Novel Periodic Copolymers Consisting of Ester and Amide Units with the Same Carbon Numbers: Effects of Comonomeric and Sequential Structures on Crystalline Structures and Physical Properties

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ABSTRACT: Four novel series of periodic copolymers composed of ester and amide units with the same carbon numbers were synthesized by two-step polycondensation reactions using adipate, linear aliphatic diols, and diamines with various chain lengths, ranging from 3 to 6 methylene groups. Effects of the comonomeric and sequential structures on the physical properties and crystalline structures were investigated for the obtained copolymer series by means of differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and tensile testing. The thermal properties of obtained periodic copolymer series were found to be strongly dependent on both comonomeric and sequential structures, and the values showed remarkable differences between neighboring methylene numbers in the comonomer units. Such thermal behavior was strongly correlated to the wide-angle X-ray diffraction patterns, with some copolymers displaying patterns similar to homopolyesters, while other copolymers had diffraction patterns that were very different than the homopolyester, dependent on the comonomeric and sequential structures. These results suggest that the molecular chain arrangements and their intermolecular hydrogen bond interactions based on the ester-amide sequential structure play an important role in the formation of a thermally stable crystalline region. Furthermore, the mechanical properties of periodic copolymers were determined from the stress−strain curves of film samples.

Introduction

Recently, aliphatic poly(ester-amide)s are attracting strong interest for environmental and biomedical applications because of their suitable biodegradability, biocompatibility, and favorable physical properties, which result from combining of the advantageous characteristics of both aliphatic polyester and polyamide. While the ester linkages in the chain provide good hydrolysis properties, the amide groups can enhance the thermal and mechanical properties because of strong intermolecular hydrogen bond interactions. Enzymatic degradation of the copolymers synthesized by ester-amide interchange reaction between nylon and polycaprolactone was first reported in 1979.[1] Since then, many types of poly(ester-amide)s with random or alternate introduced amide groups in the main chain or incorporated in the polymer, either as blocks or as segments, have been prepared by various methods using aliphatic chemicals, such as dicarboxylic acids, amino acids, hydroxyl acids, diols, and their derivatives, widening the range of applications of these materials.[2−27]

In our previous work,[20] aliphatic poly(ester-amide)s with defined periodic sequence consisting of ester and amide groups were synthesized by two-step polycondensation reactions using adipate, butane-1,4-diamine, and linear diols with various chain lengths, and their structures and thermal properties were characterized. The thermal properties of these copolymer series were strongly dependent on both the monomeric and ester-amide sequential structures, and the values could be regulated in a wide temperatures range. In addition, the wide-angle X-ray diffraction patterns of the copolymers also varied with the monomeric and sequential structures, indicating that the molecular chain arrangement based on the periodic ester-amide sequence and their intermolecular hydrogen bond interactions played a decisive role in the formation of a thermally stable crystalline region. Recently, Feijen et al.[21,22] have synthesized the aliphatic segmented poly(ester-amide)s composed of well-defined amide groups using bisamide-diols and showed that the physical properties, such as melting temperature and tensile strength, of these copolymers had a strong dependence on the length and symmetry of ester-amide sequence in the main chain. Puiggalí et al.[23−26] came to the same conclusion for the poly(ester-amide)s with uniform repeating units containing the ester-amide linkages derived from amino acids. The results show that the molecular structures of crystallizable ester-amide sequences, when introduced with high regularity in the polymer, are an important factor for the regulation of thermal and mechanical properties.

In this study, we focused on the molecular structures of defined ester-amide sequences and synthesized periodic poly(ester-amide)s series consisting of ester and amide units with the same carbon numbers by two-step polycondesation reactions using adipate, aliphatic diols, and diamines (Figure 1). The structures, thermal properties, and crystalline morphologies of the obtained copolymers were characterized by NMR spectroscopy, differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD). The linear aliphatic diols and diamines containing both odd and even methylene groups were used as comonomers, and their combinations with the same methylene number were applied to prepare the copolymers in an effort to study the influences of ester-amide sequential structures on the thermal properties and crystalline structures. In addition, the mechanical properties of periodic poly(ester-amide)s were investigated by monitoring the stress−strain curves

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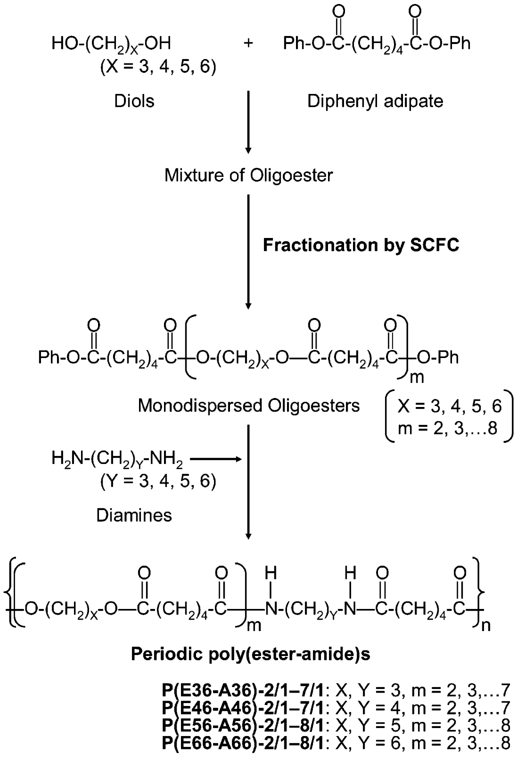

Figure 1. Synthesis and chemical structures of novel periodic copolymers consisting of ester and amide units with the same carbon numbers.

of their films. By comparison of the periodic copolymer series based on various types of ester-amide sequences, the relationships among their molecular structures, crystalline structures, and material properties were investigated.

Experimental Section

Materials. Basic materials were purchased from Kanto Chemical Co. Phenol, dimethyl adipate, diols (propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, and hexane-1,6-diol), and diamines (propane-1,3-diamine, butane-1,4-diamine, pentane-1,5-diamine, and hexane-1,6-diamine) were used as supplied without further purification.

Synthesis. Diphenyl adipate, oligoesters, and homopolyesters were prepared as previously described.[20] Diphenyl adipate synthesized by an exchange reaction between phenol and dimethyl adipate were used in order to prepare the oligoesters with nucleophilic phenyl ester end groups. Homopolyesters were synthesized by polycondensation reaction of dimethyl adipate with each diol in the presence of titanium tetraisopropoxide ($Ti(O^iPr)_4$) as a catalyst, and the reaction conditions were regulated in order to obtain homopolymers and copolymers of comparable molecular weights.

