co-isotacticity Alternating copolymer Statistical copolymer St-MMA 0.56 0.44 St-MA 0.80 0.53 St-MCA 0.69 ca. 1 St-MAN 0.19 St-MAAm 0.16 \_ 0.21 MSt-MMA 0.21 MSt-MA 0.53 0.45

Coisotacticities of various alternating styrene-acrylic copolymers

Table 3

<sup>a</sup> Copolymer abbreviations are: St–MMA, styrene– (methyl methacrylate); St–MA, styrene– (methyl acrylate); St–MCA, styrene– (methyl  $\alpha$ -chloroacrylate); St–MAN, styrene–methacrylonitrile; St–MAAm, styrene–methacrylamide; MSt–MMA,  $\alpha$ -methylstyrene– (methyl methacrylate); MSt–MA,  $\alpha$ -methylstyrene– (methyl acrylate).



Fig. 3. Finely split <sup>13</sup>C NMR absorptions due to tacticity of poly[ethylene-*alt*-(methyl methacrylate)] **22** at 100 MHz (chemical shift from HMDS).

periodic ethylene–ethylene–MMA copolymer 7 were not characterized regarding the configuration of their MMA units [14,15].

The alternating ethylene–MMA copolymer 22 is amorphous when prepared according to Eq. (4) as described in Section 2.4. The configuration of MMA units in this alternating copolymer could be studied by its <sup>13</sup>C NMR spectrum [25]. Thus the <sup>13</sup>C NMR spectrum showed very small amounts of fine splittings for the <sup>d</sup>C and <sup>e</sup>C absorptions of the MMA unit as shown in Fig. 3.



Table 4 shows the <sup>13</sup>C chemical shift differences between the highest and lowest split  $\alpha$ -CH<sub>3</sub> (<sup>d</sup>CH<sub>3</sub>) absorption peaks for **22**, **7**, as well as polyMMA. As already reported by many investigators, the  $\alpha$ -CH<sub>3</sub> absorption of polyMMA is clearly split and shows a difference of 4.423 ppm. It has been considered that this splitting is due to the diamagnetic shielding effect of the two neighboring ester–carbonyl groups. The  $\alpha$ -CH<sub>3</sub> absorption of **22**, however, shows a very small difference. It is only 0.136 ppm. The neighboring ester–carbonyl groups in **22** are separated from the  $\alpha$ -CH<sub>3</sub> group by two more carbon

Table 4 <sup>13</sup>C NMR chemical shifts of  $\alpha$ -CH<sub>3</sub> groups in methyl methacrylate (co)polymers

<sup>13</sup> C NMR chemical shifts of $\alpha$ -CH <sub>3</sub> absorption (ppm from TMS)	Poly(methyl methacrylate)	Poly[ethylene- <i>alt</i> - (methyl methacrylate)] ( <b>22</b> )	Poly[ethylene- <i>per</i> - ethylene- <i>per</i> -(methyl methacrylate)] ( <b>7</b> )
rr	16.899	20.967	No split was observed
mr	19.025	21.020	No split was observed
mm	21.322	21.103	No split was observed
Difference, mm - rr	4.423	0.136	No split was observed

(Co)polymer <sup>a</sup>	Tensile strength at	Elongation at break (%)	Tensile modulus $(10^6 \text{ N m}^{-2})$	
	$(10^6 \text{ N m}^{-2})$		(10 10 11 2)	
PolyMMA	48-75	2-10	26-31	
PolySt	48-56	2-3.5	31-33	
Poly(St-stat-MMA)	13.4	5.4	2.5	
Poly(St-alt-MMA)	11.3	3.4	3.3	

14010 0											
Mechanical	properties	for some	alternating	and	statistical a	styrene-	(methy	l methacry	(late)	copolyn	ners

<sup>a</sup> (Co)polymer abbreviations are: poly(MMA), poly(methyl methacrylate); polySt, polystyrene; poly(St-*stat*-MMA), statistical styrene– (methyl methacrylate) copolymer; poly(St-*alt*-MMA), alternating styrene– (methyl methacrylate) copolymer.

atoms than in polyMMA and thus their shielding effect on the  $\alpha$ -CH<sub>3</sub> resonance in question is weakened. The  $\alpha$ -CH<sub>3</sub> group in **7** is still more separated from ester–carbonyls and does not show any indication of splitting in various attempted <sup>13</sup>C NMR experiments. All absorptions are sharp and non-split singlets as shown in Fig. 1. However, the author considers it is very improbable that this copolymer **7** is stereo-regular with respect to its MMA unit configuration. It is interesting to recall that this periodic copolymer **7** is crystalline as pointed out in Section 2.2.

Intensity determination of the fine split  $\alpha$ -CH<sub>3</sub> absorption peaks for 22 showed this copolymer is atactic.

# 3. Properties of periodic copolymers

Table 5

Table 6

This section describes various materials properties of periodic copolymers, especially in relation to their ordered sequences. Several investigators have studied the differences between alternating and statistical copolymers with respect to various properties. Battaille and Granger [42] carried out tensile tests for alternating and statistical 1:1 styrene–MMA copolymers (Table 5). Both copolymers were soft and extendable as compared to the hard and brittle homopolymers but showed only small differences with each other. The thermal decomposition traces determined by Hurdac [43] for these copolymers seemed not to show any differences. Solution properties of statistical and alternating styrene– (benzyl methacrylate) copolymers in toluene were studied by Braun [44]. The molecular dimensions of both copolymers as expressed by the Mark–Houwink–Sakurada parameters did not show any significant differences (Table 6). Thus we often hardly find any differences between statistical and alternating

	1	5	5 / 1 5		
	Copolymer		Polystyrene	Poly(benzyl methacrylate)	
	1:1 Statistical	Alternating			
$(r^2)^{1/2}/M^{1/2}$	$6.46 \times 10^{-2}$	$6.67 \times 10^{-2}$	$7.12 \times 10^{-2}$	$5.44 \times 10^{-2}$	
$K (cm^3 g^{-1})$	$8.57 \times 10^{-3}$	$8.88 \times 10^{-3}$	$1.47 \times 10^{-3}$	$5.16 \times 10^{-3}$	
α	0.72	0.71	0.70	0.71	

Mark-Houwink-Sakurada parameters for styrene- (methyl methacrylate) copolymers in toluene at 25°C



Fig. 4. Fluorescence spectra of 2-vinylnaphthalene-(methyl methacrylate) copolymers by Webber. (a) alternating copolymer; (b) statistical copolymer.

styrene– (methacrylic ester) copolymers. The reason for this may, at least partly, come from the fact that the statistical styrene– (methacrylic ester) copolymers originally have an alternating tendency as suggested by the small product of their monomer reactivity ratios. Sequential effects on the  $T_g$  of copolymer materials will be discussed in Section 3.2.

One of a few distinct differences found between alternating and statistical copolymers concerns the fluorescence spectra of 2-vinylnaphthalene–MMA copolymers shown in Fig. 4 [45]. The alternating copolymers have essentially no excimer fluorescence unlike the random copolymers. This spectral difference is probably due to the fact that, in the alternating copolymer, all of the 2vinylnaphthalene monomer units are separated each other, whereas in the random copolymer some units are arranged as next neighbors. The MMA monomer units in the alternating copolymer separate the naphthalene chromophores and simultaneously suppress excimer formation and energy transfer processes.

