Macromolecules **1995,** *28,* 2611−2617

New High-Pressure Synthesis of Aliphatic Poly(benzoxazoles) from a Bis(*o*-aminophenol) and Aliphatic Dinitriles

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Received September 8, 1994; Revised Manuscript Received January 23, 1995®

ABSTRACT: The high-pressure synthesis of benzoxazole compounds as well as aliphatic poly(benzoxazoles) was carried out in a sealed Teflon capsule by using a piston−cylinder type hot-pressing apparatus. As the model compound study, 2-phenylbenzoxazole was obtained readily from *o*-aminophenol and benzonitrile with the elimination of ammonia under 150−400 MPa at 180−190 °C. This reaction was accelerated under high pressure. The high-pressure polycondensation of 4,4′-diamino-3,3′-dihydroxybiphenyl (AHB) with aliphatic dinitriles proceeded under 150−500 MPa at 230−300 °C, affording highly crystalline aliphatic poly(benzoxazoles) having inherent viscosities about 0.2 dL·g^{-1}. These poly(benzoxazoles) were obtained also by the high-pressure polycondensation of AHB−dihydrochloride with the dinitriles along with the elimination of ammonium chloride under 200−350 MPa at 270−320 °C. Although the latter polymerization required higher reaction temperature, the polymers with higher inherent viscosities up to 0.6 dL·g^{-1} were readily produced.

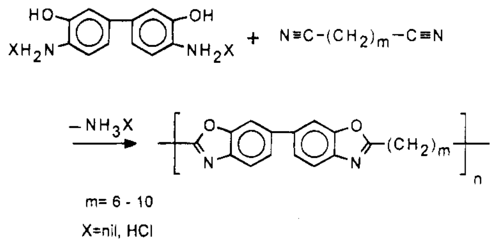
Introduction

All-aromatic poly(benzoxazoles) have been known over the past 3 decades as a class of aromatic heterocyclic polymers that exhibit high thermal stability.[1] Recently rigid-rod ordered aromatic poly(benzoxazoles) have been recognized as high-strength and high-modulus fibers[2−5] and third-order nonlinear optical materials as well.[6,7] However, the literatures are scarce on the synthesis of a series of aromatic−aliphatic poly(benzoxazoles) [hereafter aliphatic poly(benzoxazoles)].[8,9]

There have been several methods for the preparation of aromatic poly(benzoxazoles): one involves a two-step method starting from bis(*o*-aminophenol)s[10] or their trimethylsilyl-substituted derivatives[11] with aromatic dicarboxylic acid chlorides; another is a one-step method from combinations of bis(*o*-aminophenol)s and aromatic diacid diphenyl esters[12] or from aminohydroxybenzonitriles.[13] The high-temperature solution polycondensation of the bis(aminophenol) monomers with aromatic dicarboxylic acids has also been known with use of poly(phosphoric acid),[14] a mixture of phosphorus pentoxide and methanesulfonic acid,[15] and a mixture of trimethylsilyl polyphospate and chlorobenzene.[16]

In the field of synthetic organic chemistry, the application of high pressure to organic synthesis has been known as an effective means to accelerate many reactions.[17] In addition, the application of high pressure has been reported to effect a variety of polyaddition and polycondensation reactions. We have reported the high-pressure synthesis of poly(oxadiazole),[18] poly(aminoimide),[19] polycyanurates,[20] and poly(diazetidinediones)[21] through polyadditions and of polyimides[22] by polycondensation as well. The high-pressure synthesis of condensation polymers such as poly(benzimidazopyrrolones)[23,24] and polyamides[25,26] was also demonstrated by other groups.

Recently, we have developed a facile one-step method for the synthesis of aliphatic poly(benzoxazoles) from a bis(*o*-aminophenol) or its dihydrochloride and aliphatic dinitriles.[9] There is a report on the high-pressure synthesis of 2-phenylbenzoxazole from *o*-aminophenol and benzonitrile in methanol.[27] The objective of the present investigation was to elucidate the effect of high pressure on the synthesis of aliphatic poly(benzoxazoles) from the above-mentioned monomer pairs (eq 1). This paper deals with a new high-pressure synthesis of benzoxazole compounds as well as aliphatic poly(benzoxazoles).



