Synthesis of Sequence-Ordered Copolymers. 2. Synthesis of Some Alternating and Periodic Copolymers by Polymer Reactions

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ABSTRACT: Alternating styrene–allyl alcohol, styrene–allyl acetate, and styrene–propylene copolymers were synthesized from alternating styrene–methyl acrylate copolymer. Periodic ethylene–ethylene–allyl (or methallyl) alcohol and ethylene–ethylene–allyl (or methallyl) acetate copolymers were synthesized from periodic ethylene–ethylene–methyl acrylate (or methacrylate) copolymer. Glass transition temperatures of these copolymers were determined by differential scanning calorimetry and discussed in terms of their structures together with the data for some related alternating copolymers synthesized in our preceding paper.

In our preceding paper,[1] we synthesized various alternating copolymers containing an allyl derivative unit. Some copolymers were obtained by direct copolymerization of allyl and acrylic monomers, and some were by polymer reactions of appropriate precursor copolymers. The present paper will report the synthesis of some other alternating and periodic copolymers and their glass transition temperatures (T_g) and discuss the T_g's in terms of copolymer structures together with the data of copolymers in the preceding and previous papers.

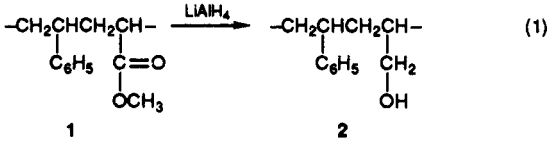
Experimental Section

Materials. Reagents were commercially available from Nacalai Tesque, Inc., Kyoto, Japan, and purified by standard method.[2] Names of solvent used are abbreviated as follows: dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *N,N,N',N',N'',N''*-hexamethylphosphoramide (HMPA), tetrahydrofuran (THF). Preparation and characterization of alternating styrene–methyl acrylate copolymer,[3] periodic ethylene–ethylene–methyl acrylate copolymer,[4] and periodic ethylene–ethylene–methyl methacrylate copolymer[5] were previously reported.

Measurement. Characterization of copolymers was carried out by ^1H and ^{13}C nuclear magnetic resonance (NMR), infrared spectroscopy (IR), and gel permeation chromatography (GPC). Details of each operation were the same as described in the preceding paper.[1] The retention time in the GPC experiment for each copolymer sample was read and assumed as a measure of copolymer molecular weight with reference to polystyrene standards. Correction for each copolymer structure was not made. T_g's of copolymers were determined by differential scanning calorimetry (DSC) on a Seiko I TA station with a DSC 210 unit in the range of −50 to +150 °C. Heating and cooling rates were 10 °C min^{-1}. Heating traces showed clearer and more reproducible results than cooling traces, and T_g values were taken as their inflection points.

Results and Discussion

Synthesis of Alternating Styrene–Allyl Alcohol Copolymer. Alternating styrene–allyl alcohol copolymer, P(St-*alt*-AA) (2), was synthesized by reducing alternating styrene–methyl acrylate copolymer, P(St-*alt*-MA) (1), with lithium aluminum hydride according to eq 1.



(1)

Preparation of sample 1 was as follows. A mixture of styrene (6.5 mL, 55 mmol), methyl acrylate (5.0 mL, 59 mmol), ethylaluminum sesquichloride (EASC)–toluene solution (1 mL, 4 mmol), and toluene (60 mL) was kept at 25 °C for 24 h. The mixture was poured into methanol (300 mL) containing a small amount of hydrochloric acid and hydroquinone. The precipitated copolymer was reprecipitated three times from chloroform into methanol and dried in vacuo. 1 with a molecular weight of 2.9×10^5 was obtained in 23% conversion. A copolymer with a molecular weight higher than 10^6 could easily be prepared by controlling copolymerization conditions, but it gave an undesirable result when subjected to reduction (gel formation and incomplete reduction). Identification of the alternating and atactic structure of 1 was already given.[3]

To a solution of the above 1 (3.00 g, 15.7 mmol) in THF (100 mL) was added $LiAlH_4$ (3.00 g, 79.0 mmol) portionwise under reflux. A large excess of $LiAlH_4$ was necessary to prevent a gel formation during the reaction. After 150 h of reflux, the reaction mixture was cooled at −20 °C and poured slowly into 10% HCl (500 mL). The precipitate was recovered from the solution by centrifugal separation and digested repeatedly with THF. The collected THF solution (150 mL) was concentrated at a reduced pressure to 20 mL and poured into 1% HCl (500 mL). The precipitated copolymer was reprecipitated three times from THF into 1% HCl and finally from THF into methanol–water (1:1). Dried copolymer 2 weighed 2.30 g (90% yield) and had a molecular weight of 2.4×10^5.

