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Synthesis, thermal and mechanical properties and biodegradation of branched polyamide 4

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Abstract

A series of linear and branched polyamide 4 were prepared and characterized in order to study the effect of the structure on thermal and mechanical properties. Polybasic acid chlorides were effective initiators for the synthesis of the branched polyamide 4. The melting points of the polyamide 4 for the high molecular weight region were near 265 °C and showed no significant difference depending on their chain structure. On the other hand, it was found that the branched polyamide 4 showed remarkable increase of tensile strength, compared to similar molecular weight of the linear polyamide 4 (e.g. four-branched type $M_w = 9.28 \times 10^4$, tensile strength = 72 MPa).When the initiator having branched structure were used, gel was also formed at the initiator concentration over a certain value (e.g. 3.0 mol% for 4-branched type).The biodegradation of the branched polyamide 4 was evaluated using a standard activated sludge (e.g. four-branched type $M_w = 8.25 \times 10^4$, biodegradation 41%).

Keywords: Biodegradation; Branched; Polyamides

1. Introduction

Biodegradation of natural polymer (rubber) was observed at least 70 years ago [1], then, possibilities of microbiological attack to various polymers have been studying to clarify the relationship between biodegradation and chemical structure of the polymers [2]. Besides, during the last three decades, influence of the synthetic polymers on the environment has been perceived by researchers [3,4]. As a consequence, a variety of biodegradable polymers has been synthesized and investigated [5–9]. It has been pointed out and summarized in various reviews that one of the important factors in biodegradation is the presence of hydrolysable linkage such as ester, amide, urethane and urea groups in the main chains [10,11]. In particular, various studies on syntheses and estimation of polymers have been conducted on polymers containing ester linkage in the main chain such as polyester, copolyester, copolyesterether and copolyesteramide. Most studies, however, have not focused on polymers containing only amide linkage in the main chain, namely, polyamide and copolyamide. To our knowledge, a little work is available in the published literature on the subject [12–18].

In these circumstances, it has been found that polyamide 4 is susceptible to biodegradation in composted soil [19] and in an activated sludge. According to these findings, there is a possibility that the polyamide 4 becomes attractive biodegradable materials due to their excellent thermal and mechanical properties based on their high melting point (260 °C) [20]. Furthermore, improvement in properties of the polyamide 4 makes it possible to apply in wide practical use. For this purpose, we have been attempted to modify the properties of the polyamide 4 by copolymerization since it would be expected to facilitate the synthesis of copolyesteramide by ring-opening copolymerization of 2-pyrrolidone and lactones. On the other hand, the modification of the properties includes the changing of the polymer chain's structure such as introducing the branched structure. For

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instance, there have been several investigations of introducing the branched structure into biodegradable polyesters [21–25], however, there seems to be little work for the polyamide 4. It is, therefore, important to investigate correlation between structure and the properties of the polyamide 4. This study was carried out to synthesize the polyamide 4 containing branched structure in main chain and to investigate their properties.

2. Experimental part

2.1. Materials

2-Pyrrolidone (Tokyo Kasei Kogyo Co., Japan) was distilled under reduced pressure. Sodium (Wako Pure Chemical Industries, Japan) was used after removing impurities on the surface. Tetrahydrofuran (Wako, Japan) was distilled from calcium hydride. Benzoyl chloride (Wako, Japan), Terephthaloyl dichloride (Wako, Japan), Isophthaloyl dichloride (Kanto Chemical Co., Japan), Benzene-1,3,5-tricarbonyl trichloride (Wako, Japan) were used without further purification. Biphenyl-3,3′,5,5′-tetracarbonyl tetrachloride was prepared by the method as described in synthesis part. A standard activated sludge was provided from the Chemicals Evaluation and Research Institute, Japan.

