Synthesis of Sequence-Ordered Copolymers. 1. Synthesis of Alternating Copolymers Containing Some Allyl Derivative Units

Tadamichi Hirabayashi, Kouji Yamauchi, and Kenji Yokota*

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

Received November 14, 1990; Revised Manuscript Received February 25, 1991

ABSTRACT: Alternating copolymers containing allyl chloride, allyl alcohol, and allyl acetate units were synthesized by alternating copolymerization of allyl and acrylic monomers in the presence of an organoaluminum complexing reagent or by polymer reactions of appropriate precursor copolymers. Their glass transition temperatures were determined.

In our previous papers,[1,2] an alternating ethylene–methyl methacrylate copolymer and a periodic ethylene–ethylene–methyl methacrylate copolymer, both of which could not be obtained directly by copolymerizing ethylene and methyl methacrylate monomers, were synthesized by polymer reactions (reduction) of alternating vinyl bromide–methyl methacrylate and alternating butadiene–methyl methacrylate copolymers, respectively. These copolymers were soluble, soft, and rubbery materials, and their glass transitiion temperatures (T_g) were reported.

The present paper reports the synthesis and T_g values of alternating copolymers that all contain an allyl derivative as one comonomer unit. As allyl derivatives, allyl chloride, allyl alcohol, and allyl acetate were studied. Allyl derivatives are usually unreactive in polymerizations because they are unconjugated monomers and have allyl hydrogens that often work as a degradative function for propagating species. The present copolymer synthesis involves direct copolymerization of allyl derivatives with acrylic monomers and polymer reactions of appropriate precursor copolymers. T_g values of copolymers thus synthesized were determined by thermal analysis and will be discussed in the succeeding paper[3] together with T_g's of related copolymers in terms of their structure.

Experimental Section

Materials. Most of materials were commercially available extra-pure or guaranteed reagents from Nacalai Tesque, Inc., Kyoto, Japan, and purified by standard methods.[4] Allyl trimethylsilyl ether was obtained from E. Merck. Ethylaluminum sesquichloride (EASC) was obtained from the Ethyl Corp., distilled, and used as its toluene solution (4 mol L^{-1}). Monomers were purified, dried finally over calcium hydride, distilled, and stored in a refrigerator before use.

Copolymerization. Allyl derivative monomers were generally fed in a large excess in the EASC-complexed copolymerization with acrylic monomers. In a nitrogen-purged test tube, an acrylic monomer, a solvent, the EASC–toluene solution, and an allyl monomer were mixed and copolymerized. After a given time, the content was poured into a large volume of nonsolvent. The precipitated product was collected, reprecipitated, and dried in vacuo. Details will be described for each copolymerization in the Results and Discussion section.

Polymer Reactions. Some alternating copolymers synthesized in the above paragraph were converted into other alternating copolymers as precursor copolymers by appropriate polymer reactions. Details will be described for each reaction in the Results and Discussion section.

Measurement. ^1H (200-MHz) and ^{13}C (50-MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Varian XL-200 spectrometer. The pulse sequence for ^{13}C NMR was as follows: 18-μs pulse width (90° pulse angle), 0.8-s acquisition time, and 1-s interval. Generally 800 scans were accumulated for a 12 500-Hz spectral width. ^1H (90-MHz) NMR spectra were also recorded on a Hitachi R-90 spectrometer. Most of the spectra was taken for 5–10% deuteriochloroform or dimethyl-d_6 sulfoxide solutions at room temperature. Infrared (IR) spectra were recorded for polymer films or KBr disks on a Jasco IR Report 100 spectrometer. Molecular weight determination of copolymers was carried out by using a Tosoh gel permeation chromatograph HLC 803D with GMX-, G1000-, G2000, and G4000-HXL columns in series. The eluent was tetrahydrofuran (THF), and its flow rate was 1 mL min^{-1} at 40 °C. The retention time for each copolymer sample was read simply at the peak top of each chromatogram and assumed as a measure of the copolymer molecular weight with reference to polystyrene standards. Correction for each copolymer structure was not made. A differential scanning calorimetry (DSC) study was carried out on a Seiko I TA station with a DSC 210 unit. Heating and cooling rates were 10 °C min^{-1}.