The structure of the resultant copolymer 2 was identified by ^1H and ^{13}C NMR and IR spectra in Figure 1, comparing it with the spectra (cf. lit.[3]) of precursor copolymer 1. The ^1H NMR spectrum shows that the three split absorptions of $COOCH_3$ between 3.1 and 3.5 ppm in 1 disappeared and instead a broad methylol CH_2O absorption appears at 3.2 ppm. The methylol OH absorption was observed at 11.2 ppm as a result of its proton exchange with the solvent acetic acid-d_4. The ^{13}C NMR spectrum in Figure 1b also shows the disappearance of the OCH_3 group (51.2 ppm[6]) and the appearance of the CH_2OH group (64.2 ppm). This new CH_2OH ^{13}C absorption splits into three peaks of which the intensity ratio gives a coisotacticity $\sigma = 0.5$, an identical value with that calculated[3] for 1 from the split $COOCH_3$ ^1H absorption. The IR spectrum in Figure 1c shows the disappearance of an ester C=O stretching vibration absorption at 1730 cm^{-1} and the appearance of primary alcohol O–H and C–O stretching absorptions at 3400 and 1050 cm^{-1}, respectively.

2 is a white powdery material, soluble in DMSO, DMF, HMPA, THF, and acetic acid and insoluble in methanol–water and water. It swells in toluene and cyclohexanol.

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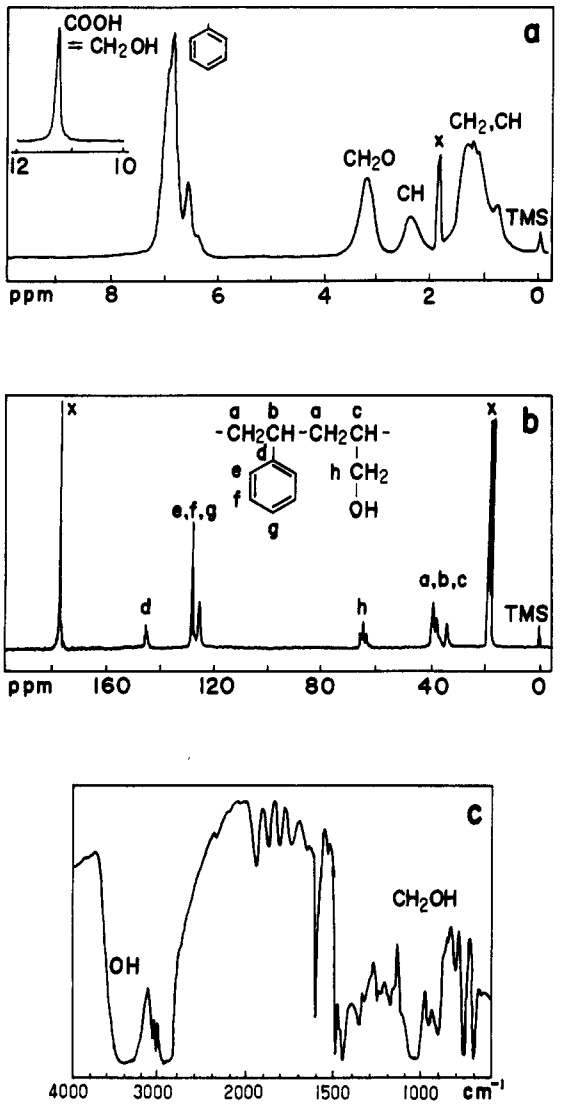


Figure 1. (a) ^1H and (b) ^{13}C NMR and (c) IR spectra of an alternating styrene–allyl alcohol copolymer. Peaks x in (a) and (b) are due to solvent, acetic acid-d_4.

