Polyamide4-block-poly(vinyl acetate) via a polyamide4 azo macromolecular initiator: Thermal and mechanical behavior, biodegradation, and morphology

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ABSTRACT: A series of polyamide4-block-poly(vinyl acetate)s were synthesized by the radical polymerization of vinyl acetate (VAc) using an azo macromolecular initiator composed of polyamide4 (PA4). The block copolymers were investigated by examining their molecular weight, structure, thermal and mechanical properties, biodegradation, and the morphology of the film surface. The compositions and molecular weights (Mw) ranging from 46,800 to 163,700 g mol^{-1} of the block copolymers varied linearly with increasing molar ratio of VAc to azo-PA4. The block copolymers have high melting points of 248.2–262.5°C owing to PA4 blocks and heats of fusion, which were linearly dependent on the PA4 content. The mechanical properties of the block copolymers were monotonically dependent on the composition, i.e., increasing the PA4 content increased the tensile strength, whereas increasing the poly(vinyl acetate) content increased the elongation at break. The morphology of the block copolymers suggested the appearance of microphase separation. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42466.

INTRODUCTION

Polyamide4 (PA4) was initially synthesized by combining 2-pyrrolidone (PRN), basic catalysts, and acyl compounds by Ney et al.[1] Since then, extensive efforts have been made to investigate PA4[2–11] and its properties. However, PA4, which is difficult to mold and has an unspecified suitability for applications, has not been put to practical use, which hampered the subsequent research.

It has been found that under inactive research circumstances, PA4 is biodegradable in various environments such as in soil, sea water, and activated sludge, in spite of its outstanding properties such as its high melting point and tensile strength.[12–19] Further, PRN, which is the monomer of PA4, can be derived from glucose using glutamic acid and γ-aminobutyric acid by a combination of biochemical and chemical processes.[20,21] Of late, these significant features have gradually reawakened the interest in the study of syntheses, properties, structure,[22] biodegradation, and biosynthesis of PA4 monomers.

It should additionally be noted that PA4 is synthesized by the anionic ring-opening polymerization of PRN, which progresses via an activated monomer mechanism. In this mechanism, the PA4 chains propagate from the active carboxyl groups on the initiator, thereby facilitating the design of polymeric structures.

For example, when benzene-1,3,5-tricarbonyl trichloride is used as the initiator, the chain propagation reaction is initiated from the three acyl groups on the aromatic ring to form three-branched PA4. This branched compound showed an improvement in its ability to form a film and a remarkable increase in tensile strength, compared to linear PA4, which has a comparable molecular weight.[14] These peculiar properties presumably arose due to the entanglement resulting from the branched structure.

It should also be pointed out that the synthesis of PA4 is possible at temperatures near the melting point of PRN (25°C). Because of this mild synthetic reaction condition, the initiator, which contains the thermolabile group, can be used in polymerization without thermal decomposition. Considering one example of the use of such an initiator, when 4,4′-azobiscyanopentanoyl chloride is used to initiate the polymerization, the PA4-containing azo group (azo-PA4) was obtained. This azo group generates radicals with the elimination of nitrogen gas when heated to approximately 60°C, which means that the azo-PA4 functions as a macromolecular initiator.

Thus far, azo macromolecular initiators with a single azo group in the polymer chain have been employed in two types of procedures to utilize the 4,4′-azobiscyanopentanoyl group to

synthesize polyamide-block-vinyl polymers. The first type involves a three-step procedure, for example, the synthesis of 4,4′-azobiscyanopentanoyl lactam, followed by the preparation of the vinyl polymer with a lactam end-group by radical polymerization and the anionic ring-opening polymerization of lactam monomers, in this order.[23–25] The other type of procedure also includes three steps, for example, the preparation of the polyamide prepolymer by anionic ring-opening polymerization, followed by the synthesis of the azo macromolecular initiator by reacting the polyamide with 4,4′-azobiscyanopentanoyl chloride, and the radical polymerization of vinyl monomers by the azo macromolecular initiator, in this order.[26] The former type is difficult to apply to polar vinyl monomers such as vinyl acetate (VAc), and both types have the disadvantage of requiring a three-step procedure for the synthesis of polyamide-block-vinyl polymers. Modifying the procedure would make it possible to synthesize azo-PA4 by taking advantage of the low polymerization temperature of PRN and to reduce the number of steps in the synthesis of polyamide4-block-vinyl polymers to two. A previous paper has reported the synthesis of azo-PA4 and its initiator activity for the radical polymerization of vinyl monomers.[27] The synthesis of azo-PA4 made it possible to polymerize various vinyl monomers and the formation of the block copolymer was confirmed by conducting an experiment using styrene as the monomer.

For the present investigation, VAc was selected from among the various vinyl monomers, because it offers the following two beneficial features when polymerized: poly(vinyl acetate) (PVAc) are amorphous polymers with a softening point of 35–50°C,[28] while PA4 are crystalline polymers with a high melting point of 260°C.[29] Moreover, PVAc differs from PA4 in terms of its solubility parameter (δ)[30] and the difference may result in immiscibility. Thus, the combination of a crystalline block consisting of PA4 and an amorphous block consisting of PVAc is expected to exhibit specific properties originating from the phase formed by two immiscible blocks.[31–34] Therefore, the purpose of the present study was to establish the synthesis of polyamide4-block-poly(vinyl acetate) by using azo-PA4 and to investigate its thermal and mechanical properties, biodegradability, and morphology.