Results and Discussion

Alternating Copolymerization of Allyl Chloride. Alternating copolymerization of allyl chloride and ethyl acrylate was carried out as follows. Ethyl acrylate (0.9–2.2 mL) was taken in a test tube and degassed by freeze–thaw cycles. An equimolar EASC–toluene solution was added at −78 °C and stirred for some time at room temperature to complete complexation. Toluene solvent was added, rinsing the inner wall of the vessel. Finally a large excess of allyl chloride was added, and the mixture was stirred gently at −20 °C. After 50 h, the mixture was cooled again at −78 °C and mixed slowly with a large volume of methanol containing small amounts of hydroquinone and hydrochloric acid. The precipitated copolymer was collected and reprecipitated three times from chloroform solution into methanol and dried in vacuo. Alternating copolymerization of allyl chloride and acrylonitrile was also carried out by the same procedure. The solvent for reprecipitation in this case was dimethyl sulfoxide (DMSO). Tables I and II summarize the results of both copolymerizations.

Allyl chloride–ethyl acrylate copolymers, obtained in moderate yields in runs 1–5 of Table I, had molecular weights of 20 000–60 000. The allyl chloride content in the copolymer (mol %) determined by ^1H NMR peak areas increased with its content in the monomer feed. With 93.8 mol % allyl chloride content in the monomer feed in run 4, a 50 mol % allyl chloride –50 mol % ethyl acrylate copolymer was obtained. This copolymer, however, had no completely alternating sequence, as revealed by its ^{13}C NMR spectrum in Figure 1. The absorption in a 36–44 ppm region can be assigned to the α-carbon to which

0024-9297/91/2224-4538$02.50/0

Table I
Copolymerization of Allyl Chloride (AC) and Ethyl Acrylate (EA)[a]

run	monomer feed, mol % AC	monomer feed, mol % EA	convn,[b] %	copolymer,[c] mol % AC	copolymer,[c] mol % EA	sequence distribution,[d] % EA-EA-EA	sequence distribution,[d] % EA-EA-AC + AC-EA-EA	sequence distribution,[d] % AC-EA-AC	mol wt, $\times 10^{-4}$
1	47.0	53.0	25.6	24.4	75.6	40	45	15	4.4
2	80.0	20.0	24.0	44.7	55.3	0	21	79	4.2
3	90.0	10.0	30.8	46.4	53.6	0	15	85	5.7
4	93.8	6.2	59.0	49.7	50.3	0	10	90	2.6
5	98.0	2.0	40.5	49.9	50.1	0	0	100	1.6
6	98.0	2.0	*e*	100.0	0.0	0	0	0	1.0

[a] With EASC in toluene at −20 °C for 50 h. [b] Conversion was based on EA feed (0.9–2.2 mL). [c] Composition was determined by ^{1}H NMR. [d] Sequence was determined by ^{13}C NMR. [e] Friedel–Crafts type polymerization occurred.

Table II
Copolymerization of Allyl Chlorides (AC) and Acrylonitrile (AN)[a]

run	monomer feed, mol % AC	monomer feed, mol % AN	convn,[b] %	copolymer,[c] mol % AC	copolymer,[c] mol % AN	copolymerizn mixture turned	mol wt, $\times 10^{-4}$
1	32.7	67.3	1.0				
2	49.2	50.8	9.9	33.3	66.7		1.6
3	80.2	19.8	2.8	45.4	54.6		1.7
4	90.7	9.3	8.0	49.2	50.8		1.7
5	95.0	5.0	8.6	49.7	50.3		2.0
6	66.0	34.0	*e*	100.0	0.0	reddish brown after 3 h	0.3
7	98.0	2.0	*e*	100.0	0.0	reddish brown after 5 h	0.2
8[d]	98.0	2.0	*e*	100.0	0.0	reddish brown immediately	

[a] With EASC in toluene at −20 °C for 50 h. [b] Conversion was based on AN feed (1–2 mL). [c] Composition was determined by ^{1}H NMR. [d] Ethylaluminum dichloride was used instead of EASC. [e] Friedel–Crafts type polymerization occurred.