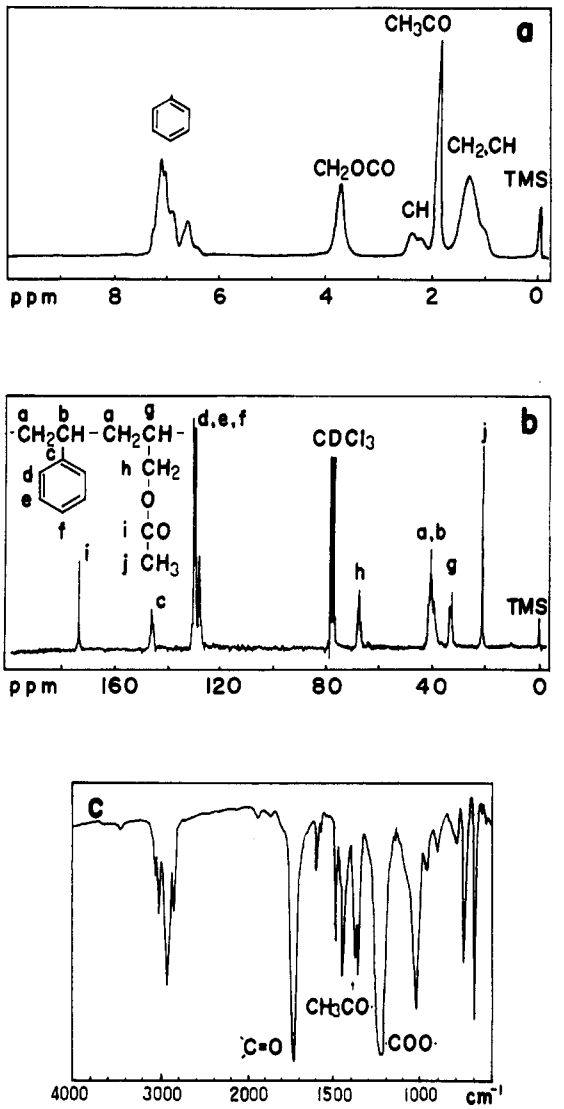
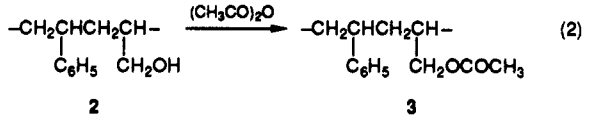


Figure 2. (a) ^1H and (b) ^{13}C NMR and (c) IR spectra of an alternating styrene–allyl acetate copolymer.

Synthesis of Alternating Styrene–Allyl Acetate Copolymer. Alternating styrene–allyl acetate copolymer, P(St-*alt*-AAc) (**3**), was synthesized from **2** according to eq 2.



(2)

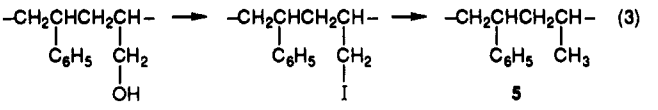
2 **3**

A mixture of **2** (200 mg, 1.23 mmol), acetic anhydride (0.5 mL, 5.3 mmol), and acetic acid (6 mL) was warmed at 70 °C for 24 h. Then the excess of acetic anhydride was reacted with added methanol, and the mixture was concentrated by evaporation and poured into water. The precipitate was reprecipitated three times from acetone into water and dried in vacuo. The dried copolymer **3** weighed 210 mg (85% yield) and had a molecular weight of 2.0×10^5.

The structure of **3** was identified by its ^1H and ^{13}C NMR and IR spectra in Figure 2. All spectra show the disappearance of CH_2OH absorptions, which are observed for **2** in Figure 1 and instead of them the appearance of CH_2OCOCH_3 absorptions of **3**.

3 is a white powdery material, soluble in DMSO, DMF, HMPA, THF, acetic acid, acetone, and chloroform and insoluble in methanol and ethanol.

Synthesis of Alternating Styrene–Propylene Copolymer. Alternating styrene–propylene copolymer, P(St-*alt*-P) (**5**), cannot be obtained by copolymerizing the monomers. In this paper, **5** is synthesized starting from **2** via alternating styrene–allyl iodide copolymer, P(St-*alt*-AI) (**4**), according to eq 3.