Fractionation of Monodispersed Oligoesters with Symmetric Structure. Fractionation of monodispersed oligoesters was performed on a JASCO supercritical fluid chromatography (SCFC) system with an MD-2010 plus multiwavelength detector. A stainless steel column (200 × 20 mm^2) containing silicagel (10−20 μm) (SFC Megapak SIL(10/20); JASCO) was used for fractionation at 60 °C. A mixture of supercritical carbon dioxide and acetonitrile was applied as eluent, and the pressure of the eluent was regulated at 12 MPa. The flow rate of carbon dioxide was maintained at 4 mL·in^{-1}, while the rate of acetonitrile was linearly increased for each condition. The oligoesters were detected spectrophotometrically at a wavelength of 210 nm. Each fraction of oligoester was collected from the eluate, and the solvent was evaporated. The purity and structure of each fractionated oligoester were evaluated by ^{1}H NMR analysis (see Table 1 and Figure 2A), MALDI-ToF MS analysis, and the reinjection analysis of oligoesters in SCFC as previously reported.[20]

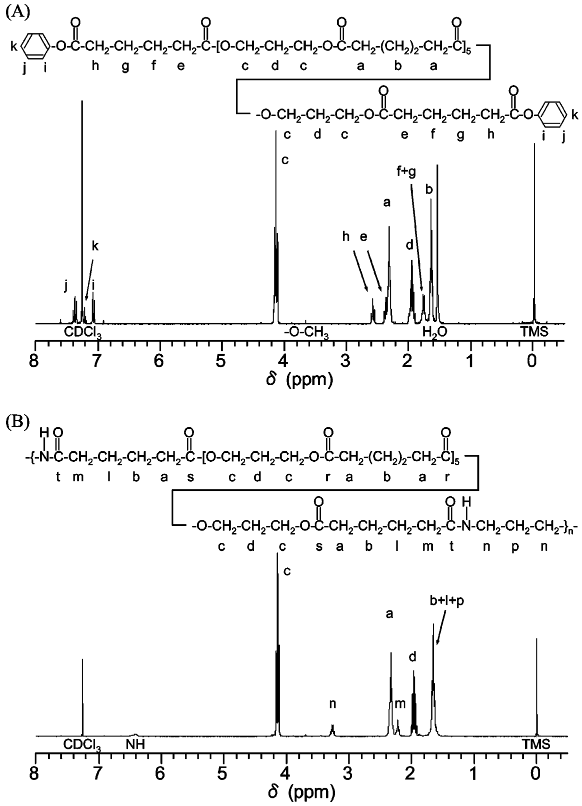

Figure 2. ^{1}H NMR spectra of fractionated oligomer of trimethylene adipate with 6 repeating units derived from diphenyl adipate and propan-1,3-diol (A), and produced copolymer (sample P(E36-A36)-6/1) from condensation of monodispersed oligomer of trimethylene adipate with 6 repeating units and propane-1,3-diamine (B).

Table 1. Purities of Isolated Oligoesters with Symmetric Structures

		purity[a]			
		oligomers of oligo-methylene adipate			
fraction no.	repeating no. of ester unit	tri- (mol %)	tetra-[b] (mol %)	penta- (mol %)	hexa- (mol %)
1	2	95	97	93	97
2	3	95	98	94	98
3	4	96	97	97	97
4	5	94	97	94	96
5	6	95	94	94	97
6	7	96	89	91	97
7	8			90	97

[a] ^{1}H NMR purities as lowest values calculated from the ratio of end groups. [b] Data from ref 20.

Copolymerization of Monodispersed Oligoesters with Diamines. Periodic copolymers were synthesized by the condensation reaction between diamine and monodispersed oligoester in the absence of catalyst. Equimolar amounts of monodispersed oligoester and diamine were placed into a reactor under nitrogen. The copolymerization was carried out at 120 °C and atmospheric pressure for 6 h. The products were dissolved in chloroform or trifluoroethanol and precipitated in cold methanol or diethyl ether at 0 °C. The precipitate was dried under vacuum at room temperature. Obtained periodic copolymer series were coded as follows; P(Exa-Ayb)-c/d: x and a show the carbon numbers of diol and adipate components respectively in ester (E) unit, y and b show the carbon numbers of diamine and adipamic acid components respectively in amide (A) unit, c and d show the repeating numbers of ester and amide units respectively in the copolymer sample. In this study, four series of copolymers, P(E36-A36), P(E46-A46), P(E56-A56), and P(E66-A66), were synthesized (see Figure 1).

Poly(trimethylene adipate-*per*-trimethylene adipamide), polymer code: P(E36-A36). ^{1}H NMR ($CDCl_3$, TMS, int ref): δ 4.15 (t,

$\mathrm{OC}H_2$), 3.27 (br q, $\mathrm{NHC}H_2$), 2.33 (br t, $\mathrm{OCOC}H_2$), 2.20 (br t, $\mathrm{NHCOC}H_2$), 1.97 (br m, $\mathrm{OCH_2C}H_2$), 1.66 (br m, $\mathrm{OCOCH_2C}H_2$, $\mathrm{NHCOCH_2C}H_2$, and $\mathrm{NHCH_2C}H_2$). ^{13}C NMR ($\mathrm{CDCl_3}$, TMS, int ref): δ 173.37 ($\mathrm{NH}C\mathrm{O}$), 173.21 ($\mathrm{O}C\mathrm{O}$), 60.94 ($\mathrm{O}C\mathrm{H_2}$), 36.35 ($\mathrm{NH}C\mathrm{H_2}$), 35.65 ($\mathrm{NHCO}C\mathrm{H_2}$), 33.78 ($\mathrm{OCO}C\mathrm{H_2}$), 27.98 ($\mathrm{OCH_2}C\mathrm{H_2}$), 25.17 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 24.42 ($\mathrm{NHCOCH_2}C\mathrm{H_2}$), 24.32 ($\mathrm{OCOCH_2}C\mathrm{H_2}$).

Poly(tetramethylene adipate-*per*-tetramethylene adipamide) in our previous research,[20] polymer code: P(E46-A46). ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, int ref): δ 4.09 (t, $\mathrm{OC}H_2$), 3.26 (br q, $\mathrm{NHC}H_2$), 2.33 (br t, $\mathrm{OCOC}H_2$), 2.20 (br t, $\mathrm{NHCOC}H_2$), 1.70 (br m, $\mathrm{OCH_2C}H_2$), 1.66 (br m, $\mathrm{OCOCH_2C}H_2$ and $\mathrm{NHCOCH_2C}H_2$), 1.53 (br m, $\mathrm{NHCH_2C}H_2$). ^{13}C NMR ($\mathrm{CDCl_3}$, TMS, int ref): δ 173.56 ($\mathrm{NH}C\mathrm{O}$), 173.31 ($\mathrm{O}C\mathrm{O}$), 63.85 ($\mathrm{O}C\mathrm{H_2}$), 39.01 ($\mathrm{NH}C\mathrm{H_2}$), 36.26 ($\mathrm{NHCO}C\mathrm{H_2}$), 33.86 ($\mathrm{OCO}C\mathrm{H_2}$), 26.94 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 25.30 ($\mathrm{OCH_2}C\mathrm{H_2}$), 25.12 ($\mathrm{NHCOCH_2}C\mathrm{H_2}$), 24.38 ($\mathrm{OCOCH_2}C\mathrm{H_2}$).