#### 3.1. Materials properties of periodic copolymers

Poly(ethylene-*per*-ethylene-*per*-MMA) **7** may be considered as a hybrid of polyethylene and poly-MMA. It shows both the properties of polyethylene and polyMMA. It is soluble in benzene, chloroform, and tetrahydrofuran as polyMMA and can form films when cast from solution. These films are transparent, soft, and extendable materials just like a low-density polyethylene, which is not soluble in the above solvents. The thermal decomposition curve for **7** in Fig. 5, determined by thermogravimetry, is a polyethylene-type and not a polyMMA-type [15]. PolyMMA decomposes rapidly above 300°C to regenerate the monomer and shows a steep weight loss, but **7** as well as polyethylene gradually decomposes around this temperature.

Poly[ethylene-*per*-ethylene-*per*-(methyl ( $\alpha$ -chloroacrylate)] **9** has  $T_g$  and  $T_m$  values at 76°C and 120°C, respectively, as indicated in Table 7 [19]. These  $T_g$  and  $T_m$  values are about 30°C higher than those for poly(ethylene-*per*-ethylene-*per*-MMA) **7**. The polar chlorine substituent in **9** instead of the non-polar methyl substituent in **7** gives stronger intermolecular forces to the copolymer **9** and makes this



Fig. 5. Thermal decomposition of: (a) poly[ethylene-*per*-ethylene-*per*-(methyl methacrylate)] **7**; (b) polyethylene; and (c) poly(methyl methacrylate).

material a little harder and more brittle than 7. The hydrogen-substituted homologue, i.e. poly[ethyleneper-ethylene-per-(methyl acrylate)] 8 shows lower  $T_g$  and  $T_m$  values at -30 and 40°C, respectively, and is softer and more extendable than 7. Crystallization is most pronounced for 7 among these three copolymers as indicated by their DSC peak shapes.

The properties for various other poly[ethylene-*per*-ethylene-*per*-(methacrylic ester)]s are also given in Table 7 [19]. The benzyl methacrylate copolymer **18** is crystalline whereas ethyl, isopropyl, and phenyl methacrylate copolymers **15–17** are amorphous. Mechanical properties seem to parallel their  $T_{gs}$ and  $T_{ms}$ . The isopropyl ester copolymer **16** is the most extendable material, of which a 10-fold stretched sample shrinks back to its original size very slowly.

In Table 7, poly[ethylene-*per*-ethylene-*per*-(methyl ( $\alpha$ -chloroacrylate)] **9** is compared to a sequencedisordered, random 2:1 ethylene-(methyl  $\alpha$ -chloroacrylate) copolymer. The "random 2:1 copolymer" was prepared by copolymerizing the calculated feed of butadiene and methyl  $\alpha$ -chloroacrylate monomers under low conversions with a radical initiator and hydrogenating the resulting 1:1 copolymer. This "random 2:1 copolymer" does not show a  $T_m$  peak in the DSC and shows a  $T_g$  at 37°C, i.e. 40°C lower than **9**. Also by its X-ray diffraction pattern in Fig. 6, while **9** shows diffraction peaks, the random 2:1 copolymer was characterized as amorphous. It is softer and more extendable than the periodic copolymer **9**.

# 3.2. Glass transition temperatures for periodic copolymers and statistical copolymers

The materials properties of a copolymer are fundamentally determined by sequence as well as by chemical structure and composition. They are primarily understood by studying the copolymer's  $T_g$  and  $T_m$  which can be conveniently determined by DSC for small samples. Hirooka and Kato [46] studied the  $T_g$ s of various alternating and statistical copolymers and found how the  $T_g$ s for alternating copolymers differed from those for statistical copolymers. When the  $T_g$ -composition relationship for a given statistical copolymer is linear as is in the case of styrene– (methyl acrylate) copolymer, the alternating and the 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 and higher  $T_g$ s than the statistical 1:1

Acylic unit in the copolymer, and its polymer number <sup>a</sup>	$d^{20}$ (g cm <sup>-3</sup> )	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	Young's modulus (kg cm <sup>-2</sup> )	Stress at yield (kg cm <sup>-2</sup> )	Stress at break (kg cm <sup>-2</sup> )	Elongation at break (%)
MMA, <b>7</b>	1.052		90	$1 \times 10^{3}$	$3 \times 10^{2}$	$3 \times 10^{2}$	300
MA, <b>8</b>	1.057	45	40	$1 \times 10^2$	$1 \times 10^{2}$	$1 \times 10^{2}$	600
MCA, <b>9</b>	1.214	30	120	$3 \times 10^{3}$	$2 \times 10^{2}$	$2 \times 10^{2}$	100
MCA, random	1.194	70	_	$3 \times 10^{2}$	$5 \times 10^{1}$	$2 \times 10x$	400
Ethyl MA, 15	1.005	-	_	$1 \times 10^{2}$	$3.5 \times 10^{0}$	$2 \times 10^{0}$	500
Isopropyl MA, 16	0.982	32	_	$1 \times 10^1$	$3.5 \times 10^{0}$	3 × 10	1100
Phenyl MA, 17	1.105	26 14	_	$1.5 \times 10^{1}$	$5 \times 10^{0}$	$5 \times 10^{1}$	600
Benzyl MA, 18	1.099	?	47	$2.5 \times 10^{2}$	$3 \times 10^{1}$	$1.5 \times 10^{2}$	500

Table 7 Thermal and mechanical properties for periodic ethylene-ethylene-acrylic copolymers

<sup>a</sup> Abbreviations of the acrylic units in the periodic ethylene–ethylene–acrylic copolymers are: MMA, methyl methacrylate; MA, methyl acrylate; MCA, methyl  $\alpha$ -chloroacrylate; Ethyl MA, ethyl methacrylate; Isopropyl MA, isopropyl methacrylate; Phenyl MA, phenyl methacrylate; Benzyl MA, benzyl methacrylate. As to the polymer numbers, see the text.



Fig. 6. X-ray diffraction pattern of (a) poly[ethylene-*per*-ethylene-*per*-(methyl  $\alpha$ -chloroacrylate)] **9** and (b) "random" 2:1 copolymer.

copolymer, respectively. Styrene–MMA and styrene–acrylonitrile copolymers are examples for each of these cases.

The periodic 1:1 and 2:1 ethylene–acrylic copolymers were studied with respect to their  $T_{gs}$  in comparison to statistical copolymers. Since the acrylic units were methyl acrylate, MMA, and methacrylonitrile, the following six alternating and periodic copolymers were evaluated. Poly[ethylene-*alt*-MMA] **22** here is the hydrogenated poly(methyl 2-methyl-2,4-pentadienoate) [25].



The corresponding statistical copolymers to be compared containing various mole fractions of ethylene and acrylic monomer units were prepared according to the following Eq. (8).

 $CH2=CCl2 + CH2=CXY \rightarrow -[-CH2CCl2-]_p-[-CH2CXY-]_q-$ 

(C4H9)3SnH

-[-CH2CH2-]p-[-CH2CXY-]q-

X=H or CH3, Y=COOCH3 or CN

(8)

The radical copolymerization of vinylidene chloride with each of the acrylic monomers was carried out by warming the monomer mixtures of various feed compositions with  $\alpha, \alpha'$ -azobisisobutyronitrile initiator. Small volumes of appropriate solvent were added for the homogeneous copolymerizations. The resulting vinylidene chloride copolymers were reduced with tri-*n*-butyltin hydride and  $\alpha, \alpha'$ -azobisisobutyronitrile in tetrahydrofuran at 30°C to obtain statistical ethylene copolymers having a wide range of compositions. Copolymer molecular weights were about 10<sup>5</sup>. When reducing (vinylidene chloride)– MMA copolymers, it was essential to conduct the reaction between 0 and -20°C to prevent a marked decrease in the molecular weight for the product copolymers.

