Releasing Polyacrylonitrile from Poor Biodegradability by Insertion of a Highly Biodegradable Chemical Structure into the Main Chain

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ABSTRACT: Polyacrylonitrile turned biodegradable by incorporation of *N*-benzyl-4-vinylpyridinium chloride (BVP), a highly biodegradable chemical structure, into the main chain. Oligomers of acrylonitrile are biodegradable dissimilar to polyacrylonitrile, and connection of them by BVP produced biodegradable polymers. The half-life of a copolymer of acrylonitrile with BVP (PAN-*co*-BVP) in a molar ratio of 97 : 3 was 21 days when treated with activated sludge in soil. The average number of acrylonitrile units in the oligo-acrylonitrile portion was 32. Degradation at the BVP portion appeared predominant, but the oligo-acrylonitrile portion also underwent exhaustive degradation when the portion was sufficiently short. Even though biodegradable, oligo-acrylonitriles are not useful as polymeric materials, but connection of them by BVP produces useful polymeric materials possessed of sufficient biodegradability. Such bridged polymer is different from conventional polyacrylonitrile, and its utility may be different to some extent, but it possesses sufficient biodegradability. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 852–857, 2006

Key words: biodegradable; degradation; functionalization of polymers

INTRODUCTION

In the past 60 years, the polymer industry has provided durable materials adapted to particular uses, but considerable attention has focused on biodegradable polymers for protection of the natural wealthy environment from persistent solid wastes. These biodegradable polymers include naturally occurring polymers and their derivatives, poly(hydroxyalkanoates) produced by bacteria,[1] and biodegradable synthetic polymers, such as aliphatic polyesters[2,3] and poly(vinyl alcohol).[4] However, these polymers are not always possessed of the necessary characteristics for wide use of synthetic polymers, and it is favorable if general synthetic polymers are turned substantially biodegradable by partial modification of the chemical structure. Different from poly(vinyl alcohol), biodegradation of hydrophobic vinyl polymers having a carbon–carbon bond as the main chain is extremely difficult.

Incorporation of a biodegradable chemical structure into the main chain is effective for making synthetic polymers substantially biodegradable. Matsumura et al.[5] attempted to make poly(carboxylic acid) biodegradable by incorporation of vinyl alcohol as a biodegradable unit. Previously, we reported rapid digestion of crosslinked poly(*N*-benzyl-4-vinylpyridinium chloride) (PBVP) by activated sludge,[6] and *N*-benzyl-4-vinylpyridinium chloride (BVP) was demonstrated to be a highly biodegradable chemical structure. Poly(methyl methacrylate) and copolymer of vinyl acetate with 10 mol % of methyl acrylate showed distinct degradation by treatment with activated sludge when BVP was incorporated into the main chain.[6,7]

However, these polymers did not exhibit biodegradability in the absence of BVP, and it is difficult to exclude the possibility that biodegradation is limited only to the portion of BVP, with the residual polymer chain remaining unchanged after the treatment. On the other hand, low molecular weight oligomers of ethylene,[8] butadiene,[9] isoprene,[10] and trimer of acrylonitrile[11] and dimer of styrene[12] were reported biodegradable. Therefore, we expected exhaustive degradation of the residual oligomer portion when the chain length was sufficiently short, and attempted to elucidate the amount of BVP necessary to realize substantially exhaustive biodegradation of hydrophobic vinyl polymers using polyacrylonitrile (PAN) as an additional example.

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EXPERIMENTAL

Materials

Reagent grade acrylonitrile was purchased from Nacalai Tesque (Kyoto, Japan) and was purified by distillation under atmospheric pressure. Reagent grade 4-vinylpyridine was purchased from Nacalai Tesque, and was purified by distillation under a reduced pressure around 8 mm Hg. Reagent grade benzyl chloride, 2,2′-azobisisobutyronitrile (AIBN), dimethylformamide (DMF), ethyl acetate, and $MgCl_2 \cdot 6H_2O$ were purchased from Nacalai Tesque and were used without further purification. High pressure nitrogen provided by Izumi Sangyo (Kyoto, Japan) was used without further purification.