Poly(pentamethylene adipate-*per*-pentamethylene adipamide), polymer code: P(E56-A56). ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, int ref): δ 4.07 (t, $\mathrm{OC}H_2$), 3.23 (br q, $\mathrm{NHC}H_2$), 2.35 (br t, $\mathrm{OCOC}H_2$), 2.19 (br t, $\mathrm{NHCOC}H_2$), 1.66 (br m, $\mathrm{OCH_2C}H_2$, and $\mathrm{OCOCH_2C}H_2$), 1.52 (br m, $\mathrm{NHCH_2C}H_2$), 1.43 (br m, $\mathrm{OCH_2CH_2C}H_2$, and $\mathrm{NHCH_2CH_2C}H_2$). ^{13}C NMR ($\mathrm{CDCl_3}$, TMS, int ref): δ 173.61 ($\mathrm{NH}C\mathrm{O}$), 173.37 ($\mathrm{O}C\mathrm{O}$), 64.15 ($\mathrm{O}C\mathrm{H_2}$), 39.10 ($\mathrm{NH}C\mathrm{H_2}$), 36.26 ($\mathrm{NHCO}C\mathrm{H_2}$), 33.88 ($\mathrm{OCO}C\mathrm{H_2}$), 29.11 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 28.27 ($\mathrm{OCH_2}C\mathrm{H_2}$), 25.15 ($\mathrm{NHCOCH_2}C\mathrm{H_2}$), 24.39 ($\mathrm{OCOCH_2}C\mathrm{H_2}$), 23.88 ($\mathrm{NHCH_2CH_2}C\mathrm{H_2}$), 22.43 ($\mathrm{OCH_2CH_2}C\mathrm{H_2}$).

Poly(hexamethylene adipate-*per*-hexamethylene adipamide), polymer code: P(E66-A66). ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, int ref): δ 4.06 (t, $\mathrm{OC}H_2$), 3.23 (br q, $\mathrm{NHC}H_2$), 2.33 (br t, $\mathrm{OCOC}H_2$), 2.20 (br t, $\mathrm{NHCOC}H_2$), 1.66 (br m, $\mathrm{OCH_2C}H_2$, and $\mathrm{OCOCH_2C}H_2$), 1.51 (br m, $\mathrm{NHCH_2C}H_2$), 1.37 (br m, $\mathrm{OCH_2CH_2C}H_2$, and $\mathrm{NHCH_2CH_2C}H_2$). ^{13}C NMR ($\mathrm{CDCl_3}$, TMS, int ref): δ 173.61 ($\mathrm{NH}C\mathrm{O}$), 173.41 ($\mathrm{O}C\mathrm{O}$), 64.31 ($\mathrm{O}C\mathrm{H_2}$), 39.01 ($\mathrm{NH}C\mathrm{H_2}$), 36.31 ($\mathrm{NHCO}C\mathrm{H_2}$), 33.91 ($\mathrm{OCO}C\mathrm{H_2}$), 29.47 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 28.52 ($\mathrm{OCH_2}C\mathrm{H_2}$), 26.04 ($\mathrm{NHCOCH_2}C\mathrm{H_2}$), 25.61 ($\mathrm{OCOCH_2}C\mathrm{H_2}$), 25.16 ($\mathrm{NHCH_2CH_2}C\mathrm{H_2}$), 24.42 ($\mathrm{OCH_2CH_2}C\mathrm{H_2}$).

Compositions of Poly(ester-amide)s. Compositions of the produced copolymers were calculated from the ^{1}H NMR spectra. The amide contents (mol %) in the copolymers were determined by integration of the proton resonances of four distinct peaks, (c) (4.06−4.15 ppm: $\mathrm{OC}H_2$), (n) (3.23−3.27 ppm: $\mathrm{NHC}H_2$), (a) (2.33−2.35 ppm: $\mathrm{OCOC}H_2$), and (m) (2.19−2.20 ppm: $\mathrm{NHCOC}H_2$) (see Figure 2B), as in the following two equations:

$$\text{Amide mol \%} = \left(\frac{\mathrm{n}}{\mathrm{c}+\mathrm{n}}\right) \times 100\% = \left(\frac{\mathrm{m}}{\mathrm{a}+\mathrm{m}}\right) \times 100\%$$

For any cases, the calculated values from two equations were in good agreement with each other.

Analytical Procedure. ^{1}H NMR analysis of oligoester and poly(ester-amide) samples was carried out on a JNM AL-300 spectrometer. The samples (5 mg·mL^{-1}) were dissolved in either $\mathrm{CDCl_3}$ or $\mathrm{CF_3CD_2OD}$, and the 300 MHz ^{1}H NMR spectra were recorded at 23 °C with a 6.2 μs pulse width (45° pulse angle), 3 s pulse repetition, 6000 Hz spectroscopic width, and 16K data points.

^{13}C NMR analysis of poly(ester-amide) samples was performed with a JNM AL-300 spectrometer. The samples (30 mg·mL^{-1}) were dissolved in either $\mathrm{CDCl_3}$ or $\mathrm{CF_3CD_2OD}$, and the 75 MHz ^{13}C NMR spectra were recorded at 23 °C with a 3.8 μs pulse width (45° pulse angle), 1.4 s pulse repetition, 20 000 Hz spectroscopic width, and 32K data points.

MALDI MS data recorded using a time-of-flight MALDI MS spectrometer (Ultraflex, Bruker) with reflector and positive-ion models. Ions were generated using a nitrogen laser operating at wavelength 337 nm. The spectra were obtained from the 250 laser shots accumulated. For the sample preparation, 0.5 mg of 2,5-dihyroxybenzoic acid as the matrix and 10 μL of methanol were added to about 10 mg of the fractionated oligoester samples in 100 μL of tetrahydrofuran. For the analysis, 0.5 μL of the mixed solution was spotted on the sample slide and dried in air.

All molecular weight data were obtained by gel-permeation chromatography at 40 °C, using a Shimadzu 10A GPC system and a 10A refractive index detector with Shodex K-806M and K-802 columns. Chloroform was used as an eluent at a flow rate of 0.8 mL·min^{-1}, and a sample concentration of 1.0 mg·mL^{-1} was applied. Polystyrene standards with a low polydispersity were used to make a calibration curves.

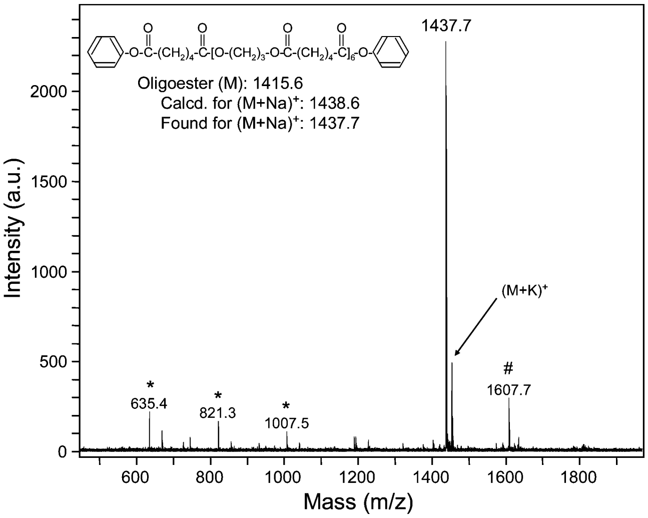

Figure 3. Time-of-flight MALDI MS spectrum of fractionated oligomer of trimethylene adipate with 6 repeating units derived from diphenyl adipate and propan-1,3-diol, (#: from impurities with an asymmetric structure; *: from decomposition products at measurement).

Differential scanning calorimetry (DSC) data of polyester and poly(ester-amide) samples were recorded in the temperature range of −100−300 °C on a Perkin-Elmer Pyris 1 equipped with a cooling accessory under a nitrogen flow of 20 mL·min^{-1}. Samples of 3−5 mg were encapsulated in aluminum pans and heated at a rate of 20 °C·min^{-1}. The melting temperature (T_m) and enthalpy of fusion (ΔH_m) were determined from the DSC endotherms of the first heating process. The T_m was taken as the peak temperature. For the measurement of the glass-transition temperature (T_g), the samples were rapidly quenched to −100 °C. They were heated from −100 to 200 °C at a heating rate of 20 °C·min^{-1}. The T_g was taken as the midpoint of the change in heat capacity.