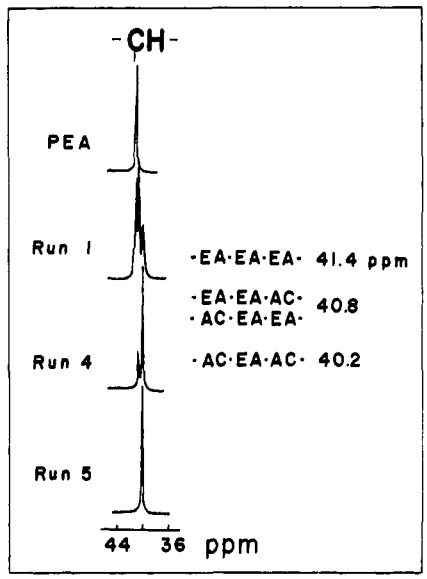


Figure 1. ^{13}C NMR spectra of allyl chloride–ethyl acrylate copolymers in the region of 36–44 ppm.

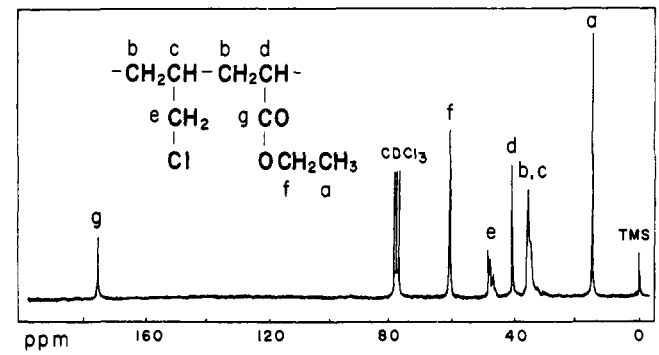


Figure 2. ^{13}C NMR spectrum of an alternating allyl chloride–ethyl acrylate copolymer.

$COOC_2H_5$ is attached. Comparison of the absorptions of the run 1 copolymer and the ethyl acrylate homopolymer (PEA) allows us an assignment of the split peaks. The peaks at 40.2, 40.8, and 41.4 ppm are assigned to the α-carbon absorption of the central ethyl acrylate unit of AC–EA–AC, EA–EA–AC, plus AC–EA–EA, and EA–EA–EA triad sequences, respectively. Here AC and EA stand for allyl chloride and ethyl acrylate units. Triad sequence distributions were calculated from the peak intensities and shown in Table I. The run 4 copolymer has a 90% AC–EA–AC sequence and a 10% EA–EA–AC plus AC–EA–EA sequence. The run 5 copolymer, which was obtained with a much larger excess of allyl chloride (98.0 mol %) in the monomer feed, shows only one sharp peak at 40.2 ppm and hence has a 100% AC–EA–AC sequence and can be considered to be an alternating copolymer.

Figure 2 shows whole ^{13}C NMR spectrum of this run 5 alternating allyl chloride–ethyl acrylate copolymer, P(AC-*alt*-EA) (1). Assignment of each absorption is also shown. The absorption e, which is assigned to CH_2Cl, splits into three peaks. This splitting could come from the copolymer tacticity but not from its sequence, because all of the allyl chloride units in the runs 1–5 copolymers can be considered to be flanked by ethyl acrylate units, and the intensity ratios of split peaks are identical for all copolymers. Therefore, we assigned the peaks at 48.0, 48.4, and 48.8 ppm to the central allyl chloride unit of cosyndiotactic, coheterotactic, and coisotactic triad, respectively. (The reverse assignment that the peaks at 48.0, 48.4, and 48.8 ppm are of coisotactic, coheterotactic, and cosyndiotactic triad, respectively, is naturally possible, but we prefer the above assignment because it indicates an advantageous cross-propagation by which the two neighboring polar substituents, $-CH_2Cl$ and $-COOC_2H_5$, come apart.) When peak areas are estimated by dividing into two parts, 48.0 + 48.4 ppm and 48.8 ppm, and a Bernouillian model for the steric course of cross-propagation is assumed, we obtain a coisotacticity $\sigma = 0.3$ for this alternating copolymerization. Here the coisotacticity, σ, is defined for the following steric structure in which both α-carbons have the same configuration.

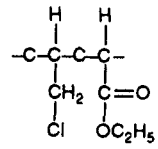


Figure 3 shows the IR spectrum of the run 5 copolymer. Characteristic absorptions due to ester and chloromethyl groups are clearly observed. ^1H NMR absorptions in $CDCl_3$ were as follows: $COOC_2H_5$ at 1.26 and 4.16 ppm, CHCOO at 2.50 ppm, CH_2Cl at 3.5–3.8 ppm, and other CH_2 and CH at 1.4–2.0 ppm.