(3)

2 **4** **5**

Iodidation of **2** to **4** was carried out by using methyltriphenoxyphosphonium iodide (MTPPI) according to the literature.[7,8] A solution of **2** (160 mg, 0.99 mmol) and MTPPI (700 mg, 1.55 mmol) in HMPA (5 mL) was stirred at 70 °C for 50 h. The reaction mixture was poured into methanol, and the precipitate was reprecipitated three times from chloroform into methanol and dried in vacuo. The dried copolymer **4** weighed 246 mg (91% yield). Its IR spectrums showed no absorptions of primary alcohol (3400 and 1050 cm^{-1}) and a new absorption of the CH_2I group at 1210 cm^{-1} (CH_2 deformation).

Reduction of **4** to **5** was carried out by using lithium aluminum hydride. A solution of **4** (200 mg, 0.73 mmol) and $LiAlH_4$ (0.57 mg, 4.3 mmol) in THF (40 mL) was re-

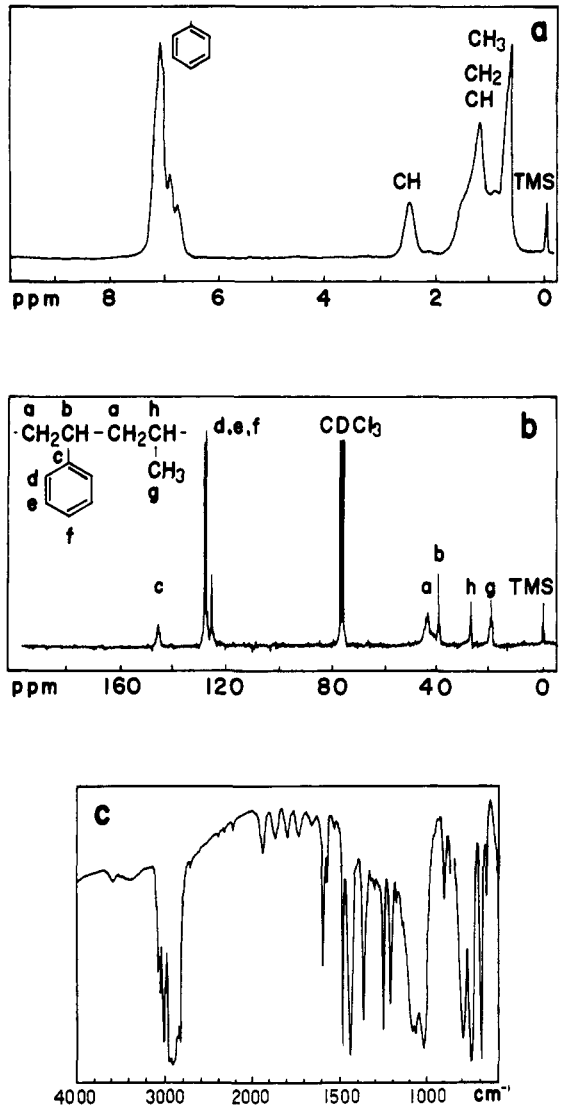


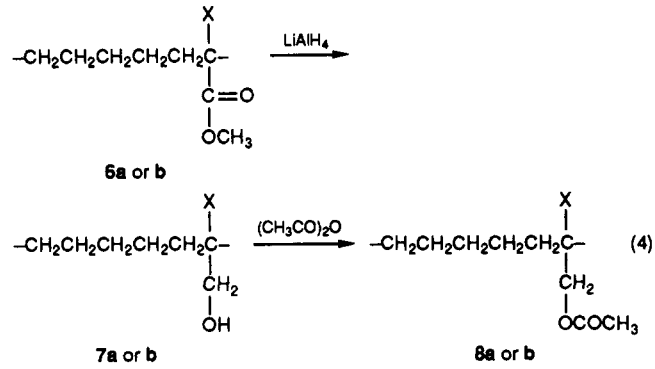
Figure 3. (a) ^1H and (b) ^{13}C NMR and (c) IR spectra of an alternating styrene–propylene copolymer.

fluxed for 200 h. Workup was the same with the procedure for isolation of **2**. The dried copolymer **5** weighed 82 mg (76%) and had a molecular weight of 2.8×10^5.

The structure of **5** was identified by its ^1H and ^{13}C NMR spectra in Figure 3. Both spectra show disappearance of CH_2I absorptions and appearance of CH_3 absorptions.

5 is a white powder, soluble in benzene, THF, and chloroform and insoluble in methanol.