Wide-angle X-ray diffraction (WAXD) patterns of polymer samples were recorded at 23 °C on a Rigaku RINT 2500 system using a nickel-filtered Cu Kα radiation (λ = 0.154 nm, 40 kV, 110 mA) in the 2θ range of 6−60° at a scanning speed of 2.0 deg·min^{-1}. The crystallinities of polymer samples were calculated from the ratio of integrals for the crystalline and amorphous areas to overall intensity of first dimensional profile according to Vonk's method.[28]

The Young's modulus, yield strength, tensile strength, and elongation at break for solvent cast films of polymer samples were determined using a tensile testing machine (EZtest, Shimadzu Co, Japan) at a crosshead speed of 10 mm·min^{-1}. The gauge length and the sample width were 10 mm and approximately 2 mm, respectively. The average of six measured values was taken for each sample.

Results and Discussion

Characterization. Oligoesters were prepared by a condensation reaction of each diol with an excess of adipate, and the products were then isolated after fractionation using supercritical fluid chromatography (SCFC) (Figure 1). In our previous research,[20] it was shown that SCFC could be used to separate the oligoesters on the basis of their specific chain length and that each fraction was a monodispersed oligoester with a defined structure. The time-of-flight MALDI MS spectra of the fractionated oligoesters (Figure 3) revealed the characteristic signal of an ionomer with the suitable mass corresponding to the chemical

Table 2. Polymerization Results, Compositions, and Molecular Weights of Periodic Copolymers and Homopolyesters

				amide fraction		molecular weight[b]	
sample no.	macromonomer (ester unit)/(*amide unit*)	repeating no. of ester unit	polymer yield (%)	mol % (theor)	mol %[a] (exptl)	M_n	M_w/M_n
P(E36-A36)-2/1	trimethylene adipate	2	66	33	33	[d]	
P(E36-A36)-3/1	/*trimethylene adipamide*	3	68	25	25		
P(E36-A36)-4/1		4	65	20	19		
P(E36-A36)-5/1		5	78	17	16	13 900	2.0
P(E36-A36)-6/1		6	72	14	14	14 900	2.0
P(E36-A36)-7/1		7	80	13	12	21 600	2.0
P(E46-A46)-2/1[c]	tetramethylene adipate	2	68	33	34		
P(E46-A46)-3/1	/*tetramethylene adipamide*	3	62	25	26		
P(E46-A46)-4/1		4	67	20	20		
P(E46-A46)-5/1		5	63	17	17	15 200	2.6
P(E46-A46)-6/1		6	71	14	15	12 800	2.2
P(E46-A46)-7/1		7	56	13	13	14 000	2.4
P(E56-A56)-2/1	pentamethylene adipate	2	86	33	34		
P(E56-A56)-3/1	/*pentamethylene adipamide*	3	76	25	25		
P(E56-A56)-4/1		4	86	20	20		
P(E56-A56)-5/1		5	84	17	16	17 100	2.0
P(E56-A56)-6/1		6	82	14	14	19 600	2.1
P(E56-A56)-7/1		7	81	13	13	20 200	2.1
P(E56-A56)-8/1		8	62	11	11	24 600	2.1
P(E66-A66)-2/1	hexamethylene adipate	2	87	33	33		
P(E66-A66)-3/1	/*hexamethylene adipamide*	3	82	25	24		
P(E66-A66)-4/1		4	76	20	20	34 000	2.4
P(E66-A66)-5/1		5	84	17	17	36 200	2.5
P(E66-A66)-6/1		6	84	14	14	51 400	2.1
P(E66-A66)-7/1		7	83	13	12	32 900	2.0
P(E66-A66)-8/1		8	79	11	11	48 600	2.0
poly(trimethylene adipate)			74	0	0	18 500	1.5
poly(tetramethylene adipate)			81	0	0	17 000	1.8
poly(pentamethylene adipate)			83	0	0	25 800	1.5
poly(hexamethylene adipate)			74	0	0	35 000	1.4

[a] Determined from ^{1}H NMR spectra. [b] Determined by GPC analysis. [c] Data from ref 20 for P(E46-A46) series. [d] Not determined

structure assigned by ^{1}H NMR spectroscopy analysis (Figure 2A). Thus, the symmetric oligoesters with a single composition could be obtained with high purity (see Table 1), although small amounts of impurities were also detected as the asymmetric oligoesters consisting of methyl ester or hydroxyl chain ends for some samples. Other fractionated oligomers of tetra-, penta-, and hexamethylene adipate were characterized in a similar way.

Subsequently, the reactions of the produced monodispersed oligoesters with diamines were carried out in the absence of catalyst at 120 °C for 6 h under nitrogen. In this study, the combinations of oligoesters and diamine with the same carbon numbers of the diol unit in the oligoesters were applied for the copolymer preparation (see Figure 1). At the initial stage of the reaction, the mixtures of oligoesters and diamine were observed in a molten state, but the viscosity of the mixtures radically increased as condensation reaction progressed. By using the oligomers with nucleophilic phenyl ester end groups as macromonomers,[27] polymeric products could be easily obtained in any case.

Table 2 lists the results of the polymerization of monodispersed oligoesters with diamines. Four series of copolymers, from trimethylene adipate and propane-1,3-diamine (P(E36-A36)), from tetramethylene adipate and butane-1,4-diamine (P(E46-A46)), from pentamethylene adipate and pentane-1,5-diamine (P(E56-A56)), and from hexamethylene adipate and hexane-1,6-diamine (P(E66-A66)), were obtained from monodispersed oligoesters with different chain lengths in satisfactory yields (56−88%). As previously reported for P(E46-A46) series,[20] the copolymer samples for P(E36-A36), P(E56-A56), and P(E66-A66) series were also characterized on the basis of ^{1}H and ^{13}C NMR spectroscopy analyses. Figure 2B shows the typical ^{1}H NMR spectrum of the products from the condensation reaction of monodispersed oligomer of trimethylene adipate and propane-1,3-diamine. The methylene proton signals and phenyl proton signals arising from adipate phenyl ester end groups (peaks (e−k) in Figure 2A) completely disappeared in the ^{1}H NMR spectra. New peaks assigned to the methylene protons of adipamic acid and propane-1,3-diamine units (peaks (l−p) in Figure 2B) were detected in addition to the methylene proton signals of adipate and propane-1,3-diol units in oligoesters. On the basis of the respective peak intensities, the molar ratios of each unit were calculated to be adipate/propane-1,3-diol/adipamic acid/propane-1,3-diamine = (m − 1):m:2:1 in any cases, and the m values constantly corresponded to the repeating numbers of ester unit, ranging from 2 to 7, in initial oligoesters. These results show that the amidation reaction between the phenyl ester chain ends of oligoesters and the diamines progressed selectively and that the obtained copolymers had a periodical sequence corresponding to the chain length of initial monodispersed oligoesters. Additionally, as shown in Figure 4, the distinct and simple signals were detected in the ^{13}C NMR spectra of copolymers for peaks (r−t) (CO: 173−174 ppm), (c) (OCH$_2$: 60−65 ppm), (n) (NHCH$_2$: 36−40 ppm), and (a) and (m) (OCOCH$_2$ and NHCOCH$_2$: 33−37 ppm), which were sensitive for the microstructure in the main chain, indicating that the identical ester-amide sequences were introduced with high regularity in the produced copolymers. Similarly, the copolymers derived from each monodispersed oligomer of pentamethylene adipate, and hexamethylene adipate with various chain lengths and the diamines were characterized on the basis of NMR analyses, and it was confirmed that all of the produced copolymers had defined periodic sequences composed of ester