EXPERIMENTAL

Materials

Reagents and starting materials were treated as follows: 2-pyrrolidone (Kishida Chemical, Osaka, Japan) was distilled under reduced pressure, followed by drying over calcium hydride; sodium (Wako Pure Chemical Industries, Osaka, Japan) was used after removing impurities from the surface; 4,4′-azobiscyanopentanoyl chloride was prepared by the halo-de-hydroxylation of 4,4′-azobiscyanopentanoic acid (Wako Pure Chemical Industries) with thionyl chloride (Kishida Chemical), as described in an earlier paper;[14] 2,2,2-trifluoroethanol (Kishida Chemical) and chloroform (Wako Pure Chemical Industries) were used as received; vinyl acetate (Wako Pure Chemical Industries) was purified by distillation. The PA4 compounds containing the azo group (azo-PA4) were prepared by anionic ring-opening polymerization of PRN using 4,4′-azobiscyanopentanoyl chloride as an initiator, as described in the literature.[27]

Polymerization of Vinyl Acetate by Azo-PA4

A typical polymerization procedure was performed as follows. To a 50 mL round-bottomed flask, azo-PA4 with Mn 17,800 g mol^{-1} (0.50 g, 0.028 mmol from 0.50/17,800) was added and dissolved in 2,2,2-trifluoroethanol (7 mL). Subsequently, VAc (1.50 g, 17.4 mmol) was added to the flask and the mixture was homogenized at room temperature. The mixture was degassed using five freeze-pump-thaw cycles in a dry ice-ethanol bath to replace the atmosphere with argon. The flask, which was equipped with an argon balloon, was maintained under an argon atmosphere and immersed into a silicone oil bath at 60°C for 24 h. Then, a vacuum pump was connected to the flask while still hot, and the solvent, 2,2,2-trifluoroethanol, and the residual VAc were removed by evaporation. In an attempt to purify the polymerization mixture, PVAc was extracted from the resulting mixture with chloroform for 2 days by using Soxhlet extraction. The resulting polymerization products were dried by storing them in a heated desiccator under reduced pressure. Aside from the polymerization products, the chloroform extract was recovered by evaporation. The desired polymerization product (insoluble in chloroform) and the extract (soluble in chloroform) weighed 1.02 g (51.0%) and 0.45 g (22.5%), respectively.

Characterization

The molecular weight (Mn, Mw) and the distribution (Mw/Mn) of the products were determined by gel permeation chromatography (GPC, HLC-8220 GPC system, Tosoh Corporation, Tokyo, Japan). Poly(methyl methacrylate) standards (Shodex Standard M-75, Shimadzu GLC Ltd., Tokyo, Japan) were used for plotting a calibration curve. All GPC measurements were carried out using two columns (TSK gel Super HM-N, Tosoh) for samples with separate double-tandem reference columns (TSK gel Super H-RC, Tosoh) connected separately and maintained at 40°C, and by using hexafluoroisopropyl alcohol (HFIP, Central Glass Co., Ltd., Tokyo, Japan) as the eluent at a 0.2 mL min^{-1} flow rate.

The structure and composition of the polymers were determined by ^{1}H nuclear magnetic resonance (NMR) spectroscopy (JNM-ECA-500 NMR spectrometer 500 MHz, JEOL Ltd., Tokyo, Japan) using deuterated methanol CD$_3$OD containing lithium chloride (0.25 g mL^{-1}) as the solvent. The concentration of the specimen was about 25 mg mL^{-1}.

The melting temperature (Tm) and heat of fusion (ΔHm) were measured by differential scanning calorimetry (DSC, DSC 3100S Calorimeter, Bruker AXS K.K., Yokohama, Japan). Samples (4–6 mg) were analyzed at a heating rate of 10°C min^{-1} and 30–350°C under a nitrogen atmosphere.

The tensile strength and elongation at break of the film specimens were measured by using a universal tensile testing machine (Auto Com/AC-50C, T.S.E Co., Ltd., Yokohama, Japan). The specimens were pulled in a vertical direction at a rate of 10 mm min^{-1} with a 100 N load cell at room temperature and the gauge length between the chucks was 10 mm. The thickness of each specimen was measured at three points before
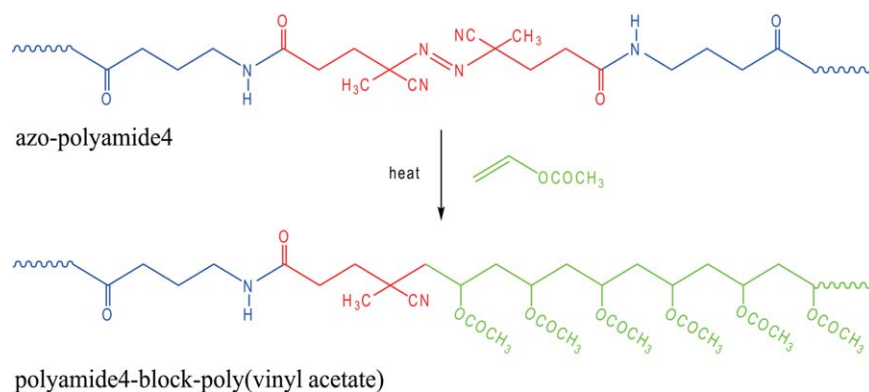
Scheme 1. Radical polymerization of VAc by azo-PA4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

testing and a minimum value was adopted. The mechanical properties reported here correspond to the average values of at least 5–15 measurements.

The biodegradation % of the polymers by a standard activated sludge metabolism was evaluated by using a closed manometric respirometer system (BOD TESTER 200F and COOLNIT CL-150R system, Taitec Co., Ltd., Koshigaya, Japan). A polymer sample (30 mg) was dispersed in 200 mL of an inorganic culture medium as described in ISO 14851, and 20 mL (dry weight: 20 mg) of a standard activated sludge (Chemicals Evaluation and Research Institute, Japan) was added to the medium. In a closed-system culture vessel, the generated carbon dioxide was absorbed at 27°C by calcium hydroxide on a pan placed in the vessel, and the amount of consumed oxygen was measured by determining the decrease in the volume by reading the scale on a burette immersed in the thermostat bath. This procedure was conducted for about one month to carry out the biodegradation test. The observed amount of oxygen consumed as a result of the condition of the polymer sample was corrected by subtracting the amount of oxygen consumed depending on the condition of the activated sludge only. The biodegradation % of the polymer sample was calculated by dividing the observed amount of oxygen consumed by the theoretical amount of oxygen required, which is the total amount of oxygen required for converting all of the carbon into carbon dioxide, nitrogen into nitrate ions, and hydrogen into water contained in the PA4 units (but not in the PVAc units) of the polymer samples when all of the PA4 units have been biodegraded.

The laser microscopy measurements presented in this article were all performed on a shape measurement laser microscope (VK-X210 + VK-X200 system, Keyence Corporation, Osaka, Japan). Thin films for laser microscopy were prepared by coating a dilute solution of 2,2,2-trifluoroethanol of the polymer sample onto a clean glass slide.