DSC experiments were carried out for these periodic and statistical copolymer samples in the temperature range from -50 to  $+100^{\circ}$ C. Reproducible and definite glass transition traces were observed when heating.  $T_{\rm g}$ s were taken as from the inflection points of the traces and averaged for three repeated experiments and are shown in Table 8. Most samples were amorphous and did not show melting peaks. For the partially crystalline copolymer 7 a quenching experiment was carried out to obtain an amorphous sample. The quenching experiment will be described in Section 3.4.

The  $T_{g}$ s of polyethylene and acrylic homopolymers were taken from a compilation in the Polymer Handbook [47]. For the  $T_{g}$  of polyethylene, many conflicting data have been given and these may be classified into three groups around -125, -80, and  $-40^{\circ}$ C. We used hereafter a  $T_{g}$  value of  $-81^{\circ}$ C according to Tobolsky [48] who estimated it by using the Fox equation [49] from the data for an amorphous polypropylene and an ethylene–propylene copolymer. Illers [50] also gave an approximate value of  $-77^{\circ}$ C through the data for ethylene copolymers with vinyl acetate, vinyl propionate, and propylene.

In Fig. 7(a)–(c), the  $T_{gs}$  of copolymers as well as homopolymers are plotted against copolymer

MMA, methyl methacrylate; MAN, methacrylonitrile)								
E–MA copolymer		E–MMA copolyme	r	E–MAN copolymer				
MA (mol%)	$T_{\rm g}$ (°C)	MMA (mol%)	$T_{\rm g}$ (°C)	MAN (mol%)	$T_{\rm g}$ (°C)			
Periodic copolym	ier							
50	- 22	50	5	50	60			
33.3	- 34	33.3	- 6	33.3	22			
Statistical copoly	mer							
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	- 10.1	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			

Glass transition temperatures of ethylene–acrylic copolymers (monomers are abbreviated as: E, ethylene; MA, methyl acrylate; MMA, methyl methacrylate; MAN, methacrylonitrile)

540

Table 8



Fig. 7.  $T_g$  vs copolymer composition for ethylene–acrylic copolymers. (a) ethylene– (methyl acrylate); (b) ethylene– (methyl methacrylate); and (c) ethylene–methacrylonitrile.  $\bigcirc$  statistical copolymers;  $\bullet$  periodic copolymers.

compositions for ethylene– (methyl acrylate), ethylene–MMA, and ethylene–methacrylonitrile pairs, respectively. Statistical copolymers and homopolymers are represented by open circles and the data for periodic copolymers are given by filled circles. Regression analysis on the data for the statistical copolymers together with the homopolymers was carried out to obtain the curves in the form of  $T_g = A + BY + CY^2$ , where Y denotes the mole percent of the acrylic units in the copolymer. The standard deviations in the regression analysis are given in Table 9 and the regression curves are drawn by solid lines in Fig. 7.

54	42

Table 9

a	• •				c	1				1			
Vtotictical	aomnomicon of	0000	tronoition	tomporofueog	+0**	altornating	ond	atotictical	oth	1000 00	1110	0000	TIMONO
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Statistical	companyon or	<b>E</b> IGDD	uanonon	comportation	101 1	anconnating	and	blaubuou	cui	, ione uo	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	20001	,
		~									~		_

	Copolymer <sup>a</sup>				
	E-MA	E-MMA	E-MAN		
Standard deviation in ordinate, °C	6.41	5.18	7.83		
Significant deviation at 95% confidence level, °C	> 12.57	> 10.15	> 15.35		
Significant deviation at 99% confidence level, °C	> 16.55	> 13.36	> 20.21		
$T_{g}$ (calcd), °C					
1:1 copolymer	- 18.8	20.5	43.7		
2:1 copolymer	- 33.3	- 11.3	7.4		
$T_{g}(\text{obsd}), \ ^{\circ}\text{C}$					
1:1 copolymer	- 22	5	60		
2:1 copolymer	- 34	6	22		
$T_{\rm g}({\rm obsd}) - T_{\rm g}({\rm calcd}), ^{\circ}{\rm C}$					
1:1 copolymer	- 3.2	- 15.5	16.3		
2:1 copolymer	- 0.7	5.3	14.6		

<sup>a</sup> Monomers are abbreviated as: E, ethylene; MA, methyl acrylate; MMA, methyl methacrylate; MAN, methacrylonitrile.

Table 9 also gives  $T_g(\text{calcd})$ ,  $T_g(\text{obsd})$ , and  $T_g(\text{obsd}) - T_g(\text{calcd})$  values.  $T_g(\text{calcd})$  denotes the calculated  $T_g$  by using the above analysis (or read from the regression curves) for 1:1 (acrylic unit, 50 mol%) and 2:1 (33.3 mol%) statistical copolymers.  $T_g(\text{obsd})$  are experimentally determined values already given in Table 8 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.

For the case of ethylene– (methyl acrylate) copolymers in Fig. 7(a), both the periodic copolymers 25 and 8 show their  $T_{gs}$  on the regression curve for statistical copolymers. In other words, both of the periodic copolymers give in Table 9  $T_{g}$ (obsd) –  $T_{g}$ (calcd) which are insignificantly small in view of the standard deviation of the regression analysis and do not show an appreciable sequential effect. The same result can be found in Fig. 7(b) for the 2:1 periodic ethylene–MMA copolymer 7. The 1:1 copolymer 22, however, shows about a 15°C lower  $T_{g}$  than the statistical copolymer of identical composition. Statistically studying Table 9,  $T_{g}$ (obsd) –  $T_{g}$ (calcd) for 22 is larger than the experimental errors in view of the standard deviation of regression analysis at a confidence level of 95% (and even at 99%). For the case of the ethylene–methacrylonitrile copolymers in Fig. 7(c), both the periodic copolymers 29 and 11 also show 15°C higher  $T_{gs}$  than the statistical copolymers. However these deviations are not that large. Statistically  $T_{g}$ (obsd) –  $T_{g}$ (calcd) for 29 is significant, and for 11 it is hardly significant at a confidence level of 95%. Both are insignificant at a confidence level of 99%.

The regression curves in Fig. 7, which show  $T_g$ -composition relationships of the three statistical ethylene–acrylic copolymers, are all gently convex. According to Hirooka and Kato's findings as described above, the  $T_g$  of a periodic copolymer should deviate above the curve when it is convex. In the case of 1:1 and 2:1 ethylene– (methyl acrylate) and 2:1 ethylene–MMA copolymers, the  $T_g$ s of the periodic copolymers did not show deviations from the regression curve. In the case of ethylene–methacrylonitrile copolymers **29** and **11**,  $T_g$  deviations are observed but are not large. Only in the case of 1:1 ethylene–MMA copolymer **22**, was its  $T_g$  was markedly deviated, but below the regression curve. A clear explanation for such results is not available but it should be pointed out that the regression curves

have very small curvatures and virtually look like straight lines. According to the results of Hirooka and Kato [46], a linear  $T_g$ -composition relationship would give an identical  $T_g$  for periodic and statistical copolymers. Another possible explanation is based on the fact that in the present copolymers one monomer unit is ethylene. Any bulky and/or polar substituent of one type of monomer unit may have an effect on the  $T_g$  of its copolymer in cooperation with neighboring substituents of another type of monomer unit. The magnitude of such a substituent effect depends on the monomer combination and on the copolymer sequences by which the two-monomer units are arranged. A copolymer containing an ethylene monomer unit would hardly show such a sequential effect since ethylene bears no substituent.