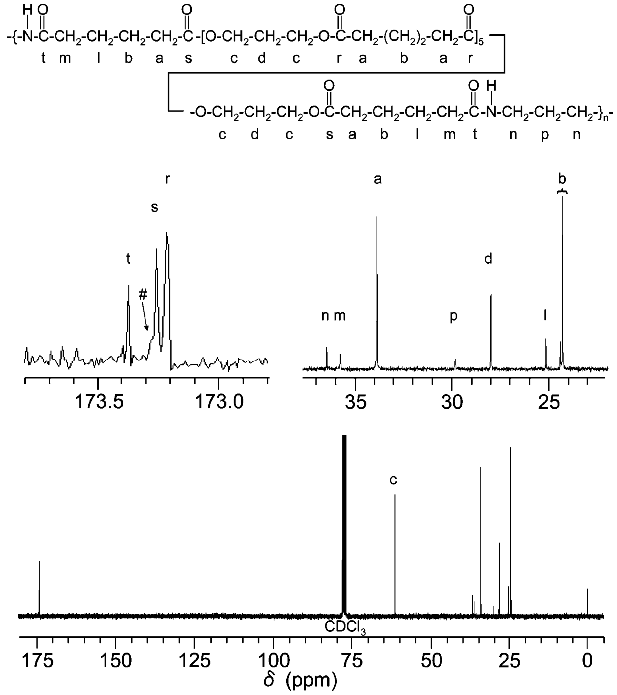

Figure 4. ^{13}C NMR spectra of produced copolymer (sample P(E36-A36)-6/1) from condensation of monodispersed oligomer of trimethylene adipate with 6 repeating units and propane-1,3-diamine, (#: from methyl ester of hydroxyl chain end).

and amide groups with the same carbon numbers (Figure 1 and Table 2). For some samples, small signals arising from methyl ester or hydroxyl chain end were detected in the ^{1}H and ^{13}C NMR spectra (Figures 2B and 4). As explained above, these signals originated from the asymmetric oligoesters left as impurities (see Figures 2A and 3), which may act as a chain-stopper or slow the chain extension due to low activity in the polymerization process. However, only little loss of periodicity or uniformity for the sequential structures was observed in any of the copolymer samples (see Table 2).

Solubilities of the obtained copolymers were dependent on their compositions. Thus, the copolymers with short ester sequences ranging from 2 to 4 repeating units although soluble in trifluoroethanol were nearly insoluble in chloroform, while those having long ester sequences ranging from 5 to 8 repeating units could be dissolved in chloroform. The solubility behavior may be due to the hydrogen bonds formed with amide groups, which have a strong relation to the structures of ester-amide sequences.

The molecular weights (M_n) and polydispersity indices (M_w/M_n) of chloroform-soluble samples for the produced periodic copolymers were determined by means of GPC using a calibration with polystyrene standards (Table 2). For the P(E36-A36), P(E46-A46), and P(E56-A56) series, copolymer samples had comparable M_n values in the range of 12 800−24 600. On the other hand, P(E66-A66) samples could be obtained with relatively high molecular weights ranging from 32 900 to 51 400 as compared with the other series. The difficulty of retaining 1:1 stoichiometry during the polycondensation reaction of oligoesters and diamines may be due to the loss of a small fraction of highly volatile diamine as the reaction progresses.[27]

Thermal Properties. The thermal properties of periodic copolymer samples were determined by DSC measurements. The results, together with the data of homopolyesters, are listed in Table 3. The glass-transition temperatures (T_g) were detected in the DSC curves for the P(E36-A36), P(E56-A56), and P(E66-A66) samples and increased with high amide content in the copolymer. However, for the P(E46-A46) samples, the distinct changes in heat capacity corresponding to the glass-transition phenomenon could not be observed in the DSC curves because the crystallization was too fast during the cooling process from the melting state.

The melting temperatures (T_m) of periodic poly(ester-amide)s series also tended to increase with high amide content in the copolymer. However, remarkable differences in the increased temperature range were observed among four series of copolymers. The T_m values of P(E46-A46) series were detected over 200 °C in any cases and were much higher than the T_m (62 °C) of poly(tetramethylene adipate) homopolyester. On the other hand, the T_m values of the P(E36-A36), P(E56-A56), and P(E66-A66) series showed a slight increase with an increase in amide content, while no great difference of the T_m values was observed between copolymer samples with less than 20 mol % amide content and homopolyesters composed of the same ester units (Table 3). For the P(E36-A36) and P(E66-A66) series, some samples had two distinct melting peaks (samples P(E36-A36)-2/1-5/1 and P(E66-A66)-2/1 in Table 3). These transitions, depending on the amide content, may be ascribed to the melting of lamellar crystals composed of single ester-amide sequences or of two or more ester-amide sequences, as reported elsewhere.[20−22]

The melting temperatures of periodic poly(ester-amide)s with each amide content showed that the T_m values of the copolymer samples with an even number of methylene groups in the comonomer units were higher than those of the copolymer samples with an odd number of methylene groups (Table 3 and Figure 5A). Previously, we synthesized another four series of periodic poly(ester-amide)s, from trimethylene adipate and butane-1,4-diamine (P(E36-A46)), from tetramethylene adipate and butane-1,4-diamine (P(E46-A46)), from pentamethylene adipate and butane-1,4-diamine (P(E56-A46)), and from hexamethylene adipate and butane-1,4-diamine (P(E66-A46)), and reported that these copolymer series had a similar odd−even effect on the T_m values.[20] However, such an effect of novel periodic copolymer series showed a larger temperature range between neighboring methylene numbers in the diol unit as compared to that of previous series because the T_m values of both P(E36-A36) and P(E56-A56) series composed of odd ester and amide units were respectively much lower than those of corresponding periodic copolymer P(E36-A46) and P(E56-A46) series composed of odd ester and even amide units, as shown in Figure 5B,C. Surprisingly, the great differences in the melting temperatures between the respective series of copolymers, P(E36-A36) and P(E36-A46), and P(E56-A56) and P(E56-A46), composed of the same ester units, were ascribed to the change of only one carbon number in the amide unit, which was a minor component in the main chain, between odd and even numbers. Unlike these copolymer series composed of odd ester units, the P(E66-A66) copolymers had almost the same T_m values compared to the corresponding P(E66-A46) copolymers (Figure 5D) because both copolymer series consisted of even ester and amide units and had the long ester-amide sequences enough to ignore the difference in the carbon number of amide units.