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Experimental Section

Apparatus. The apparatus used for the high-pressure reaction was the same as that described previously.[18]

Materials. 4,4′-Diamino-3,3′-dihydroxybiphenyl (AHB) was obtained from Wakayama Seika Co., Japan. This monomer was purified by dissolving in hot dilute hydrochloric acid, treating with active charcoal, and reprecipitating with aqueous sodium hydroxide through neutralization. AHB−dihydrochloride (AHB−HCl) was prepared by reprecipitation of the hot dilute hydrochloric acid solution of AHB, after charcoal treatment, into ice-cold concentrated hydrochloric acid. *o*-Aminophenol, benzonitrile derivatives, and aliphatic dinitriles having 6−10 methylene units were obtained from Tokyo Chemical Industry Co., Japan, and purified by distillation under reduced pressure. Commercial *o*-aminophenol hydrochloride was used without further purification.

Model Reaction. Synthesis of 2-Phenylbenzoxazole from *o*-Aminophenol. The high-pressure reaction was carried out by using a piston−cylinder type hot-pressing apparatus.[18] A mixture of 0.272 g (2.5 mmol) of *o*-aminophenol and 0.270 g (2.62 mmol) of benzonitrile was placed into a Teflon capsule (10 mm inside diameter), and then the capsule was loaded into the cylinder. The piston−cylinder was placed in the furnace, and pressure was applied at room temperature to the capsule; then the temperature was raised. The reaction was carried out under a pressure of 150−400 MPa at a temperature of 180−190 °C for 15 h, giving 2-phenylbenzoxazole. The reaction time was recorded from the point where the temperature reached the prescribed one, which usually required around 1 h. After the reaction, the temperature was

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® Abstract published in *Advance ACS Abstracts,* March 15, 1995.

0024-9297/95/2228-2611$09.00/0

Table 1. High-Pressure Synthesis of 2-Substituted Benzoxazoles

reactants		reaction conditions			product	
AH[a]	nitrile, R	pressure MPa	temp, °C	time, h	yield, %	mp,[b] °C
AH	phenyl	0.1	180	15	29	103–104 (103)[28]
AH	phenyl	200	180	15	37	
AH	phenyl	200	190	15	50	
AH	phenyl	400	180	15	78	
AH	phenyl	400	190	15	80	
AH	*p*-tolyl	200	180	15	47	113–114 (114)[28]
AH	*p*-tolyl	350	180	15	73	
AH	*o*-tolyl	300	240	3	0	
AH	*o*-tolyl	540	300	3	77	67–68 (69)[33]
AH	undecyl	300	220	15	0	
AH	undecyl	360	270	15	82	32–33 (33)[34]
AH–HCl	phenyl	150	220	15	50	103–104 (103)[28]
AH–HCl	phenyl	150	240	15	70	
AH–HCl	phenyl	450	240	15	36	
AH–HCl	*p*-tolyl	150	220	15	3	113–114 (114)[28]
AH-HCl	*p*-tolyl	200	240	15	68	
AH-HCl	*p*-tolyl	350	240	15	29	
AH-HCl	*o*-tolyl	300	220	15	0	
AH-HCl	*o*-tolyl	250	240	15	11	67–68 (69)[33]

[a] AH and AH-HCl stand for *o*-aminophenol and its hydrochloride, respectively. [b] The value in parentheses is that reported in the literature.

lowered to room temperature, followed by releasing the pressure to 1 atm. The product was isolated by washing successively with 2 M hydrochloric acid and water, and then the resulting needle crystals were filtered and dried. Mp: 103–104 °C (lit.[28] mp 103 °C). IR (KBr): 1620 cm^{-1} (C=N).

Synthesis of 2-Phenylbenzoxazole from *o*-Aminophenol Hydrochloride. A mixture of 0.291 g (2.0 mmol) of *o*-aminophenol hydrochloride and 0.216 g (2.2 mmol) of benzonitrile was reacted under a pressure of 150–500 MPa at a temperature of 200–240 °C for 15 h, yielding 2-phenylbenzoxazole and ammonium chloride. The latter byproduct was removed by washing the reaction product with water. The mp and IR spectrum (KBr) were identical with those of the compound given in the preceding experiment.

The other 2-substituted benzoxazoles were synthesized from both *o*-aminophenol and its hydrochloride by the same procedure as that described above.