A number of equations that predict the  $T_g$  values for statistical copolymers have been proposed. The Fox additive equation [49] is simple but often gives unsatisfactory results. The Gordon–Taylor equation [51] considers the specific volumes of relevant homopolymers and requires data on their thermal expansion coefficients. The Gibbs-DiMarzio theory [52] 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 in question. Subsequently, this assumption has come to the Johnston [53] and the Barton [54] equations, both of which predict the  $T_g$  in terms of the dyad sequences of monomer units in the copolymer. We use the Johnston equation below.

The Johnston equation is given by

$$1/T_{gP} = \{W_{A}P_{AA}/T_{g_{AA}}\} + \{(W_{A}P_{AB} + W_{B}P_{BA})/T_{g_{AB}}\} + \{W_{B}P_{BB}/T_{g_{BB}}\}$$

wherein  $T_{gP}$  denotes the  $T_g$  of a copolymer in question containing weight fraction  $W_A$  and  $W_B$  of two monomer units A and B.  $T_{g_{AA}}$ ,  $T_{g_{BB}}$ , and  $T_{g_{AB}}$  denote the  $T_g$  contribution of the AA, BB, and AB dyads 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  $P_{BA}$  refer to the probabilities of finding AA, BB, AB, and BA dyads in the copolymer chain, respectively, and can be calculated by using the monomer feed compositions and monomer reactivity ratios. The monomer reactivity ratios should naturally be of the copolymerization with vinylidene chloride when synthesizing statistical precursor vinylidene chloride–acrylic copolymers. The calculation of  $T_{gP}$ s according to the above Johnston equation gave brokenline curves which are found in good accordance with the experimentally found curves.

Poly[ethylene-*alt*-(vinyl alcohol)] **44** and polyethylene-*alt*-(vinyl acetate)] **45** were also compared to their corresponding statistical copolymers with respect to their  $T_{g}s$  and  $T_{m}s$  [34].

The statistical ethylene–(vinyl acetate) copolymers were prepared in an autoclave by copolymerizing high pressure ethylene with vinyl acetate in solution with  $\alpha$ ,  $\alpha'$ -azobisisobutyronitrile. One copolymer sample having a high ethylene content was a commercial product. These vinyl acetate copolymers were "methanolyzed" by sodium methoxide in methanol–benzene solutions to prepare statistical ethylene– (vinyl alcohol) copolymers. Thus the statistical ethylene–vinyl acetate and ethylene–(vinyl alcohol) copolymers of 18–85 mol% ethylene contents were obtained.

Fig. 8 shows DSC traces for alternating and statistical ethylene–(vinyl alcohol) copolymers. A trace for a poly(vinyl alcohol) sample is also shown. DSC experiments were performed for the precipitated samples. Melting endotherms are observed between 90 and 230°C and at a lower temperature with increasing ethylene content. Therefore the crystallization should predominantly be due to hydrogen bonding between copolymer molecules. Glass transition inflections are observed in these traces but hardly observed for the two copolymers having high ethylene content.

To discuss the structure- $T_g$  relationship for a copolymer independently of the crystalline region, amorphous samples were considered to be desirable. Therefore a quenching experiment in which melted



Fig. 8. DSC traces of ethylene- (vinyl alcohol) copolymers as precipitated. Numericals are referred to ethylene mole% in statistical copolymer.



Fig. 9. DSC traces of 1:1 ethylene- (vinyl alcohol) copolymers before and after quenching.

samples were thrown into liquid nitrogen was carried out. Fig. 9 shows the DSC traces before and after this quenching process for a 1:1 statistical copolymer and the alternating copolymer 44. The alternating copolymer shows a melting peak before quenching and an almost flat trace after quenching. Its  $T_g$  rises slightly from 46 to 52°C by quenching. However, the statistical copolymer shows melting traces both before and after the quenching step. Thus the effect of quenching seems most prominent on the crystallization 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), crystallizes easily.

The precipitated samples often showed melting peaks with a shoulder or two-peaks. When these samples were annealed at 30°C above their  $T_g$  for 30 min before DSC experiments, they turned out to show simple one-peak traces. Table 10 shows the  $T_g$ s after quenching and the  $T_m$ s after annealing for all of the samples. Table 10 shows that the  $T_m$ s for statistical copolymers become higher when their ethylene contents decrease (namely, the vinyl alcohol contents increase). The heat of melting per one vinyl alcohol unit calculated from the melting peak area and the vinyl alcohol unit contents suggested that the hydrogen bonding force between vinyl alcohol units is roughly the same for both alternating and statistical copolymers. In Fig. 10(a),  $T_m$ s are plotted against the copolymer composition in ethylene mol%. The plots for statistical copolymers give a rough correlation curve and the plot for the alternating copolymer **44** falls on this curve. In Fig. 10(b), the  $T_g$  for **44** also falls on the  $T_g$ -composition curve for statistical copolymers. Thus the sequence-ordering in ethylene–(vinyl alcohol) copolymer does not affect either  $T_m$  or  $T_g$  of the copolymer while it does affect the ease of crystallization.

The ethylene- (vinyl acetate) copolymers as precipitated were non-crystalline. They showed  $T_{\rm g}$ 

Run <sup>a</sup> Ethylene in copolymer (mol%)	Ethylene in	Ethylene- (vinyl alcohol) copolymer			Ethylene-vinyl acetate copolymer			
	$T_{\rm g} (^{\circ}{\rm C})^{\rm b}$	$T_{\rm m}$ (°C) <sup>c</sup>	$\Delta H_{\rm m}  ({\rm mJ}  {\rm mg}^{-1})^{\rm d}$	$T_{\rm g} (^{\circ}{\rm C})^{\rm e}$	$T_{\rm m}$ (°C) <sup>e</sup>	$\Delta H_{\rm m} ({\rm mJ} {\rm mg}^- 1)^{\rm f}$		
	100 <sup>g</sup>	- 81	113		- 81	113		
1	85.3	37	92	249	- 63	36	5	
2	61.1	39	124	180	- 24			
3	46.0	42	126	76	-4			
4	34.7	50	184	91	11			
5	26.3	55	185	104	13			
6	18.3	53	197	98	22			
	$0^{\rm h}$	59	227	98	32			
	$50^{i}$	42	140	80	- 40			

Table 10 DSC study of ethylene– (vinyl alcohol) and ethylene– (vinyl acetate) copolymers

<sup>a</sup> Runs 1–6 are statistical copolymers.

<sup>b</sup> After quenching.

° After annealing.

<sup>d</sup> Per vinyl alcohol unit in the copolymer.

<sup>e</sup> As precipitated.

<sup>f</sup> Per copolymer.

<sup>g</sup> Polyethylene.  $T_{\rm g}$  and  $T_{\rm m}$  data are taken from literatures.

<sup>h</sup> Poly(vinyl acetate) was prepared in this paper and hydrolyzed to poly(vinyl alcohol).

<sup>i</sup> The alternating copolymers, **44** and **45**.



Fig. 10.  $T_{\rm m}$  and  $T_{\rm g}$  vs copolymer composition for ethylene– (vinyl alcohol) copolymers.  $\bigcirc$ : statistical copolymers;  $\bullet$ : alternating copolymer 44.

values between -60 and  $+30^{\circ}$ C. They are plotted against the copolymer composition to give a good correlation curve in Fig. 11. The  $T_g$  of the alternating copolymer **45** appears 30°C lower from the correlation curve for the statistical copolymers. A sequence-ordering effect on the  $T_g$  of a copolymer is apparent in this case. The strong intermolecular force due to hydrogen bonding in the vinyl alcohol copolymers may cover the sequence-ordering effect in Fig. 10(b) and the weak intermolecular forces in the vinyl acetate copolymers uncover it in Fig. 11.