RESULTS AND DISCUSSION

Synthesis, Purification, and Analysis

VAc was polymerized with azo-PA4 in 2,2,2-trifluoroethanol at 60°C for about 24 h (Scheme 1). Besides the formation of copolymer, the radical polymerization of VAc by azo-PA4 causes

a chain transfer reaction and recombination, such that both the homopolymers PVAc and PA4 may be produced. Therefore, to separate the copolymer from the obtained polymerization product mixture, a Soxhlet extraction with chloroform was performed to remove PVAc from the mixtures.

The molecular weights and weight distributions of the separated polymerization products were measured by GPC. Figure 1 shows the GPC profiles for azo-PA4 (a) and the obtained copolymers (b, c, and d) with different monomer feed ratios using the same azo-PA4 initiator (I3 series in Table I). The GPC traces of each product showed broadened elution peaks and were eluted faster than the original azo-PA4. The molecular weight distribution between azo-PA4 and the series of separated products was clearly different. Although a few examples of the obtained GPC curves showed a very faint shoulder, the shape of the curves was nearly unimodal. This suggested that the separated products almost consisted of the block copolymers.
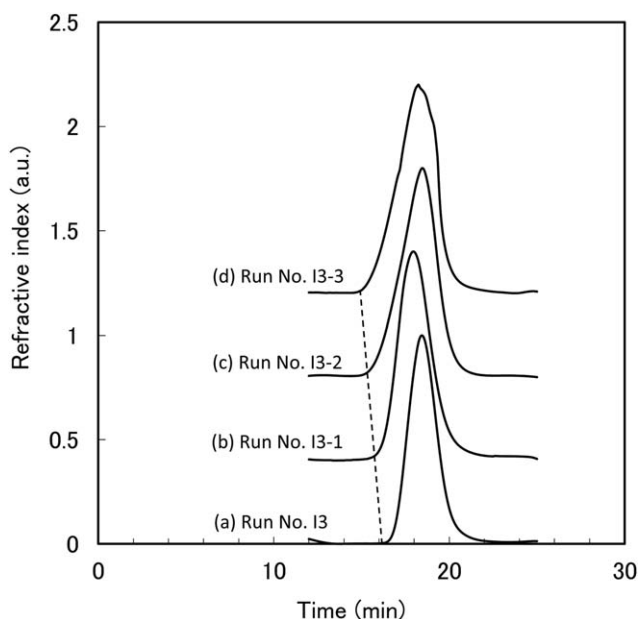
Figure 1. GPC profiles for azo-PA4 (Run No. I3) and separated polymerization products (Run No. I3-1, I3-2, I3-3 in Table I).

Table I. Results of Radical Polymerization of Vinyl Acetate by azo-PA4 Initiator

Run No.	Azo-polyamide4 [I] (g); (mmol)	Vinyl acetate (g); (mmol)	Feed ratio [PRN]/[VAc]	Total yield (%)	Soluble part in CHCl$_3$ (g); (%)	Insoluble part in CHCl$_3$ [P] (g); (%)	Increments [P] − [I] = VAc unit (g); (mmol)	Copolymer composition from increments [PRN]/[VAc]	Copolymer composition from NMR [PRN]/[VAc]	Mn × 10^{-3b}	Mw × 10^{-3b}	Mw/Mn^b
I1^a										13.1	21.9	1.68
I1-1	0.50; 5.88	0.49; 5.69	50.8/49.2	88.9	0.09; 9.1	0.79; 79.8	0.29; 3.37	64/36	56/44	16.5	46.8	2.85
I1-2	0.50; 5.88	1.48; 17.19	25.5/74.5	84.8	0.29; 14.6	1.39; 70.2	0.89; 10.34	36/64	32/68	20.6	104.0	5.05
I1-3	0.50; 5.88	2.93; 34.03	14.7/85.3	81.6	0.79; 23.0	2.01; 58.6	1.51; 17.54	25/75	23 77	25.8	136.7	5.29
I2^a										15.8	26.9	1.70
I2-1	0.50; 5.88	0.49; 5.69	50.8/49.2	91.9	0.10; 10.1	0.81; 81.8	0.31; 3.60	62/38	56/44	20.4	56.6	2.78
I2-2	0.50; 5.88	1.48; 17.19	25.5/74.5	90.5	0.50; 25.3	1.29; 65.2	0.79; 9.18	39/61	37/63	36.7	117.7	3.20
I2-3	0.50; 5.88	2.97; 34.50	14.6/85.4	83.0	1.07; 30.8	1.81; 52.2	1.31; 15.22	28/72	26/74	27.3	133.0	4.86
I2-4	0.50; 5.88	4.45; 51.69	10.2/89.8	91.1	2.20; 44.4	2.31; 46.7	1.81; 21.02	22/78	20/80	19.7	163.7	8.32
I3^a										17.8	31.5	1.77
I3-1	0.50; 5.88	0.50; 5.81	50.3/49.7	73.0	0.07; 7.0	0.66; 66.0	0.16; 1.86	76/24	64/36	24.3	62.2	2.56
I3-2	0.50; 5.88	1.50; 17.42	25.2/74.8	73.5	0.45; 22.5	1.02; 51.0	0.52; 6.04	49/51	42/58	21.5	79.7	3.72
I3-3	0.50; 5.88	3.00; 34.85	14.4/85.6	73.1	0.98; 28.0	1.58; 45.1	1.08; 12.55	32/68	28/72	23.2	106.8	4.60
I4^a										18.3	33.8	1.85
I4-1	0.50; 5.88	0.50; 5.81	50.3/49.7	77.0	0.11; 11.0	0.66; 66.0	0.16; 1.86	76/24	58/42	21.7	74.3	3.43
I4-2	0.50; 5.88	2.25; 26.14	18.4/ 81.6	69.8	0.76; 27.6	1.16; 42.2	0.66; 7.67	43/57	32/68	25.7	99.7	3.88
I4-3	0.50; 5.88	3.00; 34.85	14.4/85.6	69.4	1.10; 31.4	1.33; 38.0	0.83; 9.64	38/62	29/71	21.8	114.6	5.26
I5^a										18.1	36.6	2.02
I5-1	0.50; 5.88	1.49; 17.31	25.4/74.6	76.9	0.46; 23.1	1.07; 53.8	0.57; 6.62	47/53	40/60	25.5	97.7	3.83
I5-2	0.50; 5.88	2.23; 25.90	18.5/81.5	78.7	0.94; 34.4	1.21; 44.3	0.71; 8.25	42/58	33/67	24.7	110.9	4.49
I5-3	0.50; 5.88	4.47; 51.92	10.2/89.8	82.3	2.48; 49.9	1.61; 32.4	1.11; 12.89	31/69	27/73	34.9	142.1	4.07