1 is a rubbery material that is soluble in chloroform, acetone, and tetrahydrofuran (THF) and insoluble in methanol and water.

In the run 6 experiment where ethyl acrylate and EASC solution were added without thorough mixing and allyl chloride was added in succession, the mixture turned reddish brown immediately and an exothermic reaction took place with an evolution of hydrogen chloride. The product showed in its ^1H NMR and IR spectra the presence of aromatic, vinylene, and vinylidene groups. A small amount of chloromethyl group was also detected. This product could be formed from allyl chloride and toluene by a complicated "Friedel–Crafts type polymerization", which was reported earlier by Murahashi et al.[5] and not studied further.

Table II shows the copolymerization of allyl chloride with acrylonitrile. As in the copolymerization with ethyl acrylate, a large excess feed of allyl chloride was necessary to obtain a 50 mol % allyl chloride–50 mol % acrylonitrile copolymer. The copolymers, however, were obtained in very low yields and so could not satisfactorily be identified. Besides, occasionally and suddenly the copolymerization mixture turned reddish brown during the reaction, and the Friedel–Crafts type polymerization again occurred in runs 6–8. Therefore, the desired alternating allyl chloride–acrylonitrile copolymer was synthesized by a polymer reaction from an alternating allyl alcohol–acrylonitrile copolymer as will be described later. As a result, both copolymers here and later described showed identical ^1H and ^{13}C spectra.

Alternating Copolymerization of Allyl Trimethylsilyl Ether. Copolymerizations of allyl trimethylsilyl ether (ATSE) in place of allyl chloride in the preceding paragraph were carried out by the same procedure. After a given time of copolymerization, the reaction mixture was poured into methanol containing 1 vol % hydrochloric acid and stirred for 1 h. While stirring in the acidic methanol, removal of a trimethylsilyl group (desilylation) occurred and hence allyl alcohol copolymers were precipitated.

Attempted alternating copolymerizations of ATSE and ethyl acrylate with EASC followed by desilylation gave insoluble gelled copolymers. A special treatment that a precipitated and wet polymer was acetylated with excess acetic anhydride gave a small amount of soluble product. Its characterization showed the presence of lactone linkage, which could be formed by an intramolecular ester-exchange reaction between the neighboring allyl alcohol and ethyl acrylate units. Therefore, the gel formation is considered as due to a possible intermolecular ester-exchange reaction during the workup. The analysis of this soluble product showed that a 50 mol % ATSE–50 mol % ethyl acrylate copolymer was originally formed when a large excess of ATSE to ethyl acrylate was fed and copolymerized.

Alternating copolymerization of ATSE and acrylonitrile with EASC is shown in Table III. Desilylated

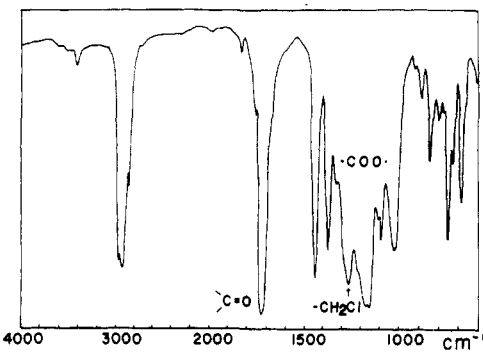


Figure 3. IR spectrum of an alternating allyl chloride–ethyl acrylate copolymer.