Some branching reactions occur during the group transfer polymerization of **41** via 3,4-propagation. These also occur in the radical-initiated statistical copolymerization of ethylene and vinyl acetate. Both reactions form appreciable branches in the copolymers and they might affect the  $T_g$  of the copolymers to some extent.

#### 3.3. Structure-property relationships for periodic copolymers

Materials properties of a polymeric material can be primarily understood by studying  $T_g$  and  $T_m$ . Both



Fig. 11.  $T_g$  vs copolymer composition for ethylene– (vinyl acetate) copolymers **45**. O: statistical copolymers;  $\bullet$ : alternating copolymer.

the characteristic temperatures often parallel each other and can be conveniently determined by using a DSC apparatus for a small piece of the sample. In this section, the structure–property relationship of alternating and periodic copolymers will be discussed in terms of substituent effects on their  $T_{\rm g}$ s. Simple sequences in alternating and periodic copolymers facilitates the understanding of substituent effects on copolymer properties.

Table 11 collects  $T_g$  values for various alternating and periodic copolymers. Roughly speaking, the  $T_{gs}$  of these copolymers can be understood by generally accepted substituent effects. Bulky and rigid substituents hinder the segmental motion of copolymer molecules. Polar and hydrogen-bonding substituents increase intermolecular forces among copolymer molecules. Thus both kinds of effects increase the  $T_g$  of a copolymer in question. Methyl and phenyl groups are bulky substituents and increase the  $T_g$  of a non-substituted (namely hydrogen-substituted) copolymer. Ester, nitrile, amide, and carboxyl groups are polar substituents and also increase  $T_g$ . Amide, carboxyl, and hydroxyl groups have hydrogen-bonding capacity as well as polar character and further increase  $T_g$ . The chlorine atom is a polar substituent and is bulkier than the hydrogen atom. Introduction of a methylene group in the repeating unit, in either the side-chain or the main-chain, makes the polymer molecule flexible and decreases  $T_g$ .

In Fig. 12,  $T_{g}s$  for alternating and periodic copolymers in Table 12 are plotted against their substituents X. Substituents X include COOCH<sub>3</sub>, CH<sub>2</sub>OH, and CH<sub>2</sub>OCOCH<sub>3</sub>. The latter two substituents were derived from the first substituent by reduction and reduction-and-acetylation, respectively. The partially crystalline **7** copolymer was heated and quenched to be amorphous before determining the  $T_{g}s$ . The other copolymers were all amorphous and the  $T_{g}$  were determined for the samples as prepared. One series of homopolymers, poly(methyl acrylate) and its derivatives, is also plotted by open circles. Fig. 12 shows a general tendency for  $T_{g}$  values as to what a substituent X the copolymer (and polymer) has. The  $T_{g}$  of a copolymer with a substituent X = COOCH<sub>3</sub> increases when the substituent X is converted into CH<sub>2</sub>OH and then decreases when X is further converted into CH<sub>2</sub>OCOCH<sub>3</sub>. The changes in  $T_{g}$  accompanying substituent conversion are almost the same for all of the copolymers as indicated by the parallel lines in Fig. 12.

Table 11

Glass transition temperatures ( $T_g$ , °C) of various alternating and periodic copolymers. (<sup>a</sup>Data by Hirooka [46]. <sup>b</sup>Determined for quenched copolymer sample.)

СНз -[-CH2CH2-CH2CH-]n--[-CH2CH2-CH2C-]n--[-CH2CH-CH2CH-]nсооснз сооснз СНз сооснз -185 СНз Cl -[-CH2CH-CH2C-]n--[-CH2CH-CH2C-]n--[-CH2CH-CH2CH-]n-сооснз СНз сооснз C6H5 COOCH3 C6H5 54a 109a 56 СНз -[-CH2CH2-CH2CH2-CH2CH-]n--[-CH2CH2-CH2CH2-CH2C-]nсооснз COOCH3 45 (6<sup>b</sup>) -30CH<sub>3</sub> Cl -[-CH2CH2-CH2CH2-CH2C-]n--[-CH2CH2-CH2CH2-CH2C-]n-COOC<sub>2H5</sub> сооснз -3276 СНз СНЗ -[-CH2CH2-CH2CH2-CH2C-]n--[-CH2CH2-CH2CH2-CH2C-]n CONH<sub>2</sub> соон 99 38 СНз -[-CH2CH2-CH2CH2-CH2C-]n--[-CH2CH2-CH2CH-]n--[-CH2CH2-CH2CH-]n-ососнз CN OH 2242 -40

The substituent effects on  $T_g$  shown in Fig. 12 can be understood as follows. When a moderately polar COOCH<sub>3</sub> moiety of a copolymer is converted into a hydrogen-bonding CH<sub>2</sub>OH, group, the  $T_g$  of the copolymer increases because of the stronger intermolecular forces by hydrogen bonding. Acetylation of the CH<sub>2</sub>OH group converts it into a CH<sub>2</sub>OCOCH<sub>3</sub> group and makes hydrogen-bonding ineffective and as a result affords a decreased  $T_g$  when compared to the acetylated copolymer. The fact that a copolymer with CH<sub>2</sub>OCOCH<sub>3</sub> always shows a lower  $T_g$  than its precursor copolymer with COOCH<sub>3</sub> may be due to the presence of an additional flexible CH<sub>2</sub> group in the former copolymer. The styrene copolymers, – CH<sub>2</sub>CH(C<sub>6</sub>H<sub>5</sub>)– CH<sub>2</sub>CHX–, with bulky C<sub>6</sub>H<sub>5</sub> substituent show the highest  $T_g$ s. The acrylonitrile copolymers, –CH<sub>2</sub>CH(CN)X–CH<sub>2</sub>CHX–, with polar CN substituents come next, and the two-ethylene periodic copolymers (i.e. **8** and derivatives) with long flexible CH<sub>2</sub> main chain, show the lowest  $T_g$ s.

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Fig. 12.  $T_{\rm g}$  values for various periodic copolymers with substituent X.

The introduction of CH<sub>3</sub> into the  $\alpha$ -position of the last periodic copolymers (7 and derivatives) increases  $T_{\rm g}$  to some extent.

# 3.4. Crystallization of periodic copolymers [55]

Some of the periodic ethylene–ethylene–acrylic copolymers are semicrystalline while the corresponding statistical copolymers are amorphous and do not crystallize [15,19,20]. The crystalline characteristic is most distinct for the poly(ethylene-*per*-ethylene-*per*-MMA) **7**. This copolymer shows a 30% degree of crystallinity when precipitated or cast as a film from a solution in benzene or chloroform. DSC and X-ray diffraction studies revealed its crystalline nature as shown in Fig. 13. As the statistical

Table 12					
Glass transition temperatures	$(T_{\rm g},$	°C) for some	e alternating	and periodic	copolymers

Copolymer	$T_{\rm g}$ (°C) for substituent X							
	-CH <sub>2</sub> Cl	-COOCH <sub>3</sub>	-CH <sub>2</sub> OH	-CH <sub>2</sub> OCOCH <sub>3</sub>				
$- [-CH_2CH(C_6H_5) - CH_2CHX - ]_n -$		58	80	39				
$- [-CH_2CH(COOC_2H_5) - CH_2CHX - ]_n -$	4			-18				
$- [-CH_2CH(CN) - CH_2CHX - ]_n -$	53		55	20				
$- [-CH_2CH_2-CH_2CH_2-CH_2CHX-]_n$		- 34	- 3	- 50				
$- [-CH_2CH_2-CH_2CH_2-CH_2C(CH_3)X-]_n -$		$45(-6)^{a}$	17	- 19				
$- [-CH_2CHX-]_n^{-b}$	31	6	24	- 9				

<sup>a</sup> Determined for a quenched copolymer sample.