Polymerization

Reactions were performed using a 500-mL round-bottomed three-necked flask equipped with a nitrogen inlet, a reflux condenser, and a mechanical stirrer. Free radical copolymerization of acrylonitrile with 4-vinylpyridine was performed using AIBN as initiator in DMF at 70°C for 24 h to produce poly(acrylonitrile-*co*-4-vinylpyridine) (PAN-*co*-VP). The copolymer was then converted to poly(acrylonitrile-*co*-*N*-benzyl-4-vinylpyridinium chloride) (PAN-*co*-BVP) by the reaction with benzyl chloride in DMF at 80°C for 6 h. For example, preparation of PAN-*co*-BVP that contained 6.6 mol % of BVP was performed as follows. Acrylonitrile (95.5 g, 1.80 mol), 4-vinylpyridine (21.0 g, 0.20 mol), and AIBN (0.32 g, 2.0 mmol) were added to 180 g of DMF under a nitrogen atmosphere and heated at 70°C with stirring for 24 h. After cooling to room temperature, benzyl chloride (25.3 g, 0.20 mol) was added, and the mixture was allowed to react with stirring at 80°C for 6 h. PAN-*co*-BVP was isolated by pouring the reaction mixture into ethyl acetate, and was dried to constant weight under a reduced pressure at room temperature. In the series of copolymerization, the total amount of acrylonitrile and 4-vinylpyridine was set to be 2.00 mol. To prepare PAN-*co*-BVP with a variety of molecular weights, the amount of AIBN was changed in the range between 0.32 g (2.0 mmol) to 1.64 g (10.0 mmol). The amount of benzyl chloride was set to be equimolar to 4-vinylpyridine contained in PAN-*co*-VP.

Composition of the copolymers was determined by elemental analyses performed at the Elementary Analyses Center of Kyoto University. We determined content of BVP based on the amount of chlorine. We determined content of acrylonitrile and 4-vinylpyridine based on the amounts of carbon and nitrogen after reduction of these amounts due to BVP, but content of 4-vinylpyridine in PAN-*co*-BVP was very low. Since we prepared PAN-*co*-VP using free radical copolymerization of acrylonitrile with 4-vinylpyridine, we expected PAN-*co*-VP and PAN-*co*-BVP to be random copolymers, and we did not investigate details of the chemical structure by spectroscopy. Intrinsic viscosities of polyacrylonitrile and PAN-*co*-VP were determined at 25°C in DMF. Viscosity average molecular weight of PAN-*co*-VP was estimated based on the viscosity–molecular weight relationship for polyacrylonitrile.[13] Intrinsic viscosity of PAN-*co*-BVP was determined at 25°C in DMF that contained 1.0 g L^{-1} of $MgCl_2 \cdot 6H_2O$. Figure 1 illustrates the relation between intrinsic viscosity of PAN-*co*-VP and that of the corresponding PAN-*co*-BVP that contained 10 mol % of 4-vinylpyridine and BVP, respectively. Viscosity average degree of polymerization of PAN-*co*-BVP was estimated using the viscosity–molecular weight relationship for PAN[13] after the intrinsic viscosity was converted to that of the corresponding PAN-*co*-VP based on the relation illustrated in Figure 1.

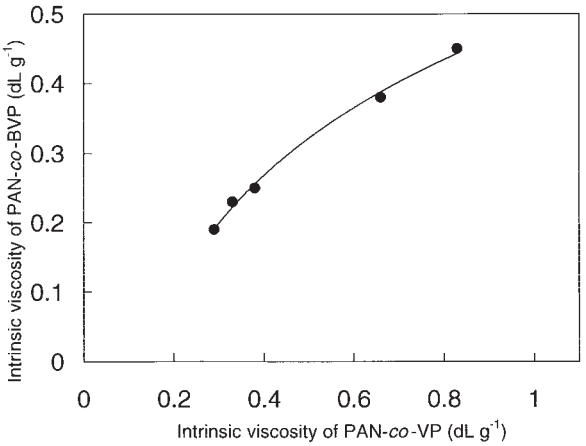

Figure 1 Relation between the intrinsic viscosity of PAN-*co*-BVP that contained about 10 mol % of BVP versus that of the corresponding PAN-*co*-VP determined prior to the reaction with benzyl chloride. Intrinsic viscosities of PAN-*co*-VP were determined at 25°C in DMF, and those of PAN-*co*-BVP were determined at 25°C in DMF that contained 1.0 g L^{-1} of $MgCl_2 \cdot 6H_2O$.