^{a} Original azo-PA4 initiator for radical polymerization.
^{b} Determined by GPC. The eluent was hexafluoroisopropyl alchohol, and the standard was poly(methyl methacrylate).
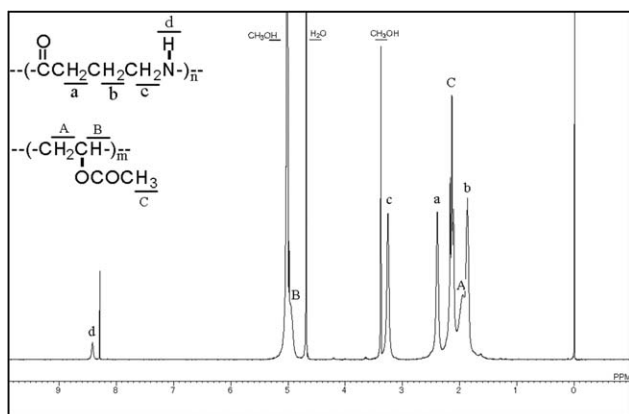
Figure 2. ^{1}H NMR spectrum of a separated polymerization product [polyamide4-block-poly(vinyl acetate)].

To verify that the separated products were in fact the block copolymers consisting of both PA4 and PVAc chains, their ^{1}H NMR spectra were recorded. A typical ^{1}H NMR spectrum of the separated products is shown in Figure 2. ^{1}H NMR (500 MHz, CH_3OH-d_4, δ): methylene protons (a), (b), (c), and amide proton (d) of PA4: 2.40 (br, 2H, CH_2), 1.87 (br, 2H, CH_2), 3.26 (br, 2H, CH_2), 8.42 (br, 1H, NH), methyl (C) and methylene protons (A) of PVAc: 2.17–2.12 (br, 3H, CH_3), 1.96 (br, 2H, CH_2). The methine protons (B) partially overlap the hydroxyl proton of methanol-$d4$ and appear as a shoulder at 4.99 ppm. There were no peaks for the microstructure based on random or alternating sequences of constitutional repeating units, whereas the simple peaks were observed independently and suggested that the separated copolymers contained both PA4 and PVAc chains.

The copolymer compositions were determined from the intensity ratio between a proton of the PA4 chain [(PRN)] and a proton of the PVAc chain [(VAc)] as follows. The integrated intensity of peak (c) provides the intensity of two protons of the PA4 repeating unit; hence, the intensity of one proton of the PA4 repeating unit is described by 0.5 × c. The intensity of peak (c) is equal to the intensity of both peaks (a) and (b), because they are all methylene protons. The integrated intensity of overlapping peaks (a + b + A + C) equals that of four protons (a + b) of the PA4 repeating unit and five protons (A + C) of the PVAc repeating unit; thus, the proton intensity of the PVAc repeating unit is described by [(a + b + A + C) − (a + b)] × 0.2, namely [(a + b + A + C) − (c × 2)] × 0.2. Here, the overlapping peaks (a + b) are approximated by substituting c into a and b, respectively. Combining these expressions, the copolymer compositions were obtained from the following formula:

$$[PRN]/[VAc] = (c \times 0.5)/[(a + b + A + C - c \times 2) \times 0.2],$$

which is the ratio of one proton intensity for the PA4 repeating unit to the PVAc repeating unit.

Based on the above facts such as the nearly unimodal shape of the GPC curves, simple peaks of the NMR spectra and preparation method, the isolated copolymers were regarded as mostly consisting of block copolymers, i.e., polyamide4-block-poly(vinyl acetate).

Features of Polymerization
The polymerization tendency and properties were examined by synthesizing other members of the series of polyamide4-block-poly(vinyl acetate)s using several azo-PA4 units with different molecular weights in a similar manner. The polymerization results are provided in Table I. The total yields of the polymerization products (both the fractions that were soluble and insoluble in chloroform) based on the feed materials were relatively high at approximately 69–92 wt %. These high yields imply that VAc was polymerized efficiently by the azo-PA4 macromolecular initiator. The soluble and insoluble fractions could be separated by Soxhlet extraction with chloroform. The above purification results indicate that the insoluble fraction largely consisted of polyamide4-block-poly(vinyl acetate).