copolymer was recovered by concentrating the methanol solution and pouring it into water. The collected copolymer was reprecipitated by using THF–cold water or DMSO–cold water. In run 1 with a 60 mol % ATSE feed, a 40 mol % allyl alcohol–60 mol % acrylonitrile copolymer was obtained. In runs 2 and 3 with over a 90 mol % ATSE feed, 50 mol % allyl alcohol–50 mol % acrylonitrile copolymers with molecular weights (determined for acetylated THF-soluble copolymers) of 10 000–20 000 were obtained. To study their sequence, ^{13}C NMR absorptions of CH_2OH and CN as shown in Figure 4 were examined. The two split CH_2OH peaks at 62.0 and 64.0 ppm have the same intensity ratios for run 1 and run 2 copolymers, and so the splitting is considered as due to tacticity. When the peak at 62.0 ppm is assigned to syndiotactic triad and the peak at 64.0 ppm to coheterotactic plus coisotactic triads of AN–AA–AN sequences (AA and AN stand for allyl alcohol and acrylonitrile units, respectively) and again a Bernouillian model for the steric course of cross-propagation is assumed, a coisotacticity $\sigma = 0.5$ is obtained. (The coisotactic diad structure is defined analogously to 1.) The CN absorption for the run 2 copolymer shows two peaks split like the CH_2OH absorption and assigns the peak at 122.0 ppm to the coisotactic triad and the peak at 124.0 ppm to the coheterotactic plus cosyndiotactic triads of AA–AN–AA sequences. The CN absorption for the run 1 copolymer seems quite complicated but, referring to the absorption fo an acrylonitrile homopolymer (PAN), can be considered as composed of the split AA–AN–AA and AA–AN–AN (and AN–AN–AA) plus AN–AN–AN sequences. Then from the above-assigned CN absorption for the run 2 copolymer, a coisotacticity $\sigma = 0.5$ is again obtained. The whole ^{13}C NMR spectrum of the run 3 copolymer is shown in Figure 5 with assignments. The IR spectrum showed CN absorption at 2220 cm^{-1} and OH absorptions at 3420 and 1040 cm^{-1}. ^1H NMR absorptions in DMSO-d_6 were as follows: CHCN at 2.93 ppm, CH_2O at 3.38 ppm, OH at 4.67 ppm, and other CH_2 and CH at 1.2–2.2 ppm.

The alternating allyl alcohol–acrylonitrile copolymer, P(AA-*alt*-AN) 2, is a white powdery material that is soluble in DMF, DMSO, *N,N,N',N',N'',N''*-hexamethylphosphoramide (HMPA), 10% hydrochloric acid, and methanol and swells in ethanol, acetic acid, and water.

Synthesis of Alternating Allyl Acetate–Ethyl Acrylate Copolymer from Alternating Allyl Chloride–Ethyl Acrylate Copolymer. 1 (run 5 copolymer in Table I; 0.150 g, 0.85 mmol) was dissolved in HMPA (2 mL) and stirred with potassium acetate (0.30 g, 3.06 mmol) at 70 °C. After 24 h, the mixture was poured into water and the precipitate was reprecipitated by using acetone–water. After drying in vacuo, a viscous liquid (0.158 mg, 93% yield) was obtained. Examination of its IR and ^1H and ^{13}C NMR spectra showed that this product was the desired

Table III
Copolymerization of Allyl Trimethylsilyl Ether (ATSE) and Acrylonitrile (AN)[a]

run	monomer feed, mol % ATSE	monomer feed, mol % AN	copolymerzn time, h	convn,[b] %	copolymer,[c] mol % ATSE	copolymer,[c] mol % AN	mol wt,[d] ×10⁻⁴
1	60.1	39.9	24	46.8	40.7	59.3	1.4
2	90.0	10.0	24	35.8	49.7	50.3	2.2
3	91.1	8.9	50	64.3	49.8	50.2	1.1

[a] With EASC in toluene at −20 °C. [b] Conversion was based on AN feed (1.3 mL) for desilylated copolymer. [c] Composition was determined by ^{1}H NMR for desilylated copolymer. [d] Molecular weight was determined for desilylated and acetylated copolymer.

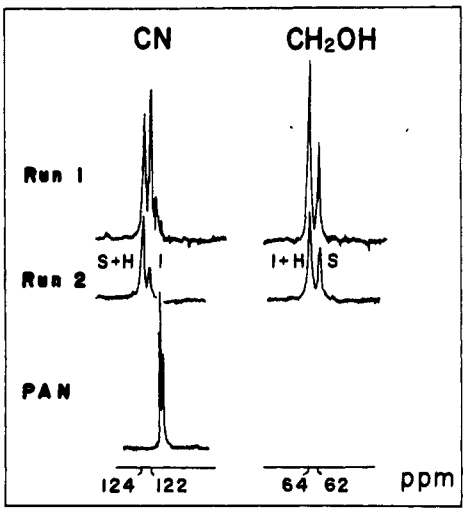


Figure 4. ^{13}C NMR spectra of allyl alcohol-acrylonitrile copolymers in the regions of CH_2OH and CN absorptions.