<sup>b</sup> Each homopolymer was synthesized by polymer reactions of poly(methyl acrylate).



Fig. 13. X-ray diffraction pattern and DSC trace of poly[ethylene-per-ethylene-per-(methyl methacrylate)] 7.

ethylene–MMA copolymers are amorphous over a wide range of their compositions as shown in Section 3.2, the crystalline nature of this periodic copolymer most likely comes from its ordered sequence.

Poly(ethylene-*alt*-MMA) **22** is amorphous when precipitated and freeze-dried. It should be recalled that this amorphous alternating copolymer has one less ethylene unit in its constitutional repeating unit than the crystalline periodic copolymer **7** has and that it is atactic with respect to the MMA unit. This copolymer **22**, however, slowly crystallizes on standing at room temperature as will be discussed below.

Poly[ethylene-*per*-ethylene-*per*-(methyl acrylate)] **8**, poly[ethylene-*per*-ethylene-*per*-(benzyl methacrylate)] **18**, and poly[ethylene-*per*-ethylene-*per*-(methyl ( $\alpha$ -chloroacrylate)] **9** are also partially crystalline materials. Their DSC melting peaks are not as clear and sharp as the peak for **7**, however.

Other various periodic ethylene–ethylene–acrylic copolymers are non-crystalline materials. These non-crystalline copolymers have the following acrylic units: methacrylonitrile, methacrylamide, *N*-methylmethacrylamide, *N*,*N*-dimethyl-acrylamide, ethyl methacrylate, isopropyl methacrylate, phenyl methacrylate, acrylic acid, and methacrylic acid. It seems curious that the periodic copolymers containing acrylic units with polar and hydrogen-bonding substituents are amorphous. We expected that the strong intermolecular forces due to polar and hydrogen-bonding substituents might have brought about some crystallization. We will discuss later why these copolymers are non-crystalline while the copolymer **7** and some copolymers are crystalline.

The degree of crystallization of poly(ethylene-*per*-ethylene-*per*-MMA) **7** is 30% as precipitated but could be intentionally controlled from 0 to 54%. Film samples of this periodic copolymer were heated, quenched, annealed, and/or stretched at various temperatures. Table 13 and Fig. 14 summarize these crystallization experiments. By quenching a small piece of sample from the melt at 100°C in an

Preparation of sample	Degree of crystallization $X_{c}$ , by WAXS %	Heat of melt $\Delta H_{\rm m}$ , by DSC (mJ mg <sup>-1</sup> )
Cast film as itself	30	31.5
Melted at 100°C and quenched in liquid nitrogen	24	21.5
As above but for a small piece of sample	a	0.3
Annealed at 65°C for 70 h	32	35.2
300% elongated and annealed at 65°C for 70 h	54	52.1

Table 13Control of crystallization for poly[ethylene-per-ethylene-(methyl methacrylate)]7

<sup>a</sup> WAXS experiment could not be carried out because the sample piece was too small.

aluminum DSC pan into liquid nitrogen, an amorphous material is formed. The same processing, however, for a larger piece of film sample does not give an amorphous material. By annealing a 300% stretched film above the  $T_g$  at 65°C for 70 h, a sample with the highest degree of crystallization, 54%, is formed. Thus samples with various degrees of crystallization between 0 and 54% are available.

The same technique was applied to the amorphous poly-(ethylene-*alt*-MMA) **22**. A film sample was prepared by casting its solution on a glass plate and this was allowed to stand at room temperature above its  $T_g$ . Then it slowly turned out to show small melting peaks in the DSC traces (Table 14). The highest



Fig. 14. X-ray and DSC experiments on a film sample of poly[ethylene-*per*-ethylene-*per*-(methyl methacrylate)] **7** after the following processing. (a) cast film as itself; (b) melted at 100°C and quenched in liquid nitrogen; (c) same as b but for a small piece of sample; (d) annealed at  $65^{\circ}$ C for 70 h; (e) 300% elongated and annealed at  $65^{\circ}$ C for 70 h.

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Table 15

Time for which a film sample was allowed to stand (h)	Heat of melt $\Delta H_{\rm m}$ by DSC (mJ mg <sup>-1</sup> )
Start	3.2
26	8.7
48	10.3
72	13.1
96	13.3
144	16.4 <sup>b</sup>

Control of crystallization for poly[ethylene-*alt*-(methyl methacrylate) **22** (a film sample was allowed to stand at room temperature for hours shown)

<sup>a</sup> This sample showed 16% degree of crystallization as determined by X-ray diffraction method.

degree of crystallization realized for 22 was 16% as determined from its X-ray diffraction pattern. This highest value for 22 is lower than for 7. We should recall again that the constitutional repeating unit of 22 contains one less ethylene unit than that of 7.

Table 15 shows the results of stress-strain experiments for the films of **7** with various degrees of crystallization. The higher the degree of crystallization, the harder and less elastomeric the material is.

The crystalline structure of the periodic copolymer **7** was studied by X-ray diffractometry. Fig. 15(a)–(c) show X-ray diffraction patterns for a biaxially stretched and annealed sample sheet. This sample had a degree of crystallization of 50%. The "through view" and "edge view" show oriented diffraction patterns but the "end view" shows unoriented, concentric Debye–Scherrer rings. Uniaxially stretched samples also gave the same diffractions. These results may identify the crystal form but at this point, we cannot draw a conclusion. We suppose a possible one in which copolymer molecules having mainchains of successive five methylenes in one repeating unit are arranged side by side as in polyethylene crystals. The periodically attached substituents, CH<sub>3</sub> and COOCH<sub>3</sub>, may modify the polyethylene crystal but basically do not alter it. Substituents, likeCN, COOH, and CONH<sub>2</sub>, which have strong intermolecular forces between themselves, will tend to disturb this molecular arrangement and give more amorphous materials.

#### 3.5. Intermolecular association of periodic acid copolymers with base polymers

By hydrolyzing periodic copolymers 22 and 7, periodic acid copolymers 21 and 20 were obtained as described in Section 2.3. Poly(methacrylic acid) 46 is available by polymerizing methacrylic acid

Sample	Degree of crystallization (%)	Heat of melt (mJ mg <sup>-1</sup> )	Young's modulus (MPa)	Stress at break (Mpa)	
Quenched	25	22.4	51	18.6	
Cast film	34	33.1	96	24.5	
Annealed	37	33.4	127	32.3	
Stretched and annealed	54	49.2	176	75.5	

Mechanical properties of poly[ethylene-per-ethylene-per-(methyl methacrylate)] 7 having various degrees of crystallization



Fig. 15. X-ray diffraction patterns of biaxially stretched poly[ethylene-*per*-ethylene-*per*-(methyl methacrylate)] **7**. (a) through view; (b) edge view; and (c) end view.

monomer. Then we have the following three acid polymers which carry their carboxyl substituents on every two, four, and six carbon atoms of their main-chains, respectively. These carboxyl groups may interact differently with the pyridyl groups of a base polymer, poly(4-vinylpyridine) **47**.