Wide-Angle X-ray Diffraction Patterns. The wide-angle X-ray diffraction (WAXD) patterns of periodic poly(ester-amide)s and those of corresponding homopolyesters are displayed in Figure 6. Detailed d-spacing data of periodic copolymer crystals calculated from the peak positions at angle of 2θ in the diagrams are listed in Table 4. All samples for P(E46-A46) series revealed different WAXD patterns from that

Table 3. Thermal Properties and X-ray Crystallinities of Periodic Copolymers and Homopolyesters

		thermal properties[a]					
sample no.	amide fraction (mol %) (exptl)	T_g (°C)	T_{m1} (°C)	ΔH_{m1} (J·g^{-1})	T_{m2} (°C)	ΔHm2 (J·g^{-1})	Xc[b] (%)
P(E36-A36)-2/1	33	−29	40	3	76	15	18
P(E36-A36)-3/1	25	−40	43	16	71	9	26
P(E36-A36)-4/1	19	−47	46	15	73	19	26
P(E36-A36)-5/1	16	−51	50	23	71	2	20
P(E36-A36)-6/1	14	−54	46	22			23
P(E36-A36)-7/1	12	−54	48	25			21
P(E46-A46)-2/1[c]	34	[d]	258	31			33
P(E46-A46)-3/1	26		255	25			38
P(E46-A46)-4/1	20		245	26			29
P(E46-A46)-5/1	17		241	19			25
P(E46-A46)-6/1	15		221	20			26
P(E46-A46)-7/1	13		209	18			28
P(E56-A56)-2/1	34	−41	65	19			24
P(E56-A56)-3/1	25	−49	47	18			23
P(E56-A56)-4/1	20	−54	38	19			24
P(E56-A56)-5/1	16	−57	34	11			18
P(E56-A56)-6/1	14	−60	35	15			20
P(E56-A56)-7/1	13	−61	35	18			23
P(E56-A56)-8/1	11	−62	36	21			24
P(E66-A66)-2/1	33	−35	77	16	108	10	32
P(E66-A66)-3/1	24	−45	68	22			25
P(E66-A66)-4/1	20	−49	63	21			25
P(E66-A66)-5/1	17	−52	58	19			23
P(E66-A66)-6/1	14	−54	56	20			24
P(E66-A66)-7/1	12	−57	55	27			31
P(E66-A66)-8/1	11	−57	52	24			27
poly(trimethylene adipate)		−63	40	33			33
poly(tetramethylene adipate)		−58	62	52			60
poly(pentamethylene adipaet)		−73	40	50			39
poly(hexamethylene adipate)		−69	56	58			43

[a] Measured by DSC. [b] Crystallinities from X-ray diffraction patterns. [c] Data from ref 20 for P(E46-A46) series. [d] Not determined.

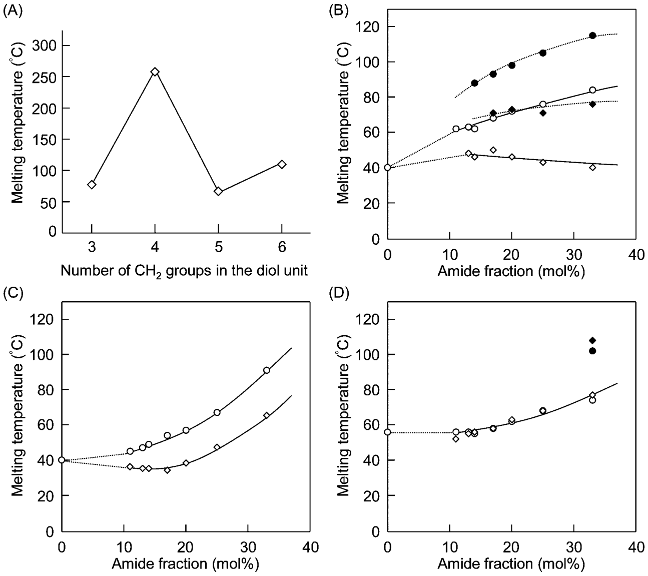

Figure 5. Melting temperatures of the periodic poly(ester-amide)s as a function of the number of CH_2 groups in the diol unit (A) (33 mol % amide unit content) and of amide fraction: (B) P(E36-A36) series (◇, T_{m1}; ◆, T_{m2}) and P(E36-A46) series (○, T_{m1}; ●, T_{m2}), (C) P(E56-A56) series (◇) and P(E56-A46) series (○), and (D) P(E66-A66) series (◇, T_{m1}; ◆, T_{m2}) and P(E66-A46) series (○, T_{m1}; ●, T_{m2}), P(E36-A46), P(E56-A46), and P(E66-A46) data from ref 20. The symbols at the 0 mol % amide fraction show the T_m values of homopolyesters.

of poly(tetramethylene adipate) homopolyester, and three main diffraction peaks at 2θ values of about 20°, 23°, and 26° were detected in the diagrams (Figure 6B). In the cases of the P(E56-A56) and P(E66-A66) copolymer series, the diffraction patterns were strongly dependent on the amide content (Figure 6C,D), and the samples with amide content exceeding 20 mol % gave different WAXD patterns from those of homopolyesters, whereas the samples with amide content lower than 17 mol % had nearly identical 2θ values as compared to the homopolyesters. Unlike these copolymer series, any of the P(E36-A36) copolymer samples showed relatively broad diffraction patterns in which some parts were located at nearly identical 2θ values as compared to poly(trimethylene adipate) homopolyester (Figure 6A). Such differences in the diffraction patterns strongly correlated to the thermal behavior determined from DSC measurements. In fact, the P(E46-A46) samples or the P(E56-A56) and P(E66-A66) samples with more than 20 mol % amide content had apparently higher T_m values, but samples with less than 17 mol % amide content for the P(E56-A56) and P(E66-A66) series had little change in T_m values as compared to the homopolyesters (see Table 3 and Figure 5). Moreover, most of the P(E36-A36) copolymer samples had two distinct melting peaks with temperature intervals ranging from about 20 to 40 °C, and the lower peaks were observed in the identical temperature range as compared to the homopolyester. Because the crystalline structures of these periodic poly(ester-amide)s have not been defined, further research is needed to elucidate the relations between the thermal properties and crystalline structures. However, these results indicate that the formations of chain-packing structures in the crystalline region of periodic poly(ester-amide)s are strongly dependent on both the comonomeric and ester-amide sequential structures. The differences in chain packing structures are facilitated by the intermolecular hydrogen bond interactions of crystallizable ester-amide sequences and lead to higher T_m values compared to those of the