2.2. Synthesis

5-Iodo-*m*-xylene (10.0 g, 43.1 mmol), copper powder (10.0 g, 157 mmol) was heated to 280 °C for about 1 h, and then copper powder (5.0 g, 79 mmol) was added. The mixture was allowed to stand for 20 h at 270–280 °C, the stirring being continued throughout. Finally, copper powder (5.0 g, 79 mmol) was added again and the mixture was maintained at the same temperature for 3 h. After cooling to room temperature, acetone (80 ml) was poured into the reaction vessel and the solid residue was removed by using glass filter and filter paper. The filtrate was purified by the use of silica gel column chromatography. The solvent was removed from the purified filtrate to yield a colorless crystals, 3,3′,5,5′-tetramethylbiphenyl, 2.56 g, in 57% yield.

The mixture of 3,3′,5,5′-tetramethylbiphenyl (0.30 g, 1.43 mmol), water 100 ml, potassium permanganate (2.26 g, 14.3 mmol) was slowly heated to boiling with continual stirring until the permanganate color disappeared or paled. This required 3 days. The mixture was filtered through glass filter and the filter cake washed with hot water. The combined filtrate was filtered through a filter paper. When the filtrate was slightly acidified by cautiously adding concentrated hydrochloric acid, white fluffy precipitate was formed. The precipitate was filtered off, washed with water, and dried in vacuo. Biphenyl-3,3′,5,5′-tetracarboxylic acid obtained was 0.12 g (yield 25%).

To a small round-bottom flask was charged Biphenyl-3,3′,5,5′-tetracarboxylic acid (0.66 g, 2.0 mmol), thionyl chloride (20 ml, 274 mmol) and toluene (20 ml). The suspension was refluxed till it became almost homogeneous (it took about 1 day). The mixture was filtered through a filter paper to remove a small amount of insoluble solid. After the filtration, the excess of thionyl chloride and toluene were removed by evaporation under reduced pressure. The ivory powder, Biphenyl-3,3′,5,5′-tetracarbonyl tetrachloride (0.67 g) was obtained in a 83% yield.

2.3. Polymerization

A typical procedure is as follows. 2-Pyrrolidone (4.26 g, 50 mmol) and sodium (0.0345 g, 1.5 mmol) were placed in round-bottom flask equipped with a magnetic stirrer. The reaction mixture was heated to 50 °C under reduced pressure. After the sodium was reacted completely with 2-pyrrolidone, a carboxylic acid derivative (benzoyl chloride 0.105 g, 0.75 mmol) dissolved in tetrahydrofuran (0.2 ml) was added into the flask. The mixture was maintained at 50 °C under reduced pressure for approximately 24 h. The polymerization mixture was dissolved in formic acid and precipitated in acetone followed by washing with water and with methanol.

2.4. Processing

All the films of the polyamide 4 were prepared by dissolving in 2,2,2-trifluoroethanol (8–14%, w/v), subsequently drying at room temperature for 2 days. The films were cut into rectangles (5×30 mm^2) and both edges of the specimens were fixed by square card board (25×25 mm^2) taking gauge distance 10 mm.

2.5. Characterization

The Jeol alpha-500 NMR spectrometer was used to obtain ^{1}H NMR spectra (500 MHz). A saturated methanol-d_4 with calcium chloride was used as a solvent with tetramethylsilane as internal standard. Weight-average molecular weights and molecular weight distributions were determined by gel permeation chromatography using the Tosoh HLC-8220 GPC system. Two columns (TSK gel Super HM-N, TSK gel Super H-RC; Tosoh Co., Japan) were used with hexafluoroisopropyl alcohol (HFIP; Central Glass Co., Japan) as an eluent (0.2 ml min^{-1}) at 40 °C. The thermal property of the synthesized polymers was investigated by DSC, using a DSC3100S (Bruker AXS K.K., Japan). All the scans were carried out from 30 to 275 °C at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. Data for melting temperature (T_m) were taken from the peak top of the first heating scan. The mechanical property of the polymers was measured by a tensile testing. The tensile testing of the test piece was carried out using a TENSILON/UTM-4-100 testing machine (Toyo Baldwin

Co., Ltd, Japan) with a 5 kg load cell and the cross speed was maintained 10 mm min^{-1} at room temperature. The gauge length was maintained at 10 mm. The thickness of each test piece was measured at three points before testing and a minimum value was adopted.