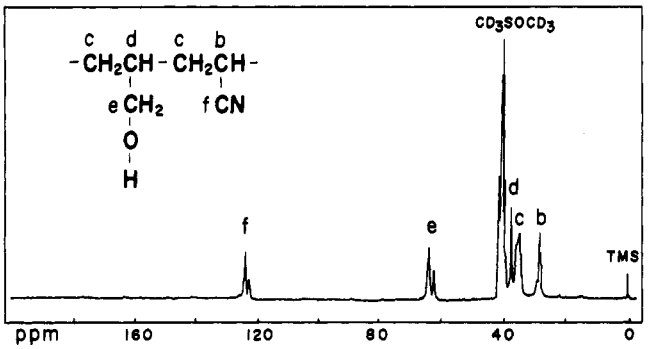


Figure 5. ^{13}C NMR spectrum of an alternating allyl alcohol–acrylonitrile copolymer.

alternating allyl acetate–ethyl acrylate copolymer, P(AAc-*alt*-EA) (3). Its IR spectrum showed COO absorptions at 1730, 1240, and 1170 cm^{-1}. ^{1}H NMR absorptions in $CDCl_3$ were as follows: $OCOCH_3$ at 2.07 ppm, two types of OCH_2 at 3.8–4.3 ppm, $OCCH_3$ at 1.26 ppm, CHCOO at 2.4–2.8 ppm, and other CH_2 and CH at 1.4–1.9 ppm. The ^{13}C NMR spectrum shown in Figure 6 demonstrates the complete conversion of a chloromethyl group to an acetoxymethyl group in this polymer reaction when compared with the spectrum of precursor copolymer 1 in Figure 2. The chloromethyl absorption at 48–49 ppm have disappeared, and three new acetoxymethyl absorptions at 19, 62–68, and 169 ppm have appeared. The split peaks of the CH_2 group in an acetoxymethyl group gave the same coisotacticity ($\sigma = 0.3$) as the value given above for 1. This is a natural result of the displacement reaction that occurs on the side-chain carbon. Reactions in DMF, THF, and diethylene glycol monomethyl ether proceeded much slower. The extents of conversion of a chloromethyl group to an acetoxymethyl group in these solvents were 30, 0, and 1%, respectively, after 24h.

3 is a viscous liquid, soluble in chloroform, acetone, and THF and insoluble in methanol and water. A GPC study

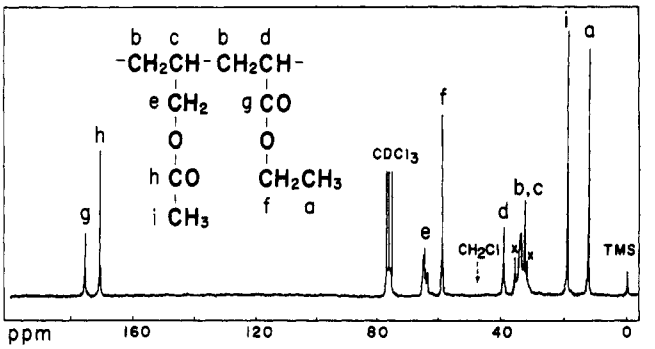


Figure 6. ^{13}C NMR spectrum of an alternating allyl acetate–ethyl acrylate copolymer. Peaks x are due to contaminating HMPA.

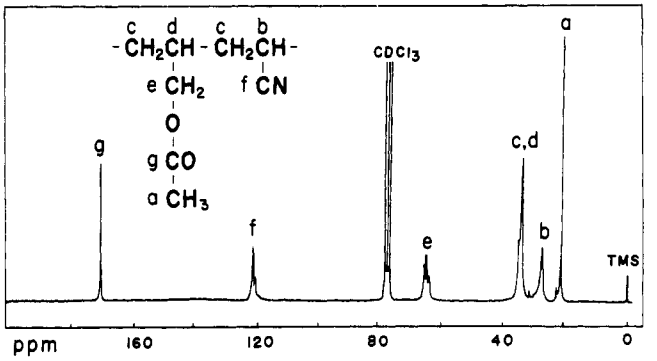


Figure 7. ^{13}C NMR spectrum of an alternating allyl acetate–ethyl acrylate copolymer.

showed that the degree of polymerization of copolymer was found unchanged during the polymer reaction (88 before and 84 after the reaction). Direct alternating copolymerization of allyl acetate–ethyl acrylate with EASC was also tried, but no polymeric product was obtained.