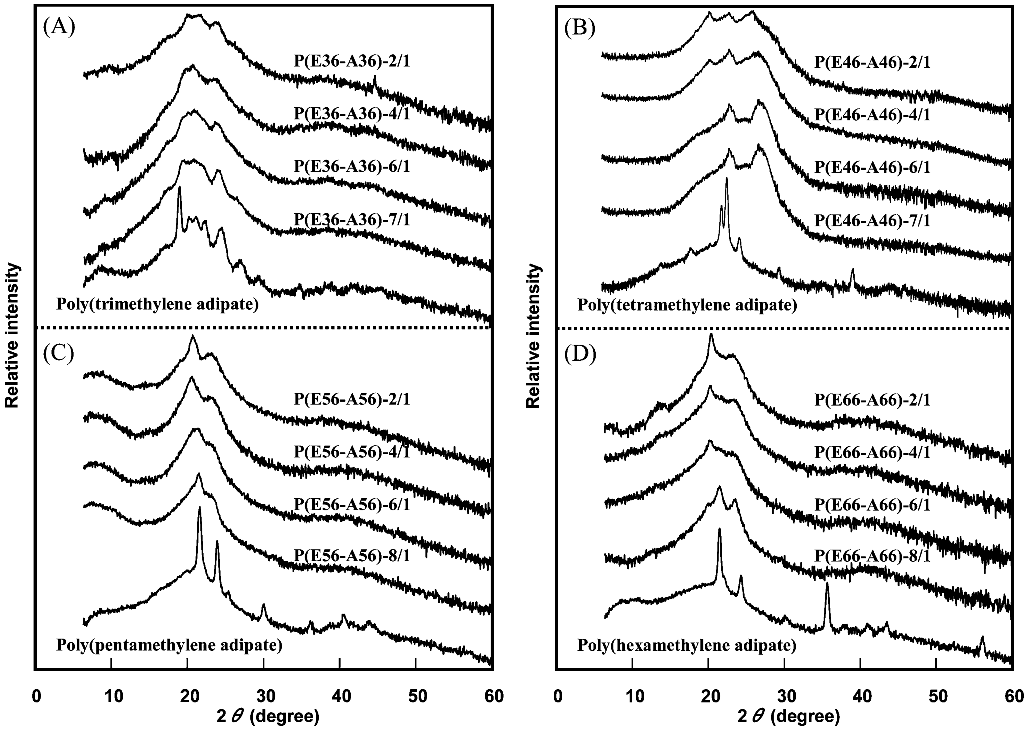

Figure 6. Wide-angle X-ray diffraction patterns of periodic copolymers and homopolyesters: (A) samples P(E36-A36)-2/1, -4/1, -6/1, -7/1, and poly(trimethylene adipate), (B) samples P(E46-A46)-2/1, -4/1, -6/1, -7/1, and poly(tetramethylene adipate), (C) samples P(E56-A56)-2/1, -4/1, -6/1, -8/1, and poly(pentamethylene adipate), and (D) samples P(E66-A66)-2/1, -4/1, -6/1, -8/1, and poly(hexamethylene adipate).

Table 4. *d*-Spacing Values of Periodic Copolymer Crystals and Homopolyester Crystals from X-ray Diffraction Patterns

sample no.	*d*-spacing[a] (nm)						
P(E36-A36)-2/1		0.446		0.413	0.374		
P(E36-A36)-4/1		0.448	0.432		0.378		
P(E36-A36)-6/1		0.441	0.428		0.375		
P(E36-A36)-7/1		0.458	0.429		0.373		
poly(trimethylene adipate)	0.471	0.446	0.426	0.404	0.367	0.332	
P(E46-A46)-2/1		0.440		0.389		0.342	
P(E46-A46)-4/1		0.437		0.389		0.341	
P(E46-A46)-6/1		0.444		0.390		0.334	
P(E46-A46)-7/1		0.442		0.390		0.334	
poly(tetramethylene adipate)			0.408	0.395	0.368		0.303
P(E56-A56)-2/1		0.435		0.387			
P(E56-A56)-4/1		0.435		0.386			
P(E56-A56)-6/1		0.432	0.419	0.388			
P(E56-A56)-8/1		0.431	0.418	0.389			
poly(pentamethylene adipate)			0.417		0.375	0.299	0.249
P(E66-A66)-2/1		0.440		0.385			
P(E66-A66)-4/1		0.442		0.382			
P(E66-A66)-6/1		0.441		0.385			
P(E66-A66)-8/1		0.440	0.413	0.378			
poly(hexamethylene adipate)			0.419		0.370	0.298	0.253

[a] Calculated from the peak positions at angle of 2θ according to Bragg's law ($d = n\lambda/2 \sin \theta$).

corresponding homopolyesters, while the formations of crystals based on the intervals of ester sequences may also occur due to the increase in the ester sequential length and to the similarity of molecular structure between ester and amide units.

Molecular Chain Arrangements. For a better understanding of the significant differences in the melting properties and crystalline structures among these copolymer series, the possible chain arrangements based on the periodic ester-amide sequences and their intermolecular interactions were considered. Figure 7 shows the schematic illustration of the speculated chain arrangements constructed from the molecular chains with a planar zigzag structure. In this model, all of the copolymers were drawn as antiparallel sheet structures because the many types of polyamides and polyesters generally form antiparallel chain-folded sheets in the stable crystalline state.[29] The molecular chains of periodic poly(ester-amide)s can arrange into two main types dependent on the intermolecular hydrogen bond interactions (between amide−amide groups for model I and between amide−ester groups for model II), as shown in Figure 7. Here, it may be expected that the periodic poly(ester-amide)s mainly form the chain arrangement of model II rather than model I because the amide unit is a minor component compared to the ester unit. P(E46-A46) copolymers in Figure 7A can form excellent interchain arrangements on the basis of the intermo-

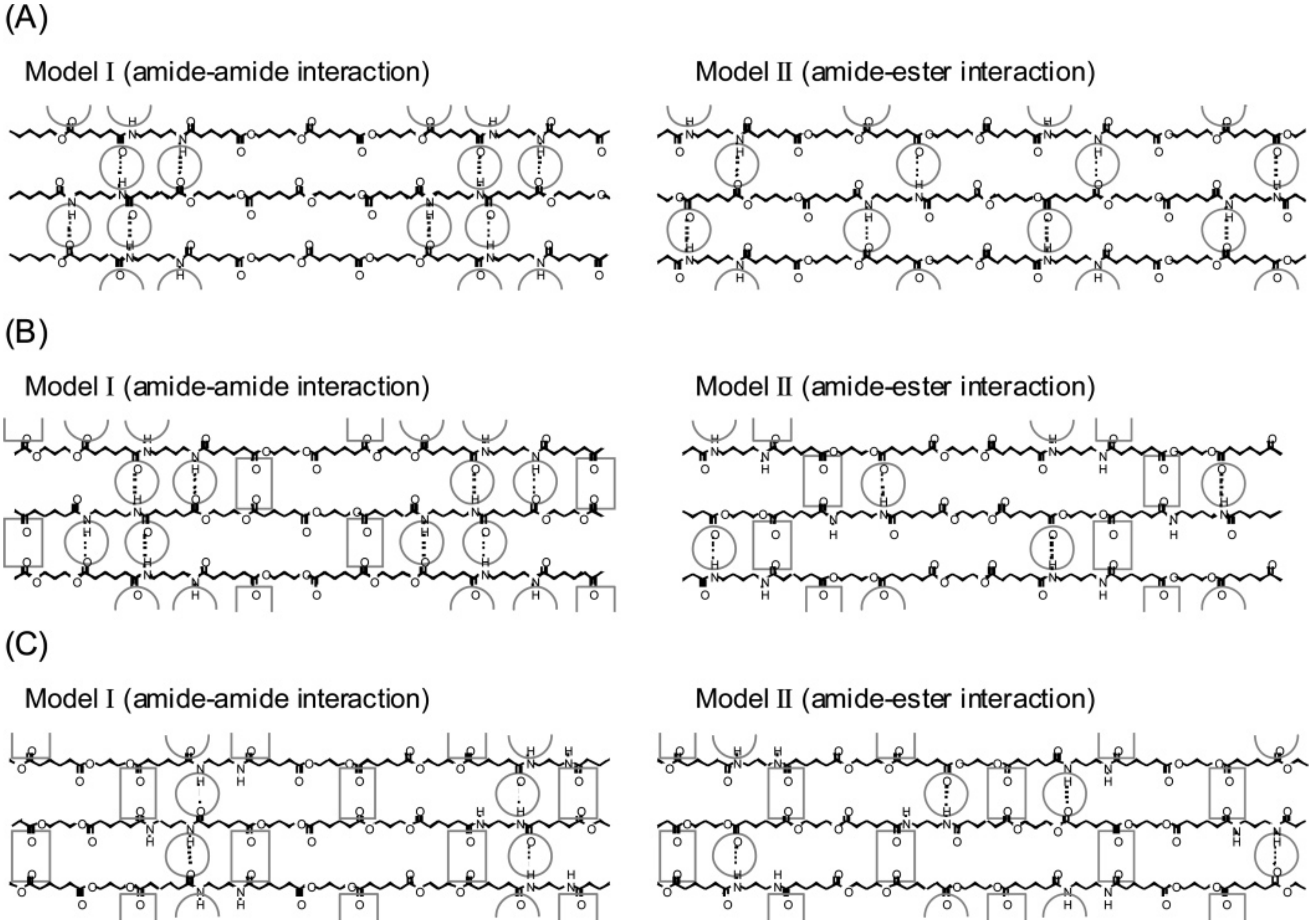

Figure 7. Speculated chain arrangements for periodic poly(ester-amide)s: (A) P(E46-A46) series, (B) P(E36-A46) series, and (C) P(E36-A36) series (○, intermolecular hydrogen bond interaction; □, steric hindrance).