2.6. Biodegradation by an activated sludge

Biodegradability of the polyamide 4 was evaluated from determination of the amount of carbon dioxide (CO_2) evolved by a standard activated sludge metabolism in conformity to the procedure reported in ISO14852 and a previous paper [26]. The evolving CO_2 was trapped by sodium hydroxide solution (0.025 mol l^{-1}) and determined as inorganic carbon with a total organic carbon analyzer, TOC-5000 (Shimadzu Co., Japan). The duration of the biodegradation test was about 1 month and the amount of CO_2 was measured every week. Biodegradation of the polyamide 4 was calculated by the following equation:

$$\text{Biodegradation in } \% = (\text{amount of observed } CO_2/\text{amount of theoretical } CO_2) \times 100$$

The observed CO_2 amount was corrected by subtraction of the CO_2 amount of the blank experiment. The theoretical CO_2 amount was calculated from the structural formula of the polyamide 4 assuming that degraded products are completely mineralized to CO_2.

Furthermore, the polyamide 4 also contains nitrogen, and hence nitrite ion and nitrate ion seem to form in culture media when the polyamide 4 was degraded and metabolized by the activated sludge. In order to confirm and determine the formation of nitrite ion and nitrate ion, ion chromatography was performed. An ion chromatography system (conductivity monitor CM-8020, dual plunger pump DP-8020, column oven CO-8020; Tosoh Co., Japan) was operated as follows. Columns (TSK gel IC-Anion-PWXL; Tosoh Co., Japan) were used with TSK eluent IC-Anion-A (Tosoh Co., Japan) as an eluent (1.2 ml min^{-1}) at 40 °C.

3. Results and discussion

Linear and branched polyamide 4's were prepared by the ring-opening polymerization of 2-pyrrolidone. In order to examine an influence on yields and molecular weights, the polymerizations were carried out using benzoyl chloride (BzC), terephthaloyl dichloride (Bz14DCC), isophthaloyl dichloride (Bz13DCC), benzene-1,3,5-tricarbonyl trichloride (Bz135TCC) and Biphenyl-3,3′,5,5′-tetracarbonyl tetrachloride (Bp3355TCC) as the initiators at various concentrations.

Table 1 shows the effects of concentration of individual initiators on yield and molecular weights of polymers. BzC, Bz14DCC and Bz13DCC were used for synthesizing the linear polyamide 4 (end type, straight type, bent type) as the initiators. In both case, there was a faint tendency for the yields to decrease when the initiator concentration was low. However, the yields did not decrease abruptly up to the concentration 0.75 mol%. The weight-average molecular weights remained about 40,000 for using BzC, even if the initiator concentration was 0.75 mol%.

Next, Bz135TCC was used for synthesizing a three-branched polyamide 4 as the initiator. In the case of using Bz135TCC, the yields of the polymers showed concentration dependence of the initiator and of the catalyst. The polymer yields hardly changed from 3.0 to 0.75 mol% of the initiator concentration, below which it decreased abruptly. In such a case of low initiator concentration (under 0.45 mol%), the yields remained a few percentages even the polymerization was continued for a long time. This low yield is probably due to deactivation of active site for propagation by very small amounts of impurities in the reaction system. On the other hand, in the case of the initiator at concentrations higher than 4.5 mol%, a gelation occurred. Consequently, the yields of soluble parts of the polymerization products were decreased, however, the total yields of the products were almost the same as the initiator concentration at 3.0–0.75 mol%.

Furthermore, Bp3355TCC was used for synthesizing a four-branched polyamide 4 as the initiator. In this case, the yield also decreased when the initiator concentration was low. On the other hand, raising the initiator concentration (3.0 mol%) resulted in gelation similar to Bz135TCC initiated polymerization.