Degradation of PAN-*co*-BVP by treatment with activated sludge in soil

Activated sludge was obtained from Sewage Works of Hiking City immediately before the experiments of biological degradation, and was washed three times with sterilized physiological saline. Test soil used for the biological degradation was obtained from the shore of Lake Biwa, and was washed with water using a Soxhlet extraction apparatus for 30 h. The washed soil was dried to constant weight before use.

Specially prepared reagent of meat extract was purchased from Nakalai Tesque and was used without further purification. Reagent grade peptone, urea, sodium chloride, potassium chloride, calcium chloride,

magnesium sulfate, and sodium hydrogenphosphate were purchased from Nakalai Tesque and were used without further purification. An artificial sewage prepared according to a literature recipe[14] was used to assist the biodegradation. Peptone (6.0 g), meat extract (4.0 g), urea (1.0 g), sodium chloride (0.30 g), potassium chloride (0.14 g), calcium chloride (0.14 g), magnesium sulfate (0.10 g), and sodium hydrogenphosphate (1.0 g) were dissolved in 1.0 L deionized water, and pH was adjusted to 8.5. The chemical oxygen demand (COD) of this undiluted solution was about 10,000 mg L^{-1}. This solution was diluted with an appropriate amount of deionized water to prepare artificial sewage of prescribed COD concentration.

Biodegradation was performed by treatment with activated sludge in soil. A polymer sample (100 mg) was dissolved in DMF (10 mL), and was mixed with the washed soil (50 g). The mixture was then placed in a desiccator, and DMF was removed by drying under a reduced pressure to constant weight.

Washed activated sludge (0.71 g in wet weight) and an artificial sewage (100 mg in COD) were mixed with the test soil (50 g). Total amount of water in the test soil was 200 mL kg^{-1}. The mixture was allowed to stand at room temperature.

After a prescribed time, the remaining polymer was recovered by extraction with DMF using a Soxhlet extraction apparatus at room temperature for 100 h. Fine soil particles contained in the extractive were removed by centrifugation. The supernatant was placed in a rotary evaporator, and DMF was removed by evaporation. Ethyl acetate was added to the residue and the recovered polymer was precipitated, and was dried to constant weight under a reduced pressure. A series of control experiments were performed to ascertain reliability of the recovery procedure. We performed a series of experiments where activated sludge was not used, and ascertained quantitative recovery (generally more than 98% and at least 95%) of the polymer sample from the soil mixture. Since recovered PAN-*co*-BVP did not exhibit a perceivable change of elementary composition, viscosity average degrees of polymerization of the recovered PAN-*co*-BVP were approximated based on intrinsic viscosities of the corresponding PAN-*co*-VP evaluated by using a relationship illustrated in Figure 1 and the viscosity–molecular weight relationship for polyacrylonitrile.[13]

RESULTS AND DISCUSSION

Degradation of PAN-*co*-BVP by treatment with activated sludge in soil

Degradation of PAN-*co*-BVP was performed by treatment with activated sludge in soil at room temperature. Figure 2 shows the time course of weight reduction during the biological treatment. Here, residual weight is the total weight of polymeric materials recovered after the treatment by precipitation using ethyl acetate, and low molecular weight oligomers and other organic materials soluble in ethyl acetate were not included. Recovered polymer samples were dried to constant weights under a reduced pressure.