Synthesis of Periodic Ethylene–Ethylene–Allyl (or Methallyl) Alcohol Copolymers and Periodic Ethylene–Ethylene–Allyl (or Methallyl) Acetate Copolymers. The tilted periodic copolymers were synthesized starting from the previously reported periodic ethylene–ethylene–methyl acrylate copolymer, P(E-*per*-E-*per*-MA) (**6a**), or periodic ethylene–ethylene–methyl methacrylate copolymer, P(E-*per*-E-*per*-MMA) (**6b**), by firstly reducing with $LiAlH_4$ and then acetylating with acetic anhydride. Synthetic experimental procedures were almost the same as in the above synthesis of alternating styrene copolymers **2** and **3**. **6a**, 0.70 g (4.93 mmol), with a molecular weight of 4.6×10^4 was reduced with $LiAlH_4$, 0.90 g (23.7 mmol), in THF (100 mL) to give **7a**, 0.62 g (81%). **6b**, 0.23 g (1.45 mmol), with a molecular weight of 1.4×10^5 was reduced with $LiAlH_4$, 0.20 g (5.30 mmol), in THF (10 mL) to give **7b**, 0.20 g (81%). Because **7a** and **7b** were soluble only in very large volumes of THF, DMSO,



X = H for **6a**, **7a** and **8a**
X = CH_3 for **6b**, **7b** and **8b**

DMF, HMPA, and acetic acid, the identification of the structures of these two periodic copolymers was difficult. Identification was carried out on the next acetylated periodic copolymers **8a** and **8b**. **7a**, 0.27 g (2.37 mmol), was reacted with acetic anhydride, 5.0 mL (52.9 mmol), in acetic acid (10 mL) to give **8a**, 0.36 g (90%), with a molecular weight of 4.8×10^4. **7b**, 0.17 g (1.30 mmol), was reacted with acetic anhydride, 1.0 mL (10.6 mmol), in acetic acid (3 mL) to give **8b**, 0.15 g (68%), with a molecular weight of 1.5×10^5. Identification of the copolymer structure was given by ^1H and ^{13}C NMR and IR spectra. Figure 4 shows spectra for **8b**. Upon their comparison to the spectra for **6b** previously given,[5] conversion of $COOCH_3$ to CH_2OCOCH_3 is evident in each spectrum.

7a and **7b** are rubbery and hardly soluble materials. **8a** is a highly viscous liquid, and **8b** is a rubbery material. Both are soluble in chloroform, acetone, and THF and insoluble in methanol.

Copolymer Structures and Their Glass Transition Temperatures. In the preceding papers and this paper, various alternating and periodic copolymers containing allylic derivative units have been synthesized by direct copolymerizations or polymer reactions. Glass transition temperatures (T_g) of these sequence-ordered copolymers were determined by DSC as the inflection points of heating traces and are summarized in Table I. Allylic homopolymers in the last line of Table I were synthesized starting from poly(methyl acrylate) by the same polymer reactions as described above. T_g of a copolymer is generally determined by its combination and composition of involved monomer units as well as their sequence distribution. Table I compares T_g's only for sequence-ordered copolymers containing various allylic monomer units, and the copolymer compositions are fixed at 1:1 or 2:1 monomer unit ratios. A study on T_g's of sequence-ordered and sequence-unordered (statistical) copolymers will be reported by us elsewhere in the near future.

The T_g values in Table I are plotted against the substituents X in copolymers are shown in Figures 5 and 6. In Figure 5, substituents X are $-COOCH_3$, $-CH_2OH$, and $-CH_2OCOCH_3$. Although some plots are lacking, the copolymers (and a homopolymer) show a general tendency of T_g as to what a substituent X they have. T_g of a copolymer with a substituent X = $-COOCH_3$ increases when the substituent X is converted into $-CH_2OH$ and then decreases when X is further converted into $-CH_2OCOCH_3$. The increments or decrements of T_g accompanied with the substituent conversion are almost the same for all of copolymers, as indicated by the paralleled lines in Figure 5. The T_g of **6b** as precipitated and dried shows an abnormally high plot but shows a normal plot for a quenched sample. Quenching was made as follows. A

Table I
Glass Transition Temperatures of Some Sequence-Ordered Copolymers

copolymer	T_g (°C) for substituent X = –CH_2Cl	–$COOCH_3$	–CH_2OH	–CH_2OCOCH_3
–$CH_2CH(C_6H_5)CH_2C(X)H$–		58	80	39
–$CH_2CH(X)CH_2C(COOC_2H_5)H$–	4			–18
–$CH_2CH(X)CH_2C(CN)H$–	53		55	20
–$CH_2CH_2CH_2CH_2CH_2C(X)H$–		–34	–3	–50
–$CH_2CH_2CH_2CH_2CH_2C(CH_3)(X)$–		45 (–6[a])	17	–19
–$CH_2C(X)H$–[b]	31	6	24	–9

[a] Determined for a quenched copolymer sample. [b] Each homopolymer was synthesized from poly(methyl acrylate).