As mentioned above, the ^{1}H NMR analysis provided the copolymer compositions; however, these compositions can also be estimated by obtaining the weight change by subtracting the weight of the amount of azo-PA4 that was used from the weight of the insoluble fraction. The difference obtained in this way provides the increments of the VAc units in polyamide4-block-poly(vinyl acetate). Although several data points for the content lie to low, the content obtained from the weight increments were largely in agreement with that obtained from the ^{1}H NMR spectra. The reason for the lower ratio of VAc units seems to be the removal of block copolymers with a high content of VAc units by Soxhlet extraction. The validity of the estimated copolymer compositions was verified by plotting the compositions obtained from the increments and those obtained from the ^{1}H NMR spectra, as shown in Figure 3. The VAc content obtained from the weight increment above ca. 70 mol % coincides approximately with the composition obtained from ^{1}H NMR; however, below ca. 70 mol %, the composition obtained from the weight increment deviated from the straight dotted line. The reason for the deviation seems to be that the accuracy with which the
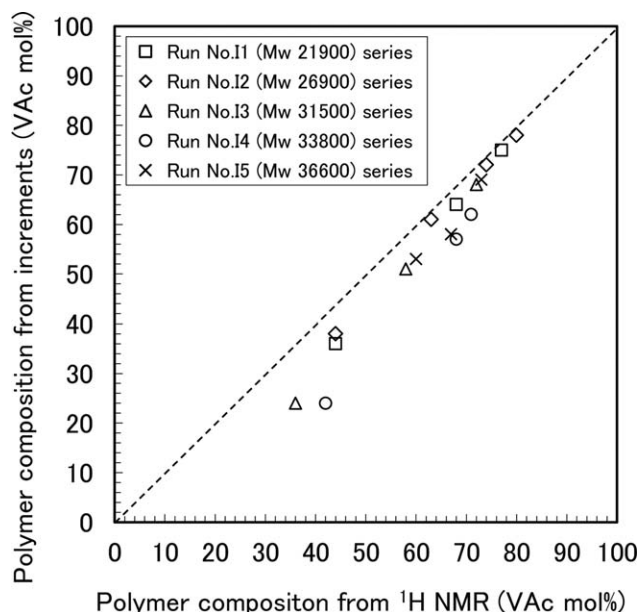
Figure 3. Polymer composition from increments against polymer composition from ^{1}H NMR for polyamide4-block-poly(vinyl acetate).
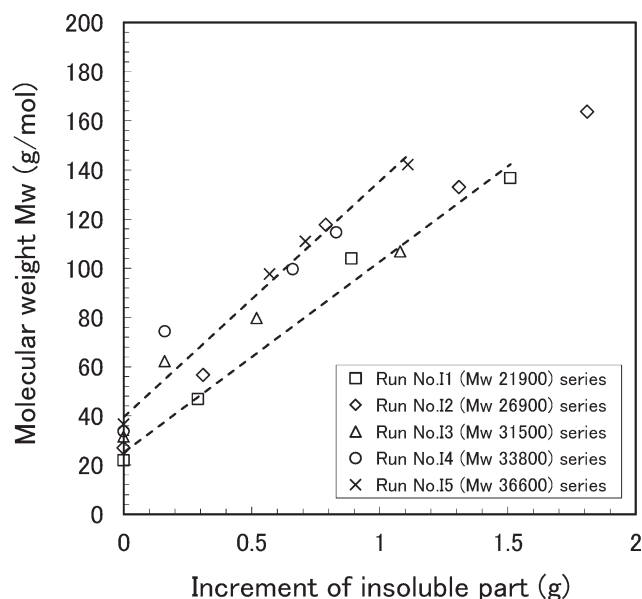
Figure 4. Relationship between the molecular weight and weight increment for polyamide4-block-poly(vinyl acetate).

recovered amount of copolymer strongly affects the weight increments of the copolymer in situations when the copolymer compositions are low in VAc content. For example, consider the case of Run Nos. I3-1 and I3-3: assuming that the recovery loss is 0.01 g, the errors are 6.3% (from 0.01/0.16 × 100) for the increments of 0.16 g of I3-1 and 0.9% (from 0.01/1.08 × 100) for the increments of 1.08 g of I3-3, respectively.

The dependence of the weight-average molecular weights (Mw) on the increments for the copolymers is shown in Figure 4. The data also included the Mw of each original azo-PA4 before polymerization for reference. Although the data points show some scatter, the Mw of the copolymers increases monotonically with the increments of the insoluble fractions. In contrast, the increments do not depend on the number-average molecular weight (Mn). This irregularity against Mn is a result of the sensitivity of the low-molecular-weight component in the copolymers. The approximate relationships for copolymers containing an azo-PA4 unit with a range of different molecular weights (Run No. 11 series and Run No. I5 series) are shown in comparison to the straight dotted lines, which correspond to the Mw of the original azo-PA4. The dependence of the molecular weights on the increments of the insoluble fractions provides further evidence for the formation of the block copolymers. For the Mw and the molecular weight distribution (Mw/Mn) shown in Table I, the Mw increased as the feed quantity of VAc was increased for azo-PA4 and polydispersity broadened as the Mw was increased. The increase in the feed quantity of VAc led to a relative increase in the concentration of the produced copolymers, because the same quantity of solvent was used, which caused the viscosity in the polymerization system to increase. Increasing the viscosity increases the Mw because of the auto-acceleration effect. There is also the possibility that chain transfer occurred on the copolymers to form a partially branching structure. Besides, cleavage of azo-PA4 continuously generates

radicals throughout the polymerization process. Therefore, the polymerization systems simultaneously contain copolymers of various molecular weights to broaden the polydispersity.

The relationship between the feed ratios of the monomer and polymer compositions was clarified by plotting the compositions against the feed ratios, as shown in Figure 5, in which the straight dotted line is fitted by using linear approximation. As seen in the figure, the polymer composition varies linearly with the feed ratio of the monomers and can therefore be controlled by the feed ratio. The VAc unit content of the copolymers is smaller than that in the original feed. The reason for the difference is that PVAc was formed partially by chain transfer and removed during the Soxhlet extraction process. Compared to the higher-molecular-weight azo-PA4 (Mw 36,600) polymers, the lower-molecular-weight azo-PA4 (Mw 21,900) polymers tended to form copolymers containing a slightly higher number of VAc units. Those with a lower molecular weight appear to achieve the radical polymerization of VAc more efficiently.

Thermal and Mechanical Properties

Table II summarizes the thermal and mechanical properties, namely the melting point (Tm), heat of fusion (ΔHm), and tensile strength and elongation at break, along with the compositions and molecular weights obtained by characterizing the block copolymers.