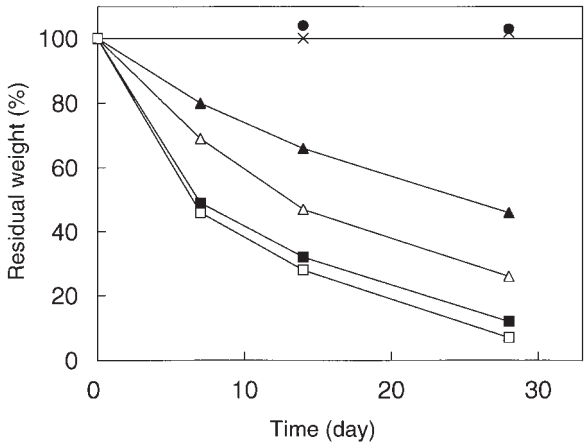

Figure 2 The time course of the weight of the polymer recovered after treatment with activated sludge in soil at room temperature. Initial amount of polymer sample, 2.0 g kg^{-1}; amount of artificial sewage added to the treatment system, 2.0 g kg^{-1} in COD; water, 200 mL kg^{-1}. Intrinsic viscosities of polymers determined before biological treatment are given in parentheses in dL g^{-1}. In the cases of PAN-*co*-BVP, the given viscosities are those of the corresponding PAN-*co*-VP determined prior to the reaction with benzyl chloride. (×) Polyacrylonitrile (0.65); (●) PAN-*co*-VP that contained 13.2 mol % of 4-vinylpyridine (0.75); (▲) PAN-*co*-BVP that contained 3.0 mol % of BVP (0.69); (△) PAN-*co*-BVP that contained 6.6 mol % of BVP (0.59); (■) PAN-*co*-BVP that contained 12.3 mol % of BVP (0.66); and (□) PAN-*co*-BVP that contained 33.0 mol % of BVP (1.10).

As shown in Figure 2, weight reduction was not observed in the cases of polyacrylonitrile (cross marks) and PAN-*co*-VP that contained 13.2 mol % of 4-vinylpyridine (closed circles), respectively. In the absence of BVP, biodegradation was not observed, similar to the cases of poly(methyl methacrylate)[6] and poly(vinyl acetate-*co*-methyl acrylate).[7]

On the contrary, PAN-*co*-BVP that contained 3.0 mol % BVP exhibited an obvious weight reduction during the treatment, as shown in Figure 2 (closed triangles). Polyacrylonitrile turned biodegradable by incorporation of BVP in 3 mol % as a biodegradable chemical structure into the main chain. In this particular case, the average number of acrylonitrile units in the oligo-acrylonitrile portion was 32. Viscosity average degree of polymerization was estimated 770, and the average number of BVP contained in a polymer chain was 24.

Weight reduction of PAN-*co*-BVP became more distinct when it contained 6.6, 12.3, and 33.0 mol % of BVP, as shown by open triangles, closed squares, and

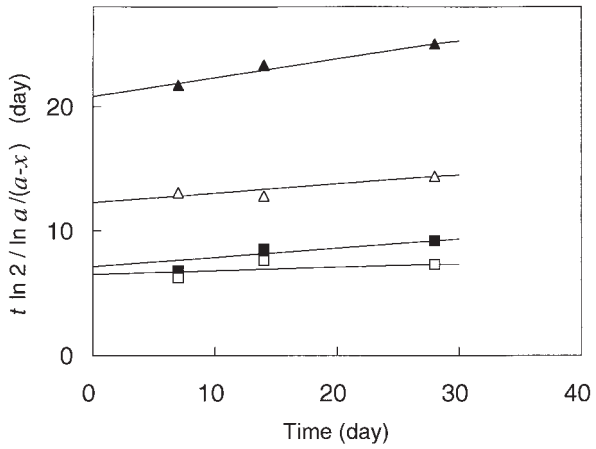

Figure 3 Time course of t ln 2 / ln $a/(a - x)$ during the treatment of PAN-*co*-BVP with activated sludge in soil: (t) treatment time; (a) initial amount of polymer; (x) weight loss during treatment time t. Content of BVP (mol %): (▲) 3.0; (△) 6.6; (■) 12.3; and (□) 33.0.

open squares in Figure 2, respectively. In these cases, the average numbers of acrylonitrile units in the oligo-acrylonitrile portion were 14, 7, and 2, respectively. Viscosity average degrees of polymerizations were estimated 610, 710, and 1400, respectively.