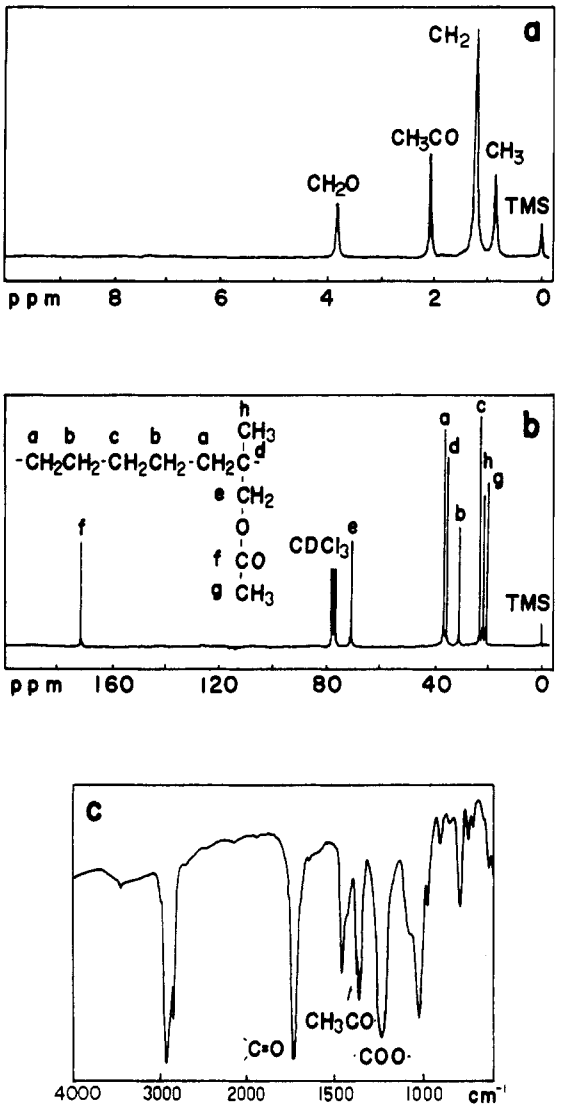


Figure 4. (a) ^1H and (b) ^{13}C NMR and (c) IR spectra of an periodic ethylene–ethylene–methallyl acetate copolymer.

copolymer sample taken in a DSC cell was first heated up to 150 °C on the DSC heating block and then cooled rapidly in air, and its heating DSC trace was recorded immediately. The unquenched, as-precipitated copolymer was already reported to show a distinct melting peak in its DSC trace and considered a partially crystalline (30%) material as a consequence of its sequence-ordered structure.[5] The quenched sample showed a very small melting peak as shown in Figure 7 and is considered almost amorphous (a less than 1% crystalline part). T_g's of many partially crystalline polymers are known to increase with its crystallinity.[9-11] Therefore, the unquenched and partially crystalline sample showed an abnormally high plot, and the quenched and almost amorphous sample showed a normal plot in Figure 5. Incidentally, 6a showed a small

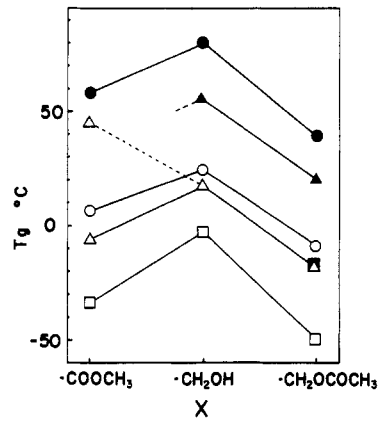


Figure 5. Glass transition temperature and copolymer structure. Copolymer symbols are as follows: ●, –$CH_2CH(X)CH_2C(C_6H_5)H$–; ▲, –$CH_2CH(X)CH_2C(CN)H$–; ■, –$CH_2CH(X)CH_2C(COOC_2H_5)H$–; □, –$CH_2CH_2CH_2CH_2CH_2C(X)H$–; △, –$CH_2CH_2CH_2CH_2CH_2C(CH_3)(X)$–; ○, –$CH_2C(X)H$–.