Interaction between these acid and base polymers was studied as follows [56]. Solutions of each of the acid (co)polymers 46, 21, and 20 in methanol and the solution of the base polymer 47 in the same solvent



Fig. 16. Ultraviolet absorption spectra of poly(4-vinylpyridine) **4**7 solution in methanol on addition of various ratios of poly(ethylene-*alt*-(methacrylic acid) **21**. Numericals given denote the feed acid-to-base ratios  $R = [A]_0/[B]_0$ .

were mixed at room temperature. When the concentration of solutions was  $10^{-1}$  mol  $1^{-1}$  with respect to the functional groups, precipitates were rapidly formed for various ratios of acid–base pairs. The acid-to-base ratios in the dried precipitates were about 1:1 for all three acid–base pairs. The  $T_g$  values for these precipitates were  $20-30^{\circ}$ C higher than predicted by the Fox additive equation [49]. This phenomenon may indicate some interaction between the acid and the base polymers. Fourier-transform IR absorption spectra for the precipitates showed absorptions at 2515 and 1930 cm<sup>-1</sup> which may be ascribed to hydrogen-bonding interactions between the carboxyl and pyridyl groups [57]. Absorptions due to anionic carboxylate groups at 1650–1600 cm<sup>-1</sup> were not observed.

When the concentration of the solutions was made lower  $(10^{-4} \text{ mol } 1^{-1})$ , no precipitate was obtained for the three pairs. Instead, the ultraviolet absorption of the pyridyl group increased its intensity according to the acid-to-base ratios (Fig. 16). It has been established [58] that the absorption of the pyridyl group enhances its intensity by interacting with a hydrogen-donating group and the enhancement depends on the degree of interaction. We determined the ultraviolet absorption intensities at 256 nm,  $A_{256}$ , for various mixed solutions and plotted them against the feed acid-to-base ratios,  $R = [A]_0/[B]_0$ . When hydrogen-bonding interaction occurs between the carboxyl group A and the pyridyl group B with an association equilibrium constant  $K_{AB}$ ,

species	А	+	В	$\stackrel{K_{AB}}{\rightleftharpoons}$	AB
concentration at the equilibrium	[A] <sub>0</sub> -[Al	3]	[B] <sub>0</sub> -[AB]		[AB]

the concentration of hydrogen-bonded species [AB] at the equilibrium is given by  $[AB] = \{C - (C^2 - 4[B]_0^2 R)^{1/2}\}/2,$ 



Fig. 17. Plots of absorption intensities of poly(4-vinylpyridine) **21**/poly[ethylene-*alt*-(methacrylic acid)] **47** in methanol solution at 256 nm against the feed acid-to-base ratios  $R = [A]_0/[B]_0$  to determine  $K_{AB}$  and  $E_{AB}$ .

and

$$C = [A]_0 + [B]_0 + K_{AB}^{-1}.$$

Then the absorption at 256 nm is given by the sum of absorptions for the free and hydrogen-bonded pyridyl groups,

 $A_{256} = E_{\rm B}([{\rm B}]_0 - [{\rm AB}]) + E_{\rm AB}[{\rm AB}],$ 

where  $E_{\rm B}$  and  $E_{\rm AB}$  denote the molar extinction coefficients of each pyridyl groups, respectively. As  $A_{256}$ ,  $[A]_0$ ,  $[B]_0$ , and  $E_{\rm B}$  were known, various  $E_{\rm AB}$  and  $K_{\rm AB}$  were assumed to find out the values, which would give a best fit to the experimental plot as shown in Fig. 17. Table 16 gives the determined  $E_{\rm AB}$  and  $K_{\rm AB}$  values for three pairs of acid and base (co)polymers. It is a natural result that the found  $E_{\rm AB}$  values are identical for all pairs. On the contrary, the  $K_{\rm AB}$  values are  $10^5-10^2$  and vary with the acid-base pairs. Because a solution of isobutyric acid and 4-ethylpyridine in methanol did not show the absorption enhancement, the  $K_{\rm AB}$  values found for the (co)polymer pairs are considered to be large. These large  $K_{\rm AB}$  values could be due to the so-called polymer effect. Carboxyl groups, being consecutively substituted on the (co)polymer main-chain, effectively interact with the pyridyl groups of 47. Among the found  $K_{\rm AB}$ , the  $K_{\rm AB}$  value for the pair 20–47 is relatively small and about  $1/10^2$  of the  $K_{\rm AB}$ s for the pairs 46–47 and 21–47. While the carboxyl groups in 46 and 21 appear on every two and four main-chain carbon atoms and can interact effectively with pyridyl groups in 47, the carboxyl groups in 20 are

Table 16 Association of acid (co)polymers and a base polymer, poly(4-vinylpyridine) **47**, in methanol at room temperature

Polymer pair <sup>a</sup>	$E_{ m AB}$	$K_{\rm AB}$ (l mol <sup>1</sup> )	
46-47 21-47 20-47	$2 \times 10^{3}$ $2 \times 10^{3}$ $2 \times 10^{3}$	$> 5 \times 10^4$ $> 5 \times 10^4$ $2 \times 10^2$	

<sup>a</sup> Acid (co)polymer numbers are: **46**, poly(methacrylic acid); **21**, poly[ethylene-*alt*-(methacrylic acid); **20**, poly[ethylene-*per*-ethylene-*per*-(methacrylic acid)].

further separated by the intervening five methylene groups and these wide spaces are unfavorable for effective interaction with **47**.

#### 3.6. Dissociation constants of periodic acid copolymers

Kawaguchi and his coworkers [59] determined the apparent dissociation constants for poly(maleic acid) and poly(acrylic acid) in water. Fig. 18(a) and (b) shows while the  $pK_a$  of poly(acrylic acid) monotonously increases with the degree of dissociation, the  $pK_a$  of poly(maleic acid) increases in stepwise fashion. They explained this phenomenon as follows. Poly(maleic acid) carries carboxyl groups on every main-chain carbon atom and therefore the already dissociated and negatively charged COO<sup>-</sup> groups strongly suppress the dissociation of neighboring carboxyl groups. However, the carboxyl groups in poly(acrylic acid) are separated and appear on every two main-chain carbon atoms and the effect of dissociated carboxylate groups is weakened.

They also studied [60,61] the dissociation for the poly[ethylene-*per*-ethylene-*per*-(acrylic acid)] **19**. In this copolymer, the carboxyl groups are further separated from each other and appear on every six main-chain carbon atoms. A quite different  $pK_a$  vs degree of dissociation relationship from the above two polymers is observed as shown in Fig. 18(c). The  $pK_a$  steeply increases until 20% dissociation and then decreases monotonously to 90% dissociation. In the region of low dissociation, the intervening hydrophobic five methylene groups between the carboxyl groups probably coagulate in water and take on a compact conformation. Because of this low dielectric hydrocarbon domain, the suppressing effect by the already dissociated carboxylate groups on a dissociating carboxyl groups repel each other by Coulombic forces and the copolymer molecule takes on a zig–zag conformation. In the region between 20% and 90% dissociation, the copolymer molecule occupies a mix of the two conformations and we observe the monotonous decrease of  $pK_a$  in Fig. 18(c).

Thus the functional groups in many periodic copolymers can show a different behavior from those in more conventional vinyl polymers.



Fig. 18. Apparent dissociation constant  $pK_a$  of (a) poly(maleic acid); (b) poly(acrylic acid); (c) poly[ethylene-*per*-ethylene-*per*-(acrylic acid)] **19** against the degree of dissociation  $\alpha$  in dilute NaCl solutions.

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### 3.7. Side-chain crystallization of widely spaced comb-like polymers

Vinyl polymers having long alkyl side-chains are often designated as comb-like polymers after their peculiar molecular structure. Alkyl groups are usually straight  $C_{10}$ – $C_{22}$  chains and are regarded as teeth of the comb which appear on every two carbon atoms of the polymer main-chain. Vinyl polymers may be poly(alkyl acrylate), poly(alkyl methacrylate), poly(alkyl vinyl ether), poly(vinyl alkanoate), poly(4-alkanoylstyrene) and so on. Comb-like polymers have a characteristic that their long alkyl side-chains crystallize even when their methyl-substituted analogue polymer is amorphous. Detailed reviews have been written by Shibaev and Platé [62,63].