Figure 3 shows the time course of t ln 2 / ln $a/(a - x)$ during the biological treatment. Here, t is the treatment time, a is the initial amount of polymer, and x is the weight loss during the treatment time t. The time course of weight reduction was shown to follow approximately first order kinetics, although the above function increased a little bit with t, and we evaluated half-lives of these polymers by extension of the relation to the treatment time zero. Figure 4 shows the relation between thus evaluated half-lives of PAN-*co*-BVP and the average number of acrylonitrile units in the oligo-acrylonitrile portion.

These results indicate that biodegradation of PAN-*co*-BVP is not limited to the portion of BVP, and the oligo-acrylonitrile portion of PAN-*co*-BVP still exhibits exhaustive biodegradation when the chain length is sufficiently short. For example, in the biodegradation of PAN-*co*-BVP that contained 3.0 mol % of BVP, closed triangles of Figure 2 indicate that the weight loss during 28 days (54%) much surpassed the amount of BVP (3.0 mol %, which corresponded to about 12 wt %). Biodegradation of oligomers of acrylonitrile seems to be not limited to trimers,[12] and even 32-mer still shows significant biodegradability when BVP was incorporated into the polymer chain. The half-life of PAN-*co*-BVP that contained 3.0 mol % of BVP was about 21 days. This half-life means that 99.9% of the polymer will disappear during 7 months of biological treatment.

Trimer of acrylonitrile is biodegradable, dissimilar to polyacrylonitrile.[11] Even so, trimer and other oligomers of acrylonitrile are not useful as polymeric materials. However, connection of many oligomers using BVP as a highly biodegradable chemical structure may produce useful polymeric materials possessed of sufficient biodegradability. Such bridged polymers are different materials from conventional polyacrylonitrile, and the utility of PAN-*co*-BVP may be different from polyacrylonitrile to some extent. However, incorporation of BVP into the polymer chain would be a practically useful methodology to release polyacrylonitrile from poor biodegradability and protect the natural environment from solid wastes of poor biodegradability. When incorporation of too much BVP is not desirable for practical use, it is very easy to comply with the request by adequate reduction of the content of BVP, although the biodegradability diminishes accordingly. The principal purpose of this work was to elucidate the limit of the length of the oligo-acrylonitrile portion of PAN-*co*-BVP for substantially exhaustive biodegradation. Based on the relation shown in Figure 4, the half-life of PAN-*co*-BVP that contains 2 mol % of BVP can be expected to be in the range between 40 to 50 days. In this case, the average number of acrylonitrile units in the oligo-acrylonitrile portion is 50, that is, 50-mers of acrylonitrile are connected by BVP. This half-life means that 99.9% of the polymer sample will substantially disappear during 13 to 16 months of biological treatment. Incorporation of 2 mol % of BVP into the backbone chain would be sufficient to make polyacrylonitrile substantially biodegradable if we do not expect exceptionally rapid degradation in the natural environment.

Influence of molecular weight of PAN-*co*-BVP on biodegradability

Yamada et al.[11] isolated a bacterial strain utilizing acrylonitrile as a sole source of carbon and nitrogen

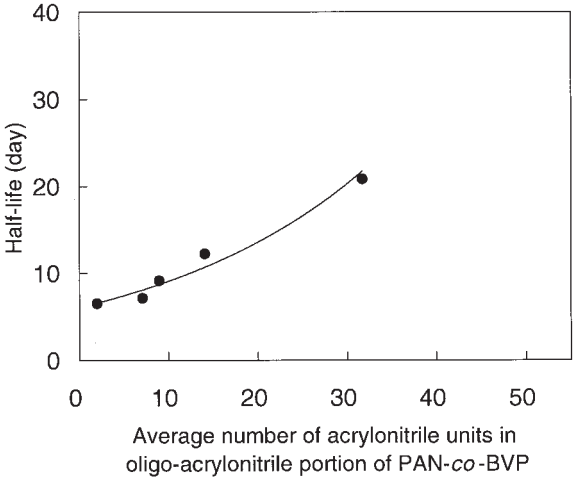

Figure 4 Relation between half-life of PAN-*co*-BVP and average number of acrylonitrile units in the oligo-acrylonitrile portion of PAN-*co*-BVP.

from an acclimated activated sludge. The bacterial strain utilized trimer of acrylonitrile. However, growth of the strain on polyacrylonitrile (Mv = 8000, i.e., degree of polymerization = 150) evaluated by the increase of turbidity was reported to be not clear. On the other hand, the half-life of PAN-*co*-BVP that contained 3.0 mol % of BVP was about 21 days (Figs. 2 and 3, closed triangles). It seems difficult to ascribe the biodegradability of this polymer solely to the biodegradability of the oligomer (32-mer in this case) of acrylonitrile. A possible explanation of the result is an enhanced biodegradation of oligo-acrylonitrile contained in PAN-*co*-BVP exerted by the chemically linked BVP.