It should be emphasized that the gelation occurred only by using the initiators having branched structure. The gelation for each of the initiators with branched structure, shown in Table 1, occurred above a certain concentration. When the initiator without branched structure (Bz14DCC, Bz13DCC) was used, no gelation occurred even if the initiator concentration was raised to 12 mol%.

Fig. 1 shows a ^{1}H NMR spectra of the polyamide 4 synthesized by using Bz135TCC and Bp3355TCC as the initiators. ^{1}H NMR spectrum in Fig. 1(a) displays characteristic signals for the methylene protons (*b*, *a*, *c*) at chemical shifts of 1.9, 2.5, 3.3 ppm and amide protons (*d*) at 8.7 ppm in the polyamide 4 chains. The peak denoted *e* at 9.1 ppm is the aromatic protons of the initiator. The mean degree of polymerization of each arm for the three-branched polyamide 4 was determined by ^{1}H NMR. In the case of initiator concentration 1.0 mol% (3.0 mol% for carbonyl chloride), the mean degree of polymerization was evaluated to be 53 from the integration ratio of signal *e* (intensity 0.188 for 3H) to signal *b* (intensity 20 for 2H). This estimation was in rough agreement with the corresponding calculated value (the calculation value = 33). In Fig. 1(b), the peaks denoted *B*, *A*, *C*, *D* were assigned to the protons on the polyamide 4 chain part that is the same as the three-

Table 1
Ring-opening polymerization of 2-pyrrolidone with several acyl chlorides as initiators

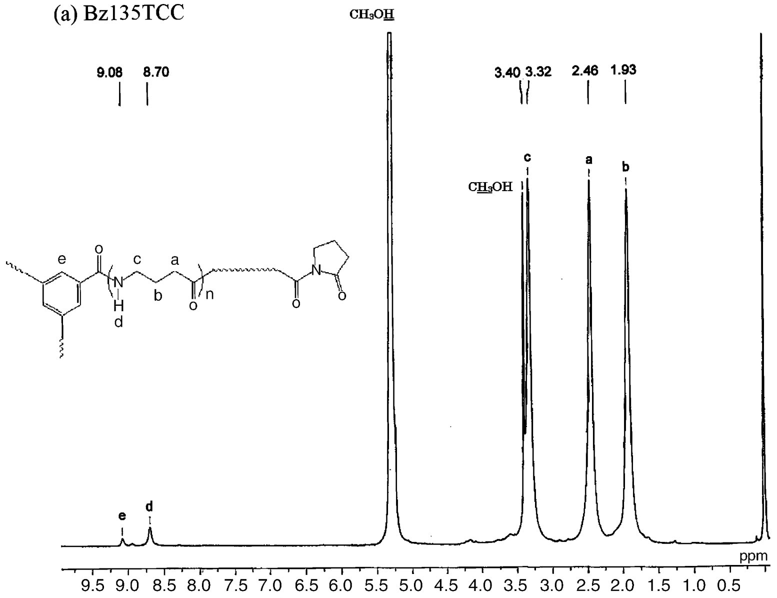
Initiator (mol%)[a]	Catalyst (mol%)[b]	Yield (%)	$M_\mathrm{n}\times10^{-4}$[c]	$M_\mathrm{w}\times10^{-4}$[c]	$M_\mathrm{w}/M_\mathrm{n}$[c]	T_m (°C)[d]
BzC: linear(end) type						
0.75	1.5	34	1.64	4.68	2.56	263.0
1.5	3.0	55	1.99	4.67	2.35	261.9
3.0	6.0	58	1.73	5.21	3.01	262.3
Bz14DCC: linear (straight) type						
0.75	1.5	70	6.50	10.93	1.68	265.6
3.0	6.0	72	1.72	5.72	3.32	260.8
6.0	9.0	76	2.09	3.99	1.91	255.9
12.0	18.0	66	1.01	1.79	1.77	239.1
Bz13DCC: linear (bent) type						
0.75	1.5	53	4.79	8.70	1.82	263.2
3.0	6.0	81	2.29	4.85	2.12	259.7
12.0	18.0	69	1.40	2.51	1.79	247.1
Bz135TCC: 3-branched type						
0.15	0.3	0	–	–	–	–
0.3	0.6	0	–	–	–	–
0.3	0.6	5.9 (4 days)[e]	1.02	1.83	1.80	256.2
0.45	0.9	3.5 (6 days)[e]	0.52	0.87	1.67	233.0
0.75	1.5	62	5.87	10.28	1.75	264.5
1.5	3.0	59	4.29	8.51	1.98	263.6
3.0	6.0	63	2.04	7.52	3.69	264.4
4.5	9.0	12, (58 gel)[f]	–	–	–	–
6.0	9.0	37, (36 gel)[f]	–	–	–	–
9.0	18.0	11, (49 gel)[f]	–	–	–	–
Bp3355TCC: 4-branched type						
1.5	3.0	32	3.94	8.25	2.09	260.8
2.0	4.0	46	2.97	9.28	3.12	262.6
3.0	6.0	(73 gel)[f]	–	–	–	–