The author and his coworkers synthesized a series of alternating butadiene– (alkyl methacrylate) copolymers **48** and their hydrogenated products, periodic ethylene–ethylene– (alkyl methacrylate) copolymers **49**, as a new type of comb-like polymer [64]. These copolymers were long alkyl homologues of **6** and **7**, and the alkyl groups were dodecyl, tetradecyl, hexadecyl, and octadecyl.



R=C12H25, C14H29, C16H33, or C18H37

We termed these as "widely spaced comb-like polymers" because their comb-teeth appeared on every six main-chain carbon atoms and therefore had wider-spaces between neighboring alkyl groups as compared to the more conventional comb-like polymers. Our main interest was to determine whether the widely spaced alkyl groups would crystallize or not.



The crystallization of the side-chains of the widely spaced comb-like polymers was studied by DSC, IR spectroscopy, and X-ray diffraction techniques. A conventional comb-like polymer **50**, poly(alkyl methacrylate)s, was also studied for comparison.





Fig. 19. DSC traces of two widely-spaced comb-like polymers, 48 and 49, and a conventional comb-like polymer, 50.

The cooling DSC curves for all samples showed single exothermic freezing peaks as shown in Fig. 19. In general, as the number of carbon atoms in the alkyl side-chain increases from 12 to 18, the freezing peaks of 48 and 49 as well as 50 shift to higher temperatures and become sharper and stronger. Widely spaced comb-like polymers 48 and 49 show somewhat broader peaks at lower temperatures than the conventional comb-like polymers 50 with the same alkyl side-chains. Determining the exothermic peak areas, the numbers of crystallized  $CH_2$  groups N in the alkyl side-chains of 48, 49, and 50 could be calculated with reference to the heat of crystallization of the hexagonal-packed alkanes in a literature [65]. These N numbers are compared with each other in Table 17. Widely spaced comb-like polymers 48 and 49 show larger N than the conventional 50. Between 48 and 49, the former which has a rigid carbon–carbon double bond in the main-chain shows smaller N than the latter.

IR spectroscopic studies of the widely spaced comb-like polymers based on their  $CH_2$  rocking mode absorption regions showed a single peak at 720 cm<sup>-1</sup> for samples **48** and **49** as well as **50**. Chapman [66] pointed out that the IR absorption spectra in this region for crystalline long alkyl compounds were correlated with the types of alkyl chain packing. Compounds showing two peaks at 727 and 719 cm<sup>-1</sup> were in the orthorhombic type packing and those showing a single peak at 720 cm<sup>-1</sup> were in the less

Number of crystallize	ed CH <sub>2</sub> groups,	Ν		
Alkyl side-chain	Je-chain Comb-like polymer <sup>a</sup>			
	48	49	50	
C12	0.6	0.9	0.5	
C14	2.7	3.4	1.9	
C16	5.4	6.3	4.0	
C18	7.5	8.2	5.6	

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Table 17

<sup>a</sup> **48**, poly(butadiene- = alt-(alkyl methacrylate)]; **49**, poly[ethylene-*per*-ethylene-*per*-(alkyl methacrylate)]; **50**, poly(alkyl methacrylate).

stable hexagonal type packing. Shibaev and coworkers [67] observed such single peaks for some conventional comb-like polymers including **50** and concluded that the crystallized alkyl side-chains of the comb-like polymers were in hexagonal packing.

X-ray diffraction studies of **48** and **49** with octadecyl side-chains by using CuK $\alpha$ -ray showed sharp diffraction peaks at  $2\theta = 21^{\circ}$ , which was the same angle as for 50.

On the basis of these results, the author proposed a possible crystallized structure for the widely spaced comb-like polymers as shown in Fig. 20 which shows a crystallizing part of alkyl side-chains and a non-crystallizing, random-coiling main-chain together with the rest of alkyl side-chains. The flexible main-chains of **48** and **49** can be coiled so as to allow for the side-chains to be packed in the crystal lattice.

Fig. 20 indicates the importance of main-chain flexibility for the side-chain crystallization of widely spaced comb-like polymers. To clarify this point, the following new type of widely spaced comb-like polymers **51** was synthesized and its crystallization behavior was studied [68].



Fig. 20. A sketch of a crystallized, widely spaced comb-like polymer.

This type of widely spaced comb-like polymer **51** was  $\alpha$ ,  $\alpha'$ -disubstituted alternating styrene– (alkyl acrylate) copolymers and hence had its comb-teeth on every four main-chain carbon atoms. The polymer was easily synthesized by copolymerizing styrene or  $\alpha$ -methylstyrene with alkyl acrylate or alkyl methacrylate in the presence of EASC. Side-chain crystallization was again studied by DSC traces and the number of crystallized CH<sub>2</sub> groups *N* were evaluated as above by determining the freezing peak areas. The *N* numbers are plotted in Fig. 21 against the carbon numbers of the alkyl side-chains for each type of copolymer. Data for poly(alkyl acrylates) **52** are also plotted in Fig. 21 for comparison. The plots for alternating styrene-(alkyl acrylate) copolymers are somewhat similar to the plots for **52**, but the indication of side-chain crystallization for **52** is observed at the dodecyl polymer. The side-chain crystallization of alternating styrene– (alkyl methacrylate) and  $\alpha$ -methylstyrene– (alkyl acrylate) copolymers is further suppressed and the indication of crystallization is just observed at the hexadecyl copolymers. Both the octadecyl copolymers give smaller *N* numbers than poly(octadecyl acrylate) and the styrene–



Fig. 21. Number of crystallized  $CH_2$  groups N of widely spaced comb-like polymers 51.

(octadecyl acrylate) copolymer. The alternating  $\alpha$ -methylstyrene– (octadecyl meth-acrylate) copolymer does not crystallize any longer and the plot is found on the abscissa.

The results in Fig. 21 can be explained on the basis of the crystallized comb-like polymer model proposed in Fig. 20, assuming a widely spaced comb-like copolymer **53**,



and considering cumulative substitution at the  $\alpha$  and  $\alpha'$  carbons by phenyl and methyl groups. Such cumulative substitution of bulky phenyl and methyl groups on the main-chain would make the polymer main-chain less flexible according to the extent of substitution. The less flexible main-chain would be unfavorable for side-chain crystallization by not allowing the side-chains to be closely packed and would give smaller *N* numbers. The substitution effects by phenyl and methyl groups on the polymer flexibility are easily understandable when we refer to the known  $T_{g}s$  of polystyrene, poly- $\alpha$ (-methylstyrene, poly(methyl acrylate), and polyMMA. Thus, the flexibility of the present type of comb-like polymers is in the order:

styrene–acrylate > styrene–methacrylate  $\simeq \alpha$ -methylstyrene–acrylate >  $\alpha$ -methylstyrene–methacrylate,

which agrees with the order of N numbers.

The alkyl side-chains of the widely spaced comb-like polymers crystallize similarly to conventional polymers that have long aliphatic paraffin chains. The intervening flexible main-chain between alkyl side-chains works preferably for the side-chain crystallization.

# 4. Concluding remarks

Various alternating and periodic copolymers were synthesized by polymer reactions of precursor polymers and alternating copolymers. Their sequence-ordered structures could be well identified in several cases. Because of the "periodic sequences", some periodic copolymers were crystalline even when the corresponding statistical copolymers were amorphous. Some materials properties of the periodic copolymers were discussed, especially in comparison to statistical copolymers. Periodically arranged substituents upon the periodic copolymer main-chain showed specific functional characteristics.

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