Synthesis of Alternating Allyl Acetate–Acrylonitrile Copolymer from Alternating Allyl Alcohol–Acrylonitrile Copolymer. To a swollen **2** (run 3 copolymer in Table III; 0.545 g, 4.90 mmol) in acetic acid (1 mL) was added acetic anhydride (1 mL, 10 mmol), and the mixture was kept at 70 °C for 24 h. The initial swollen mixture gradually turned into a homogeneous solution during the reaction. Then methanol (20 mL) was added to the solution. The precipitate was reprecipitated three times by using chloroform–methanol. The dried copolymer weighed 0.331 g (80% yield). Its molecular weight was 11 000, as already shown in Table III. Its IR and ^{1}H and ^{13}C NMR spectra showed that the copolymer was the desired alternating allyl acetate–acrylonitrile copolymer, P(AAc-*alt*-AN) (**4**). The IR spectrum showed COO absorptions at 1735, 1240, and 1040 cm^{-1} and a CN absorption at 2245 cm^{-1}. ^{1}H NMR absorptions were as follows: $OCOCH_3$ at 2.06 ppm, CHCN at 2.7–3.1 ppm, $COOCH_2$ at 3.9–4.3 ppm, and other CH_2 and CH at 1.4–2.0 ppm. Figure 7 shows CH_3, CH_2, and COO ^{13}C NMR absorptions of introduced acetoxymethyl groups at 20.7, 63–67, and 171.2 ppm, respectively. Both the split CH_2

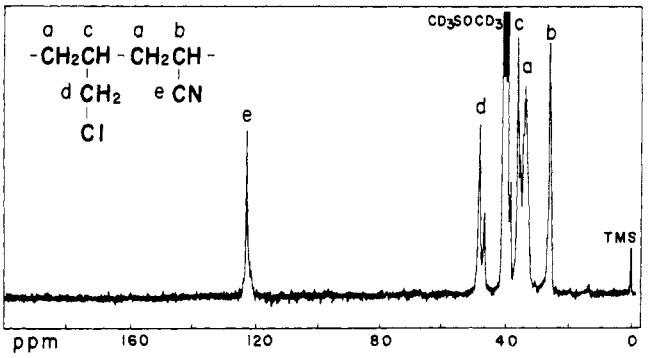


Figure 8. ^{13}C NMR spectrum of an alternating allyl chloride–acrylonitrile copolymer.

of acetoxymethyl group and CN absorptions (e and f in Figure 7) gave the same coisotacticity ($\sigma = 0.5$) as that for the precursor copolymer **2**.

4 is a white powdery material, soluble in chloroform, acetone, and THF and insoluble in methanol and water.

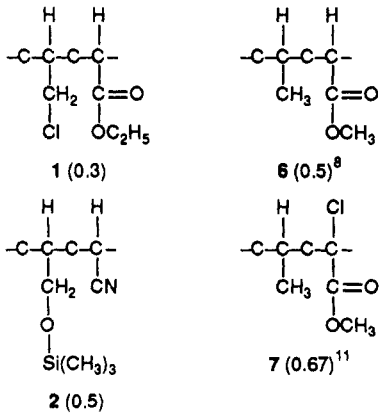
Synthesis of Alternating Allyl Chloride–Acrylonitrile Copolymer from Alternating Allyl Alcohol–Acrylonitrile Copolymer. As described above, attempted alternating copolymerization of allyl chloride and acrylonitrile gave a trace of copolymer or a complicated Friedel–Crafts type product. In this paragraph the synthesis of alternating allyl chloride–acrylonitrile copolymer, P(AC-*alt*-AN) (**5**), by a polymer reaction will be described.