These observations prompted us to consider that BVP acts as not only a highly biodegradable chemical structure for connection of oligo-acrylonitrile, but also as a functional group that initiates the biodegradation. The latter function could be derived from exceptionally strong affinity of BVP with microbial cells. Crosslinked PBVP captures microbial cells alive on the surface.[15] Oxygen consumption of living microbial cells captured on the surface of crosslinked PBVP was used for rapid determination of the population of living cells.[16] Filtration through nonwoven cloth coated with an equimolar copolymer of styrene with BVP effectively removed microbial cells from water without disinfection.[17] Not-*cross*-linked PBVP showed a strong antimicrobial activity.[18] Not-*cross*-linked PBVP exhibited an effective coagulation of microbial cells in water.[19] These phenomena indicate an extraordinarily strong affinity of BVP with microbial cells.

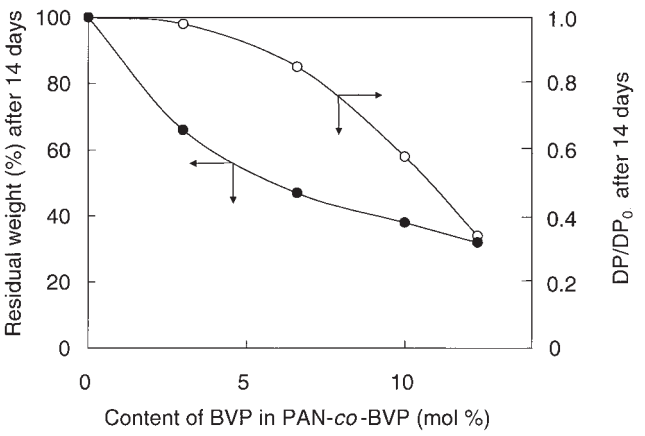

Figure 5 Influence of the content of BVP in PAN-*co*-BVP on the residual weight after two weeks of biological degradation (●) and on the rate of reduction of the estimated viscosity average degree of polymerization of polymer samples recovered after two weeks of treatment (○). Here, DP_0 and DP are the estimated viscosity average degree of polymerization before biological treatment and that of the recovered polymer sample after two weeks of biological treatment, respectively. Experimental conditions of the biological treatment are the same as in Figure 2.

Mode of chain scission of PAN-*co*-BVP during biodegradation

The mode of scission of the main chain of PAN-*co*-BVP during treatment with activated sludge in soil was investigated in detail using four polymer samples having a similar degree of polymerization and containing different amounts of BVP in the main chain. The contents of BVP in these polymers were 3.0, 6.6, 10.0, and 12.3 mol %, and viscosity average degrees of polymerization were 770, 610, 710, and 710, respectively. Experimental conditions of the biological treatment were the same as described above.

Closed circles in Figure 5 show the relation between content of BVP in PAN-*co*-BVP and residual weight after two weeks of biological treatment. Open circles in Figure 5 show the relation between content of BVP in PAN-*co*-BVP and rate of shortening of the estimated degree of polymerization, that is, DP/DP_0. Here, DP_0 and DP are the estimated viscosity average degree of polymerization before biological treatment and that of the recovered polymer sample after two weeks of biological treatment, respectively.

In the case where first scission occurs at the center of the polymer chain, the degree of polymerization may dramatically reduce to half, but decrease of weight may be negligible at this stage. Similarly, when random scission at the inside of the polymer chain predominated, shortening of the chain length of the recovered polymer may predominate over weight reduction. This mechanism of degradation was clearly rejected by Figure 5.