[a] Mol% means conversion from quantities of carboxyl chloride groups in the initiator.
[b] Calculated from quantities of sodium.
[c] Determined by GPC; eluent: hexafluoroisopropyl alcohol, standard: poly(methyl methacrylate).
[d] Determined by DSC.
[e] Polymerization time.
[f] Yield of gel part.

branched polyamide 4. The peaks denoted *E* at 8.9 ppm and *F* at 8.3 ppm come from the aromatic protons of the initiator, Bz3355TCC. The intensity of these peaks *E* and *F* weakened and the peak width broadened compared to other aromatic proton peaks of the linear polyamide 4. The reason seems to be that the aromatic molecule part was centered in the four-branched polyamide 4 chains, thereby depressed, so that uniforming of a local magnetic field did not occur [27]. Although the peak intensity of aromatic part seemed lack accuracy, the mean degree of polymerization of each arm for the four-branched polyamide 4 was also determined by ^{1}H NMR. In the case of initiator concentration 0.375 mol% (1.5 mol% for carbonyl chloride), the mean degree of polymerization was evaluated to be 78 from the integration ratio of signal *E* and *F* (intensity 0.192 for 6H) to signal *B* (intensity 20 for 2H). This estimation was in rough agreement with the corresponding calculated value (the calculation value = 67). These rough agreements for the degree of polymerization, namely the discrepancy of the degree of the polymerization can be explained as follows. Since the bulk polymerization of 2-pyrrolidone proceeds with rapid solidification, propagation of polymer chains becomes heterogeneous and the polymers of different chain length form. When these mixtures of the polymers were purified, the polymers of short length were removed.

Turning now to the effect of introducing branched architecture into the polyamide 4 chain on properties, melting point and tensile strength of the linear and branched polyamide 4's were measured. Fig. 2 summarizes the melting points at the peak top (T_m) of the polyamide 4's in Table 1 and in additional measurements. It depicts the relationships between the weight-average molecular weight (M_w) and T_m of the linear and branched polyamide 4's. The difference in melting points between the linear and branched polyamide 4 was not found over the whole molecular weight range measured ($M_\mathrm{w} > 10^4$). When the molecular weight range is in several ten thousands, difference of the polymer structure scarcely affects bulk property such as melting point. The reason seems to be that the branched polyamide 4, with high molecular weight, includes low proportion of amorphous domain, owing to chain branching. In other words, the effect of amorphous domain based on long chain