According to Cohen's method,[6] chlorination of **2** was carried out. To a stirred solution of carbon tetrachloride (1.1 mL, 11.4 mmol), triphenylphosphine (3.00 g, 11.4 mmol), and HMPA (4 mL) was added **2** (run 3 copolymer in Table III; 0.425 g, 3.82 mmol), and the mixture was stirred at room temperature. After 50 h, methanol was added to precipitate the chlorinated copolymer. Repeated reprecipitations by using THF–methanol and drying in vacuo gave **5** (0.379 mg, 76.5% yield). Its molecular weight was 1.1×10^4. The copolymer structure was identified by its IR and ^1H and ^{13}C NMR spectra. The IR spectrum showed CN anc CH_2Cl absorptions at 2245 and 1300 cm^{-1}, respectively. ^1H NMR absorption in $CDCl_3$ were as follows: CHCN at 3.10 ppm, CH_2Cl at 3.7–4.1 ppm, and other CH_2 and CH at 1.4–2.3 ppm. The ^{13}C NMR spectrum in Figure 8, when compared with Figure 5, shows complete disappearance of the CH_2OH absorption at 62–64 ppm and appearance of CH_2Cl at 45–47 ppm. The split CH_2Cl peaks again gave a coisotacticity $\sigma = 0.5$.

5 is a white powdery material, soluble in DMF, DMSO, HMPA, THF, and acetone and insoluble in chloroform and methanol.

Characteristic of Alternating Copolymerization of Allyl Derivatives. As described above, EASC-complexed copolymerization of allyl chloride or ATSE with ethyl acrylate or acrylonitrile needs a very large excess of allyl monomers in the monomer feed to obtain alternating copolymers. This is in marked contrst to the alternating copolymerization of styrene or butadiene,[7] where an alternating copolymer is obtained with a wide range of monomer feed ratios. The behavior of allyl derivatives resembles that of ethylene,[8] propylene,[9] and vinyl halides[1] in the EASC-complexed alternating copolymerization with acrylic acceptor monomers. One of the proposed mechanisms of alternating copolymerization is that it occurs via a ternary complex composed of a donor monomer, an acceptor monomer, and a complexing reagent.[7] The present unconjugated and weakly donating allyl monomers are supposedly not able to form enough of such a ternary complex to give an alternating copolymer except when they are fed in very large excess. We[10] have studied by ^1H NMR the formation of a ternary complex in the case of 1-octene–methyl acrylate–EASC copolymerization and arrived at this conclusion.

Tacticity of Alternating Copolymers. Now we have determined some coisotacticities, σ, for the following alternating copolymers.



Numerals in parentheses give σ values. Copolymers **6** and **7** are cited from our previous results.[8,11] Copolymer **2** was actually isolated as a desilylated allyl alcohol copolymer as described above. Copolymers **2** and **6** give $\sigma = 0.5$, which shows their completely atactic structure. Copolymer **1** gives a smaller coisotacticity ($\sigma = 0.3$) than copolymer **6** does. This indicates a repulsive effect of the chlorine substituent against the ester substituent in the cross-propagation step of copolymerization. The chlorine substituent at the α-position of the acrylate unit in copolymer **7** acts inversely and gives $\sigma = 0.67$.

Glass Transition Temperatures of Copolymers. T_g values of copolymers synthesized in this paper were determined by a DSC method in the range of −50 to +150 °C. Heating traces usually showed clearer and more reproducible results than cooling traces, and T_g values were taken as their inflection points. The T_g values thus determined will be given in the succeeding paper and discussed together with the data of related copolymers.

Acknowledgment. This study is partly supported by a Grant-in-Aid fcr Co-operative Research (A), The Ministry of Education, Science and Culture, Japan.

References and Notes

(1) Hirabayashi, T.; Yamauchi, K.; Yokota, K. *Macromolecules* **1990**, *23*, 935.
(2) Yokota, K.; Hirabayashi, T. *Macromolecules* **1981**, *14*, 1613.
(3) Hirabayashi, T.; Yamauchi, K.; Yokota, K. Following paper in this issue.
(4) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; 2nd ed.; Pergamon Press: Oxford, 1980.
(5) Murahasi, S.; Nozakura, S.; Hatada, K. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 631.
(6) Cohen, H. I. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1993.
(7) Bamford, C. H. In *Alternating Copolymerization*; Cowie, J. M. G., Ed.; Plenum Press: New York, 1985.
(8) Yokota, K.; Hirabayashi, T. Unpublished data.
(9) Logothetis, A. L.; McKenna, J. M. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2797.
(10) Yokota, K.; Iida, Y.; Hirabayashi, T. Unpublished data.
(11) Hirabayashi, T.; Yokota, K. *Polym. J.* **1988**, *20*, 1031.