The thermal properties of the block copolymers were determined with DSC. Typical DSC thermograms of polyamide4-block-poly(vinyl acetate) are shown in Figure 6. From the DSC traces, the melting points ($Tm \sim$ ca. 260°C) suggested that the block copolymers included PA4 blocks. The broad strong peaks indicate thermal decomposition of the copolymers ($Td \sim$ ca. 300°C). The data in Table II indicate that the melting temperatures of PA4 blocks depend on the molecular weight of azo-PA4. For the lower-molecular-weight PA4 polymers (Mw 21,900), the average melting point is 249.2 ± 0.5°C, whereas it is 260.0 ± 0.3°C for those with higher molecular weight (Mw
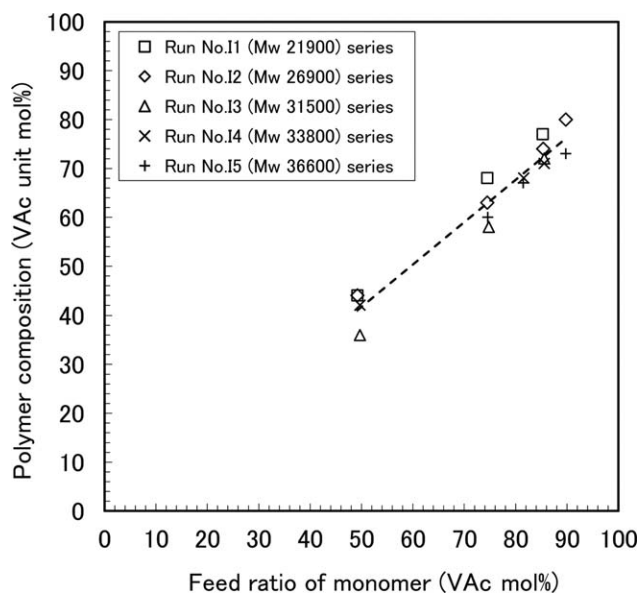
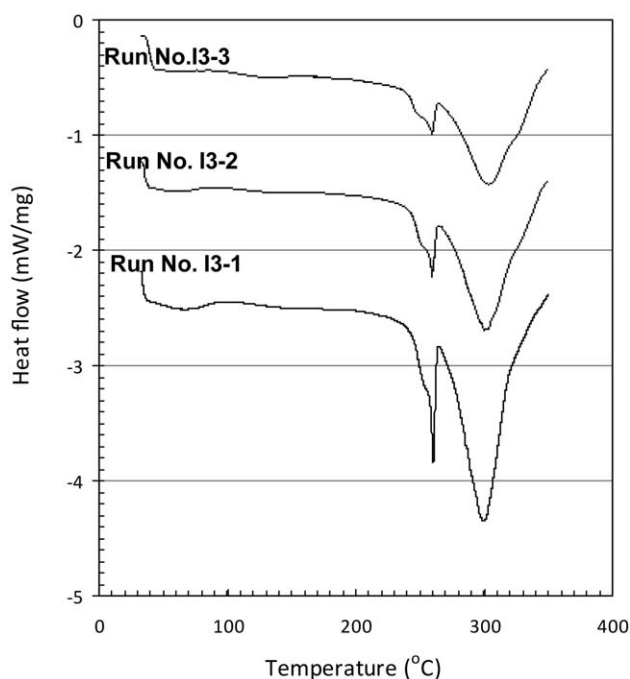**Figure 5.** Polymer composition of polyamide4-block-poly(vinyl acetate) against feed ratio of monomers.

Table II. Thermal and Mechanical Properties of Various Polyamide4-block-poly(vinyl acetate) Copolymers

| Run No.	Copolymer composition from NMR [PRN]/[VAc]	$Mn \times 10^{-3b}$	$Mw \times 10^{-3b}$	Mw/Mn^b	Tm (°C)	ΔHm (J/g)	Tensile strength (MPa)	Elongation at break (%)
I1[a]		13.1	21.9	1.68				
I1-1	56/44	16.5	46.8	2.85	250.4	48	***c	***c
I1-2	32/68	20.6	104.0	5.05	248.2	28	13.8	146
I1-3	23/77	25.8	136.7	5.29	249.1	16	10.9	273
I2[a]		15.8	26.9	1.70				
I2-1	56/44	20.4	56.6	2.78	258.7	41	***c	***c
I2-2	37/63	36.7	117.7	3.20	259.7	26	21.5	155
I2-3	26/74	27.3	133.0	4.86	256.4	20	14.3	322
I2-4	20/80	19.7	163.7	8.32	259.1	13	12.5	374
I3[a]		17.8	31.5	1.77				
I3-1	64/36	24.3	62.2	2.56	260.4	48	20.9	18
I3-2	42/58	21.5	79.7	3.72	259.5	31	18.2	149
I3-3	28/72	23.2	106.8	4.60	259.7	23	15.7	204
I4[a]		18.3	33.8	1.85				
I4-1	58/2	21.7	74.3	3.43	262.5	42	***c	***c
I4-2	32/68	25.7	99.7	3.88	260.9	22	17.6	255
I4-3	29/71	21.8	114.6	5.26	259.6	23	14.0	264
I5[a]		18.1	36.6	2.02				
I5-1	40/60	25.5	97.7	3.83	262.0	28	19.9	171
I5-2	33/67	24.7	110.9	4.49	259.6	25	17.5	258
I5-3	27/73	34.9	142.1	4.07	261.3	16	12.7	316

[a] Original azo-PA4 initiator for radical polymerization.
[b] Determined by GPC. The eluent was hexafluoroisopropyl alchohol, and the standard was poly(methyl methacrylate).
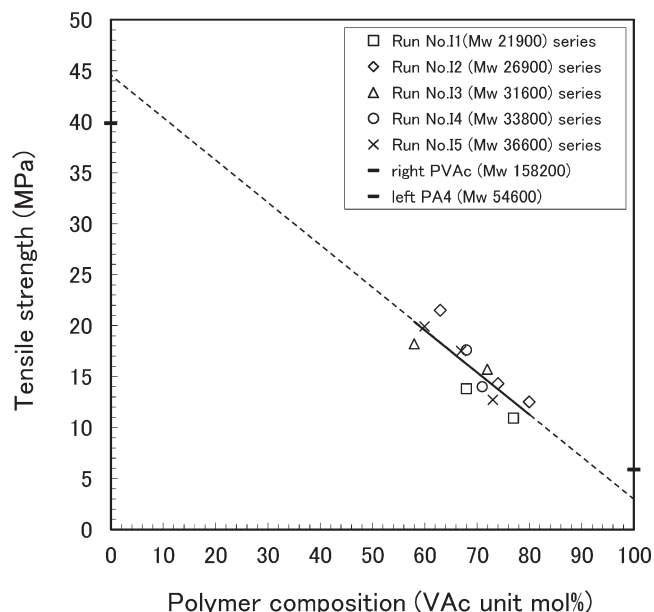[c] Good films were not obtained.