(a) Bz135TCC



(b) Bp3355TCC

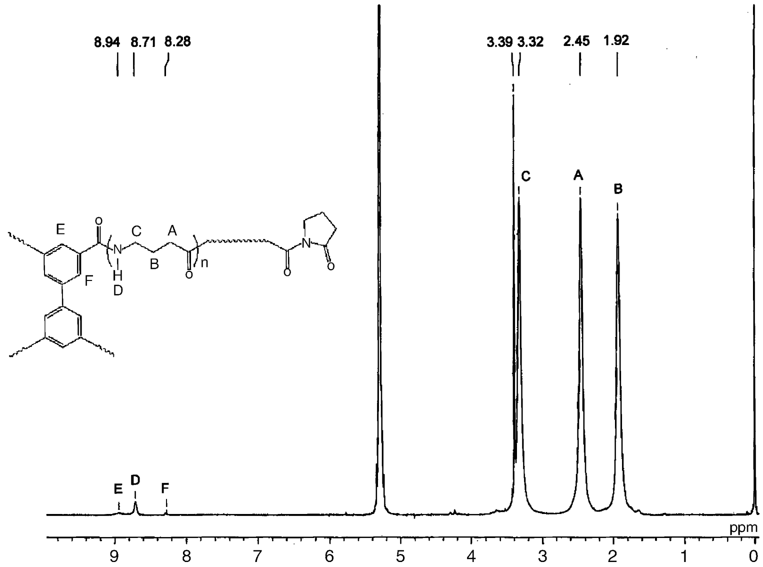


Fig. 1. ^{1}H NMR spectra of branched polyamide 4. (a) Three-branched type synthesized by using benzene-1,3,5-tricarbonyl trichloride as an initiator, (b) four-branched type synthesized by using biphenyl-3,3′,5,5′-tetracarbonyl tetrachloride as an initiator.

branching is negligible in comparison to the effect based on short branching. However, the dependence of the melting points on the molecular weight was observed clearly in low molecular weight region. The melting points showed a positive dependence for molecular weights up to 4×10^{4} above which it showed nearly constant (265 °C), even so, the plotting points slightly scattered.

Fig. 3 provides a plot of tensile strength against log M_w for the polyamide 4. The error bars indicate the probable error in measured values. The tensile strength of the polyamide 4 shows positive molecular weight dependence. As shown in Fig. 3, the tensile strength of the branched polyamide 4 is higher than that of linear polyamide 4 over the molecular weight range measured. With high molecular weight of the branched polyamide 4, the polymer chains become longer and hence the intermolecular chain entanglement of the polymer occurs. This intermolecular chain entanglement leads to a decrease of polymer chain mobility. It has been known that polymer chain mobility is a crucial factor in determining the mechanical properties of polymers. One typical example of this is that branched polymers have greater melt viscosities than those of linear

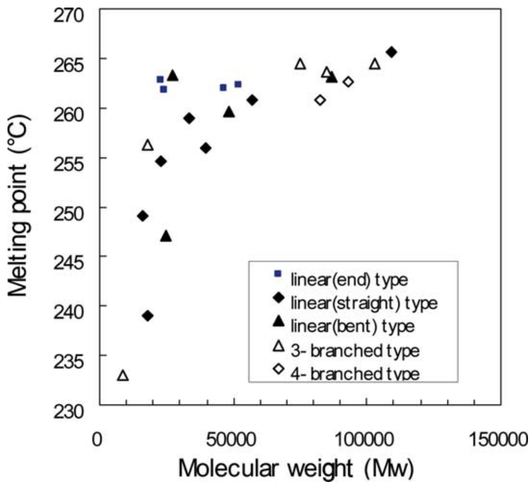


Fig. 2. Melting points of linear and branched polyamide 4 plotted against weight-average molecular weight.

chains of same molecular weight [28]. By analogy with this, the high tensile strength of the branched polyamide 4 is interpreted as the effect of the entanglement of the polymer chain.

Fig. 4 shows a plot of tensile strain against log M_w for the polyamide 4, measured at room temperature. The tensile strain of the polyamide 4 shows positive molecular weight dependence, however, the relationship between polymer chain structure and tensile strain were not clear.