On the other hand, when the first scission occurs at the end of the polymer chain, decrease of weight as well as that of the degree of polymerization may be negligible at this stage. Similarly, in the case of uniformly successive scission from the end of the polymer chain, reduction of the residual weight and shortening of the chain length of the recovered polymer may occur in parallel. This mechanism of degradation was also clearly denied by Figure 5.

Figure 5 shows that, when content of BVP was less than 6 mol %, weight reduction somewhat predominated over shortening of the chain length of the recovered polymer. For example, in the case where PAN-*co*-BVP contained 3.0 mol % of BVP, that is, the average number of acrylonitrile units in the oligo-acrylonitrile portion was 32, residual weight reduced to 66% after two weeks of treatment, but chain length of the recovered polymer was 98% of the original length at this stage. This result indicates that the amount of low molecular weight fraction was very small in the recovered polymer and reflects a characteristic feature of biodegradation. Degradation of the lower molecular weight polymer predominated.

When biodegradation once started, the shortened polymers seemed to undergo predominant biodegradation, leaving high molecular weight polymers unchanged.

In the case of PAN-*co*-BVP that contained 6.6 mol % of BVP, the average number of acrylonitrile units in the oligo-acrylonitrile portion was 14. In this case, residual weight reduced to 47% after two weeks of treatment, but chain length of the recovered polymer was 85% of the original length at this stage. Biodegradation of the shortened polymer predominated over that of higher molecular weight polymers, but to a less extent.

In the case of PAN-*co*-BVP that contained 10.0 mol % of BVP, the average number of acrylonitrile units in the oligo-acrylonitrile portion was 9. In this case, residual weight reduced to 38% after two weeks of treatment, and chain length of the recovered polymer was 58% of the original length at this stage. Biodegradation of the shortened polymer predominated over that of higher molecular weight polymers, but to a much less extent.

In the case of PAN-*co*-BVP that contained 12.3 mol % of BVP, the average number of acrylonitrile units in the oligo-acrylonitrile portion was 7. In this case, residual weight reduced to 32% after two weeks of treatment, but chain length of the recovered polymer was 34% of the original length at this stage. Weight reduction balanced with shortening of the polymer chain, and uniformly successive scission from the end of the polymer chain appeared to be suitable for the mechanisms of biodegradation. This observation suggests that biodegradability of the oligo-acrylonitrile portion stands comparison with that of BVP when the oligo-acrylonitrile portion was shorter than heptamer.

In the case where the oligo-acrylonitrile portion was larger than nonamer, uniformly successive scission from the end of the polymer chain predominated over random scission at the inside of the polymer chain, but accompanied the chain scission at the inside of the polymer chain to some extent. On the other hand, when the oligo-acrylonitrile portion was heptamer, weight reduction balanced with shortening of the polymer chain. Heptamer of acrylonitrile appeared to be a match for BVP in biodegradability. Further research is required to elucidate the mechanism of the biodegradation.

CONCLUSIONS

Polyacrylonitrile did not exhibit biodegradability at all, but PAN-*co*-BVP was degradable when treated with activated sludge in soil. The biodegradation followed first-order kinetics. The half-life of PAN-*co*-BVP increased with the average number of acrylonitrile units in the oligo-acrylonitrile portion. Biodegradation of PAN-*co*-BVP was not limited to the portion of BVP, and the oligo-acrylonitrile portion still exhibited exhaustive biodegradation when the chain length was sufficiently short. Literature suggested that biodegradation of oligo-acrylonitrile was limited to trimer, but exhaustive biodegradation of the oligo-acrylonitrile portion of PAN-*co*-BVP was possible even for 32-mer, and the half-life of PAN-*co*-BVP that contained 3.0 mol % of BVP was 21 days. In the case where the oligo-acrylonitrile portion was larger than nonamer, uniformly successive scission from the end of the polymer chain predominated over random scission at the inside of the polymer chain, but accompanied the chain scission at the inside of the polymer chain to some extent. On the other hand, when the oligo-acrylonitrile portion was heptamer, weight reduction balanced with shortening of the polymer chain. Heptamer of acrylonitrile appeared to be a match for BVP in biodegradability.

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