Figure 6. DSC thermograms of polyamide4-block-poly(vinyl acetate).
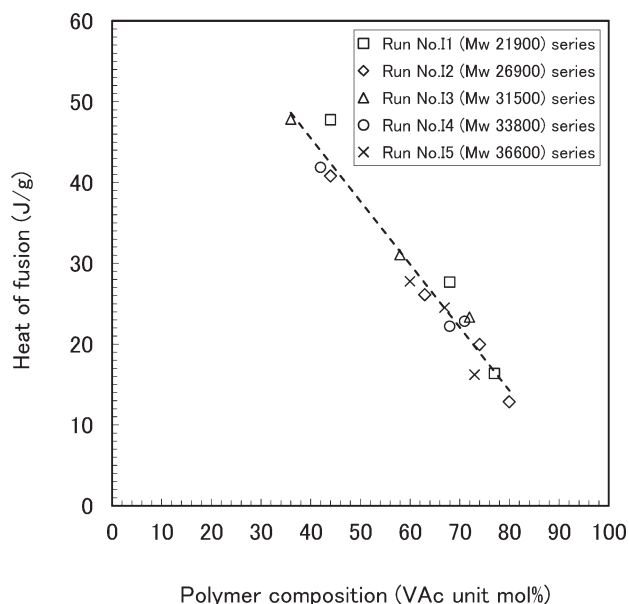
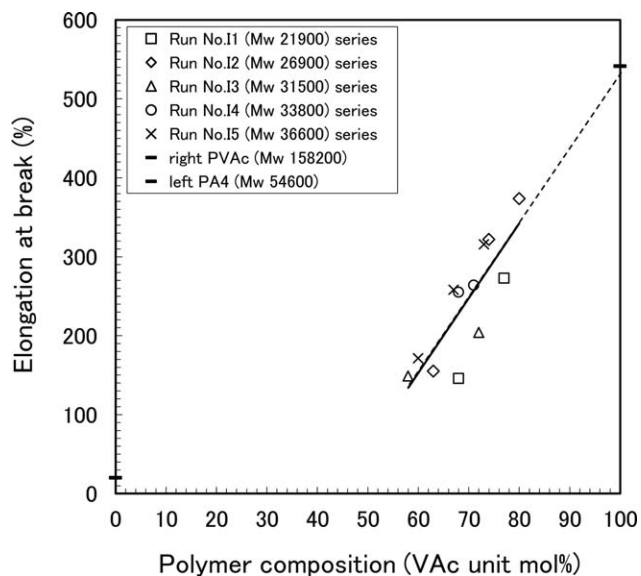**Figure 7.** Heat of fusion against composition of polyamide4-block-poly(-vinyl acetate).

Figure 8. Tensile strength against composition of polyamide4-block-poly(vinyl acetate).

Figure 9. Elongation at break against composition of polyamide4-block-poly(vinyl acetate).

26,900, 31,500, 33,800, 36,600). The measurements also indicated that the melting points of the PA4 blocks were independent of copolymer composition, whereas the heats of fusion (ΔHm) were found to depend on the polymer composition and were approximately linear (Figure 7). The linear decrease in ΔHm with decreasing PA4 content shows that the polymers are almost block copolymers. The thermal properties, including the melting point and the linear relation between ΔHm and the compositions of the PA4 polymers, suggest that phase separation arises from both the PA4 and PVAc domains.

The solvent casting method was used to prepare films of polyamide4-block-poly(vinyl acetate)s for mechanical testing by using the following method. Solutions of the polymer in 2,2,2-trifluoroethanol (ca. 10% w/v) were cast on glass Petri dishes, which were then covered. After gradual drying at atmospheric conditions for several days, films with an average thickness of ca. 100 μm were obtained. However, because of the fragility of the block copolymers with a lower VAc content, it was exceptionally difficult to obtain good quality films. The films were cut into rectangles (5 mm × 30 mm) and both ends of the rectangular specimens were fixed by square cardboard (25 mm × 25 mm) with a gauge distance of 10 mm. The specimens were thoroughly dried in a heated desiccator at 40–60°C under reduced pressure and then exposed to the atmosphere overnight before measurement of the mechanical properties.

Figure 8 (tensile strength) and Figure 9 (elongation at break) show the relation between these values and the copolymer compositions. The data for linear PA4 (Mw 54,600) and PVAc (Mw 158,200) were also included to enable comparison with the block copolymers. A straight solid line was fitted to the data of the block copolymers and the straight dotted line represents linear extrapolation on either side of the composition range. The tensile strength increases linearly with decreasing VAc content, thereby exhibiting increased strength for block copolymers

compared to PVAc. The data at either end of the dotted line, i.e., at the intercepts with the axes for PA4 and PVAc, were in rough agreement with the measured values. As for the elongation at break, the block copolymers exhibited a larger elongation than PA4. An extrapolation of the straight dotted line showed that the elongation at break of the block copolymers approaches that of PVAc with increasing VAc content. In regard to the mechanical properties, the high tensile strength of the block copolymers is attributed to the hard segment domains of PA4 blocks and the large elongation at break is attributed to soft segment domains of PVAc blocks. In general, many blends of different polymers have low miscibility, and exhibit the disadvantages of both the polymers rather than displaying a synergetic effect in terms of the mechanical properties.[35,36] Therefore,
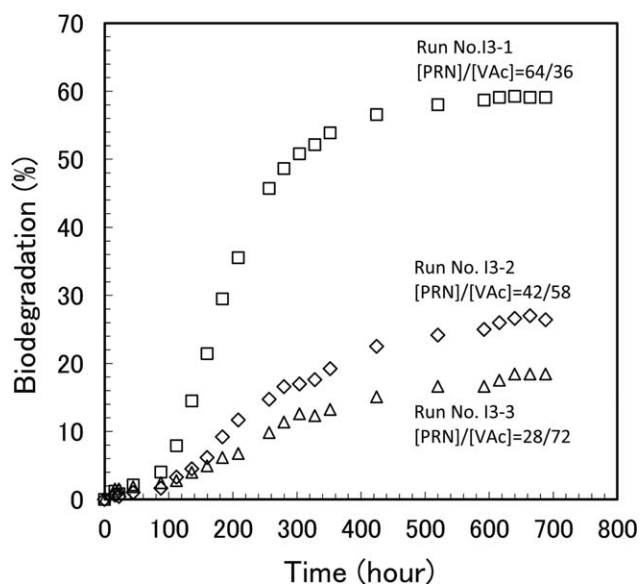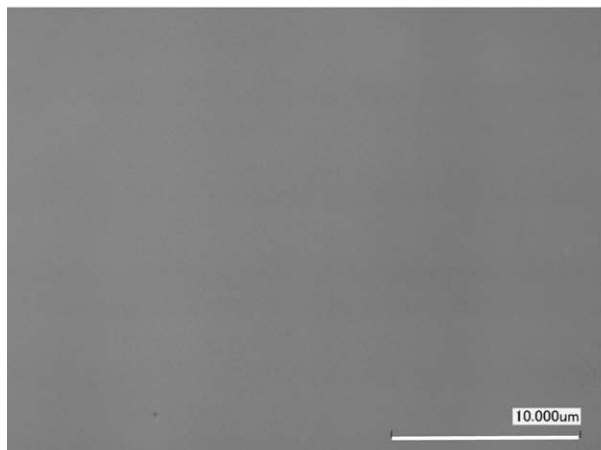