Fig. 5 shows the biodegradation profiles of the branched polyamide 4 (three-branched type: $M_w = 8.51 \times 10^4$, four-branched type: $M_w = 8.25 \times 10^4$) by the standard activated sludge. The biodegradation of the polyamide 4's reached 39, 41%, respectively, after 21 days and thereafter kept constant. It was thought that the activity of the activated sludge decreased, hence the activated sludge was added again to recover the activity. When the activated sludge was newly added to the culture media, the biodegradation of the three-branched and the four-branched polyamide 4 reached to 81, 49%, respectively, after 77 days. In the same way, the biodegradation of the linear polyamide 4 was evaluated. With linear polyamide 4's (straight type: $M_w = 10.93 \times 10^4$, bent type: $M_w = 8.70 \times 10^4$), the biodegradation were 48% (28 days), 46% (27 days), respectively.

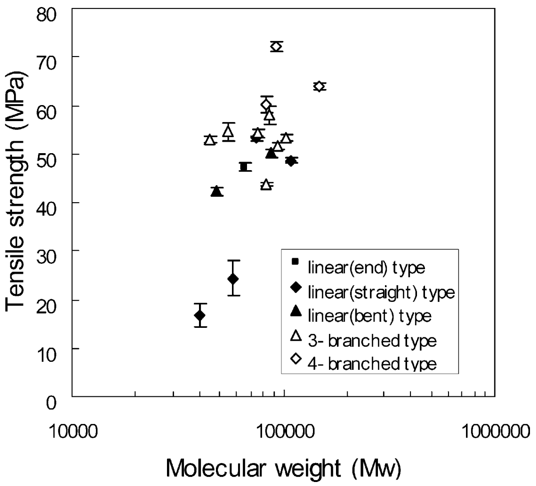


Fig. 3. Tensile strength of linear and branched polyamide 4 films plotted against weight-average molecular weight.

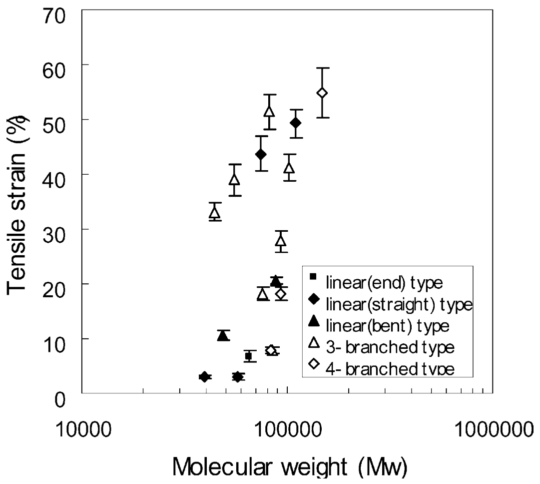


Fig. 4. Tensile strain of linear and branched polyamide 4 films plotted against weight-average molecular weight.

It is thought that the nitrogen of the polyamide 4 was metabolized by microbes in the activated sludge and was converted into inorganic compounds in the culture media. For this purpose, ion chromatography was used for measuring the concentration of inorganic nitrogen component, nitrite ion (NO_2^-) and nitrate ion (NO_3^-), in the culture media. Fig. 6 shows the time course of the concentration of the inorganic nitrogen components evolved by the biodegradation of the polyamide 4 (four-branched type: $M_w = 8.25 \times 10^4$) in the culture media. The polyamide 4 was biodegraded by the activated sludge and then (NO_2^-) and (NO_3^-) were formed. From the total concentration of (NO_2^-) and (NO_3^-), the biodegradation was estimated as follows.