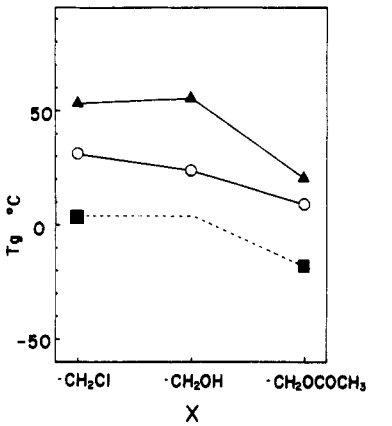


Figure 6. Glass transition temperature and copolymer structure. Copolymer symbols are the same as in Figure 5.

and indistinct melting peak at around 40 °C,[4] and other copolymers in Table I did not show any appreciable melting peak. Thus, we can discuss a substituent effect on the T_g of various sequence-ordered copolymers, all of which are amorphous or almost amorphous.

The substituent effect on T_g shown in Figure 5 may be explained as follows. When a moderately polar –$COOCH_3$ substituent of a copolymer is converted into a hydrogen-bonding –CH_2OH substituent, the T_g of the copolymer increases because of the stronger intermolecular forces by hydrogen bonding. Acetylation of the –CH_2OH substituent converts it into a –CH_2OCOCH_3 substituent and loses the hydrogen bonding and as a result gives a decreased T_g to the acetylated copolymer. Another general tendency that a copolymer with a –CH_2OCOCH_3 substituent shows a lower T_g than its precursor copolymer with a –$COOCH_3$ substituent may be explained by the presence of an additional flexible CH_2 group in the former copolymer.

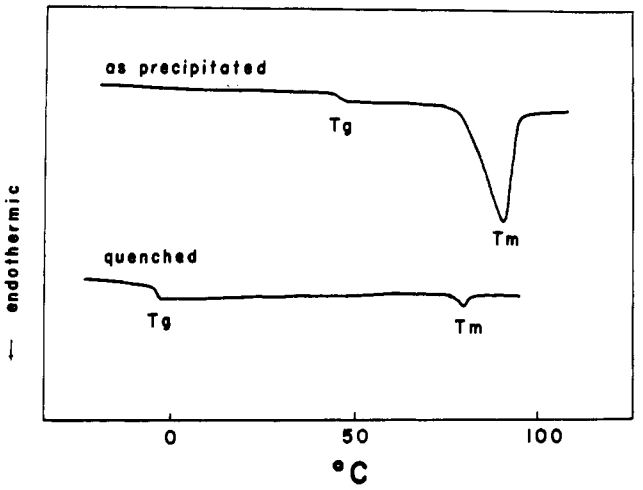


Figure 7. Heating DSC traces for a periodic ethylene–ethylene–methyl methacrylate copolymer, as precipitated and quenched samples.

In Figure 5, the styrene copolymers, $-CH_2CH(C_6H_5)-CH_2C(X)H-$, with a bulky phenyl substituent show the highest T_g's. The acrylonitrile copolymers, $-CH_2CH(X)-CH_2C(CN)H-$, with a polar cyano substituent come next, and the two-ethylene periodic copolymers, $-CH_2CH_2-CH_2CH_2CH_2C(X)H-$, with a long flexible CH_2 main chain show the lowest T_g's. Introduction of α-CH_3 into the last periodic copolymers increases T_g to some extent.

In Figure 6, T_g's of three types of copolymers are plotted against their substituents X ($-CH_2Cl$, $-CH_2OH$, and $-CH_2OCOCH_3$). The effect of substituent and backbone structure on T_g's may be explained as follows. Copolymers with the moderately polar $-CH_2OCOCH_3$ substituent show lower T_g's than copolymers with polar $-CH_2Cl$ and hydrogen-bonding $-CH_2OH$ substituents. The latter two substituents have a similar effect on T_g, as suggested by T_g's of poly(vinyl chloride) (81 °C[12]) and poly(vinyl alcohol) (85 °C[12]). The acrylonitrile copolymers show higher T_g's than the ethyl acrylate copolymers because of the more polar –CN substituent.

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References and Notes

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