lecular hydrogen bond interactions, which may lead to the higher thermal properties. On the other hand, for P(E36-A46) copolymers, the formation of intermolecular hydrogen bonds simultaneously induces the steric hindrance of carbonyl groups between neighboring chains, and conformational rearrangements must occur to form a stable chain-packing structure (Figure 7B). In addition, the number of the intermolecular hydrogen bonds was limited in the case shown as model II. As a result, the chain arrangements with less-effective intermolecular hydrogen bond interaction may form and lead to the lower improvement of the thermal stability as compared with P(E46-A46) copolymers. As shown in Figure 7C, P(E36-A36) copolymers also form the chain arrangements with limited intermolecular hydrogen bonds in both models, while the number of the steric hindrance between neighboring chains increased sharply in comparison with the P(E36-A46) copolymers, likely resulting in the slight or little increase in thermal stability. The differences in the molecular chain arrangements among three series of copolymers actually correspond with the order of the melting properties determined from DSC measurements (see Table 3 and Figure 5B). A similar model for molecular chain arrangement can be applied to the P(E56-A56) and P(E56-A46) series composed of the ester units with an odd number of methylene groups, and the T_m values of both copolymer series were considerably lower than those of P(E46-A46) copolymers, while the P(E56-A46) series showed high thermal properties as compared with P(E56-A56) series (Table 3 and Figure 5C). However, the P(E66-A66) and P(E66-A46) copolymers with an even number of methylene groups in comonomers also revealed relatively lower T_m values as compared with the P(E46-A46) copolymers, even though these copolymers can form excellent interchain arrangements without steric hindrance. These results indicate that the differences in the thermal stability of the crystalline phase for periodic poly(ester-amide)s could not simply be mentioned in terms of the intermolecular interactions of molecular chain arrangements. Because the P(E66-A66) and P(E66-A46) copolymers have longer repeating ester units and longer distances between amide linkages, the chain packing structures may form on the basis of the interaction between the ester sequences rather than of the intermolecular hydrogen bond formation.

Mechanical Properties. The mechanical properties for the copolymer samples with the highest M_n values (P(E66-A66) series, $M_n = 32\,900-51\,400$) were evaluated by monitoring the stress−strain curves of their films. Figure 8 shows the four mechanical parameters from the results of the tensile test as a function of amide content, respectively. By increasing the amide content in the P(E66-A66) copolymer samples, the Young's modulus, yield strength, and tensile strength at break increased because of the increased stiffness (Figure 8A−C), while the elongation at break tended to decrease (Figure 8D). However, all of the P(E66-A66) copolymer samples had a strain at break between about 400 and 700% and showed a high flexibility as compared with poly(hexamethylene adipate) homopolyester, which was very brittle. From these results, it has been found that the mechanical properties of periodic poly(ester-amide)s are strongly dependent on the ester-amide sequential structures and that they can be widely regulated in the elastic and plastic deformation regions.

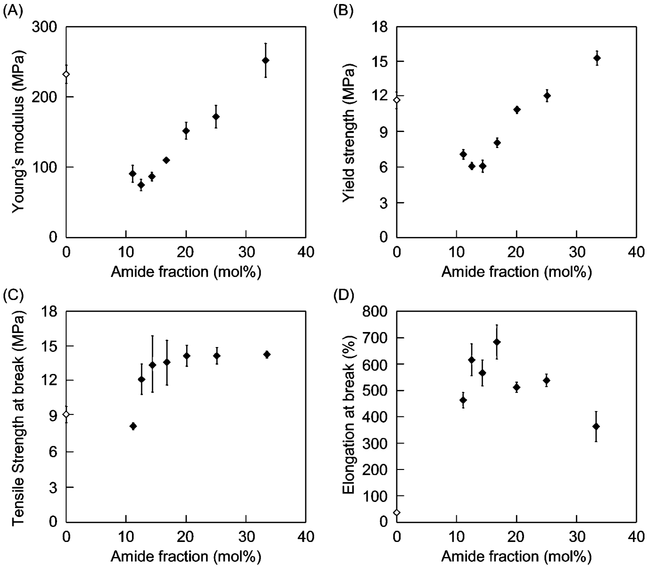

Figure 8. Mechanical properties of the periodic copolymer P(E66-A66) samples (closed symbols) and poly(hexamethylene adipate) (open symbols): (A) young's modulus, (B) yield strength, (C) tensile strength at break, and (D) elongation at break as a function of amide fraction.

Mechanical properties of polymer materials are highly dependent on several factors such as molecular weight, crystalline shape and structure, crystallinity (ratio of crystal and amorphous regions), and composition (relating to intermolecular interaction). However, in the cases of P(E66-A66) film samples, it is expected that the stress−strain data mainly showed the properties of the amorphous region in the materials because the crystallinities, which had comparable values between 23 and 32%, were very low (see Table 3). In addition, the distinct differences in the mechanical properties among the P(E66-A66) samples were observed in spite of the narrow amide content intervals between 11 and 33 mol %. The results of this study suggest that the amide units introduced with a defined periodicity into the main chains are uniformly distributed over the amorphous region in the material and that their hydrogen bonds act as crosslinking points. The change in the density of crosslinking points, depending on the amide content, may lead to the wide regulation of the mechanical properties for periodic poly(ester-amide)s. Moreover, the uniform distribution of the crosslinking points in the materials result in the high flexibility.

Conclusions

Novel periodic copolymers consisting of ester and amide units with the same carbon numbers could be synthesized by two-step polycondensation reactions from adipate, linear aliphatic diols and diamines with both odd and even methylene groups. The thermal properties of the obtained periodic poly(ester-amide)s series had a strong dependence on both the comonomeric and ester-amide sequential structures, and the values showed a very large temperature range between neighboring methylene numbers in the comonomer units. The WAXD patterns of periodic poly(ester-amide)s also varied with the comonomeric and sequential structures, and such differences were strongly correlated to the thermal behaviors. Comparing the periodic copolymer series with various types of ester-amide sequences, it has been shown that the molecular chain arrangements and the intermolecular hydrogen bond interactions on the basis of the defined ester-amide sequential structures are very important factors for the formation of a thermally stable crystalline region. In addition, according to the tensile tests, it has been found that the mechanical properties of periodic poly(ester-amide)s are also dependent on the ester-amide sequential structures and that these polymers are tough materials.

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