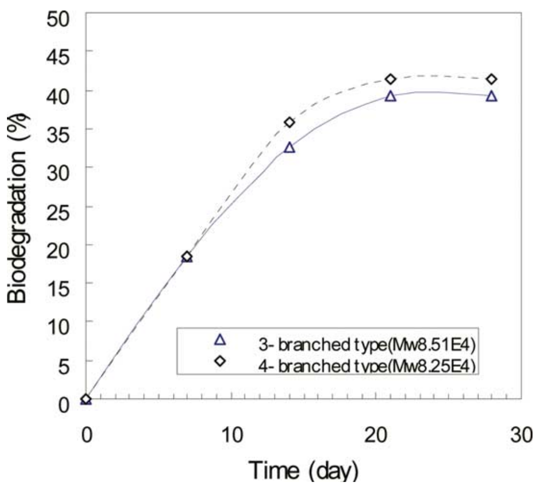


Fig. 5. Biodegradation profiles of branched polyamide 4 by a standard activated sludge.

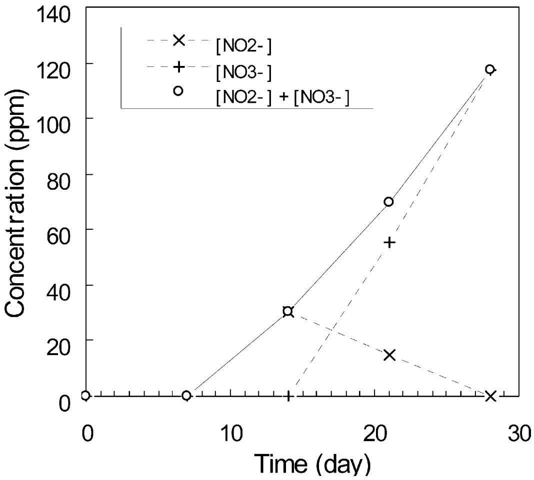


Fig. 6. Time course of concentration of NO_2^-, NO_3^- and $NO_2^- + NO_3^-$ in culture media for biodegradation by a standard activated sludge.

Constitutional repeating unit of the polyamide 4 $-(-NHCH_2CH_2CH_2C{=}O-)_n-$

formula weight of the unit 85.10, atomic weight of N 14.01

weight of N in polyamide 4 (0.2 g)

$0.2\times(14.01/85.10)=0.0329$ g.

Assuming that the polyamide 4 was mineralized completely in culture media (500 ml),

concentration of N (theoretical) is

$0.0329/0.5=0.0658$ g/l $=65.8$ ppm.

concentration of (NO_2^-) and (NO_3^-) in culture media.

(observed) (NO_2^-) 0 ppm, (NO_3^-) 117.1 ppm

content ratio of N in (NO_2^-) and (NO_3^-)

formula weight of (NO_2^-) 46.01

content ratio of N for (NO_2^-) $14.01/46.01=0.304$

formula weight of (NO_3^-) 62.00

content ratio of N for (NO_3^-) $14.01/62.00=0.226$

concentration of N (observed) is

$0\times0.304+117.1\times0.226=26.5$ ppm

hence, the biodegradation is $(26.5/65.8)\times100=40.3\%$.

In this case, the degree of biodegradation estimated from inorganic nitrogen component was identical with that estimated from CO_2 evolved (41%).

4. Conclusions

In this paper, we reported the synthesis of the branched polyamide 4 and their properties. The novel branched polyamide 4 was synthesized by using polybasic acid chloride as initiators having branched structure. When the concentration of the initiators with branched structure exceeded a certain value (4.5 mol% for three-branched type, 3.0 mol% for four-branched type), partly gelation occurred. The melting points of the polyamide 4 settled into the vicinity of 265 °C with increasing molecular weight, however, obvious difference owing to branching could not be found. The tensile strength and tensile strain showed positive molecular weight dependence over the range measured. With the same degree of molecular weight, the tensile strength of the branched polyamide 4 tended to be larger than that of the linear polyamide 4. From these results, it makes possible to improve the tensile strength by introducing branched structure into the polyamide 4 chains. Turning now to biodegradation test by an activated sludge, the polyamide 4 easily degraded regardless branched structure or linear structure. It was confirmed that the polyamide 4 was metabolized into carbon dioxide and nitrate by microbes in the activated sludge.

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