Figure 10. Time course of biodegradation for PA4-block-PVAc by an activated sludge.
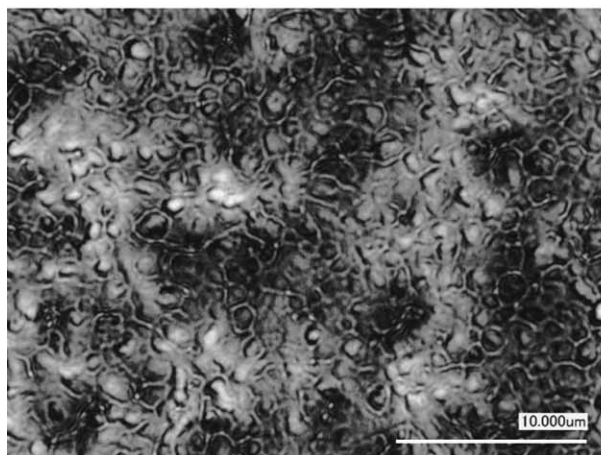
polyamide4
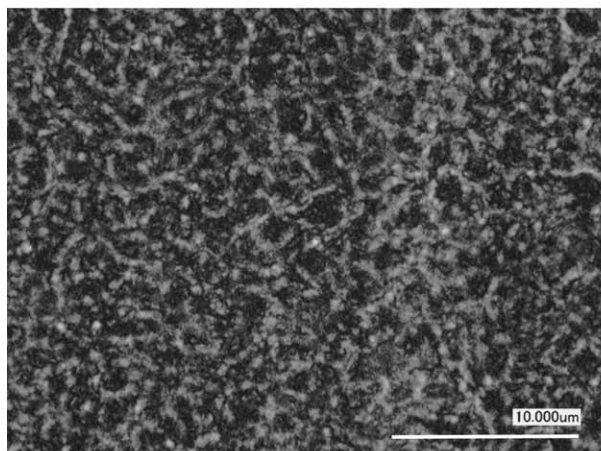
poly(vinyl acetate)

polyamide4-block-poly(vinyl acetate) (Run No.I3-2)

Figure 11. Laser micrographs of the free surface of polyamide4, poly(vinyl acetate), and polyamide4-block-poly(vinyl acetate).

the smooth continuous relation of the mechanical properties for different polymer compositions is a feature of the block copolymer, not the polymer blend.

Biodegradation

Polymer films prepared after three different polymerization runs (Run No. I3-1, I3-2, I3-3) were selected for the biodegradation test by an activated sludge. Figure 10 shows the time-course of the biodegradation results of these three block copolymers during a four-week period. When only PA4 chains were biodegraded, the percent degree of biodegradation on the basis of three different PA4 compositions of polyamide4-block-poly(vinyl acetate)'s ([PRN]/[VAc]=28/72, 42/58, and 64/36) were 18%, 27%, and 59% over 28 days, respectively. PVAc blocks with abundant block copolymers tended to suppress the biodegradation of the PA4 blocks. This means that the linking between the PVAc and PA4 chains controls the biodegradation property.

Morphology

The laser microscopic observation of the morphology of the original material was performed by preparing thin films by coating a 2,2,2-trifluoroethanol solution of the copolymers and homopolymers onto clean glass slides. Figure 11 shows the features of the free surfaces of the original PA4, PVAc, and polyamide4-block-poly(vinyl acetate). For PA4, a granite pattern was observed that seems to be based on the crystalline and noncrystalline regions. For PVAc, no observable pattern or structure was found. As for polyamide4-block-poly(vinyl acetate), a cellular wrinkled pattern was observed. From the above observation, it appeared that phase separation occurred for the block copolymers.

This could be explained by the difference in the solubility parameter (δ) for PA4 and PVAc. According to the data in the literature, the average solubility parameters are 19.74 (δ calculated by using 19.62, 19.13, 20.93, 19.2, 18, 22.61, 19.2, 19.2)[37] for PVAc and 23.96 (δ calculated by using 23.9, 24.02)[38] for PA4, respectively. The difference between the solubility parameters of these two polymers is large ($\Delta\delta = 4.22$). Furthermore, the intermolecular interaction between the two polymers is not strong because of the difficulty in forming mutual hydrogen bonds, and therefore, PVAc is not miscible with PA4. As the film was gradually formed and the disordered state was transformed into an ordered state, phase separation occurred due to immiscibility. The width of the wrinkles and the diameter of the cellular pattern were ca. 0.2 and 2 µm, respectively. The origin of the wrinkles and cellular pattern is not apparent but may be related to microphase separation rather than macrophase separation. This is because the pattern size order of macrophase separation is much more than µm order ($\gg$µm).[32,34] A possible interpretation of wrinkle formation on the free surface is the occurrence of shrinkage of the microphase separation structure of the film, presumably caused by the drying of the film.

CONCLUSIONS

Polyamide4-block-poly(vinyl acetate)s were readily synthesized by using azo-PA4, which was prepared by a simple novel method. The composition and Mw of the block copolymers, namely the content and degree of polymerization of the VAc unit, could be controlled by adjusting the feed ratio of the VAc monomers. The melting points of polyamide4-block-poly(vinyl acetate)s originated from PA4 blocks and their heats of fusion varied linearly with the PA4 content of the block copolymers.

The mechanical properties of the block copolymers showed continuous dependence on the composition. The tensile strength increased as the PA4 block content increased and the elongation at break increased with increasing PVAc block content. The biodegradation of polyamide4-block-poly(vinyl acetate)s was monotonically dependent on the composition, and the percent degree of biodegradation decreased as the PVAc block content increased. Microscopic observation of the surface of the polyamide4-block-poly(vinyl acetate) film showed that the morphology of the block copolymer film was quite different from that of both the PA4 and PVAc

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