Polymerization. Polymer from AHB and Dodecanedinitrile by High-Pressure Polycondensation. A mixture of 0.324 g (1.5 mmol) of AHB and 0.301 g (1.57 mmol) of dodecanedinitrile was placed into a Teflon capsule and then loaded into the cylinder. The polymerization was carried out under a pressure of 150–500 MPa at a temperature between 230 and 300 °C for 15 h, yielding poly(benzoxazole). After the reaction, the polymer in the form of a flat cylindrical pellet (10 mm diameter and 2–3 mm thick) was removed from the Teflon capsule, when the ammonia produced during the polymerization was liberated. IR (KBr): 1620 cm^{-1} (C=N). Anal. Calcd for $(C_{24}H_{26}N_2O_2)_n$: C, 76.98; H, 7.00; N, 7.48. Found: C, 74.70; H, 6.95; N, 7.45.

Polymer from AHB–HCl and Dodecanedinitrile by High-Pressure Polycondensation. A mixture of 0.345 g (1.2 mmol) of AHB–HCl and 0.248 g (1.26 mmol) of dodecanedinitrile was polymerized under a pressure of 200–350 MPa at a temperature of 270–300 °C for 3–40 h, giving poly(benzoxazole). After the reaction, the polymer pellet was crushed and the powdery polymer was washed with water to remove the ammonium chloride formed during the polymerization, followed by drying under vacuum at room temperature for 3 days. The IR spectrum (KBr) was identical with that of the polymer mentioned above.

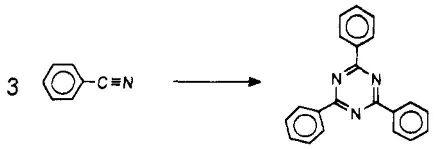
Polymer from AHB and Dodecanedinitrile by Ordinary-Pressure Polycondensation. In a 30-mL test tube were placed 0.578 g (2.00 mmol) of AHB and 0.39 g (2.03 mmol) of dodecanedinitrile. The tube was heated at 250 °C for 20 h under a nitrogen atmosphere. The polymerization proceeded in a melt state with the elimination of ammonia. After cooling to room temperature, the tube was broken away from the resultant brown polymer solid. The yield was 0.72 g (96%). The inherent viscosity of the polymer was 0.40 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C. The IR spectrum (KBr) was the same as that of the polymer described above.

The other poly(benzoxazoles) from both AHB and AHB–HCl were synthesized by similar procedures.

Measurements. Inherent viscosity was measured by using a Ostwald viscometer at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C. IR spectra were recorded on a Jasco FT/IR-5000 spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DSC-41 and TGA-40, respectively. Wide-angle X-ray diffraction patterns were obtained by using a Rigaku Denki RU 200 X-ray diffractometer with nickel-filtered Cu Kα radiation detected by scintillation counters at 50 kV and 180 mA.

Results and Discussion

Model Compound Study. 2-Arylbenzoxazoles are commonly prepared by the condensation of *o*-aminophenols with aromatic carboxylic acids or their derivatives such as acid chlorides and nitriles.[29] The reaction using nitriles in methanol was shown to be accelerated by the application of pressure.[27] However, no detailed studies on the high-pressure synthesis of 2-substituted benzoxazoles without use of a solvent like methanol have been reported so far. Naturally aromatic dinitriles themselves are known to be cyclotrimerized under a high pressure (3000–5000 MPa) at a high temperature (340–500 °C), giving triaryl-*s*-triazines (eq 2).[30,31]



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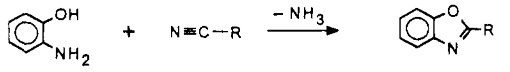
Therefore, we investigated in detail whether 2-substituted benzoxazoles were obtained from *o*-aminophenol and nitrile compounds in the absence of both solvent and catalyst under high pressure (eq 3).



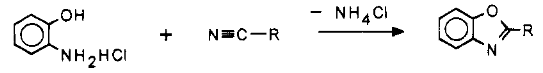
(3)

The reaction between *o*-aminophenol and benzonitrile yielding 2-phenylbenzoxazole was first examined. Table 1 shows the effect of applied pressure and reaction temperature on the yield of 2-phenylbenzoxazole formed by the reaction for 15 h. As the reaction temperature increased, the yield of 2-phenylbenzoxazole increased, and it shifted markedly higher by the application of higher pressure. When benzonitrile alone was subjected to reaction under 500 MPa at 200 and 300 °C, triphenyl-*s*-triazine was obtained in low yields of 0 and 20%, respectively, according to eq 2. Thus the *s*-triazine formation from benzonitrile required these severe conditions, and hence no side products like triphenyl-*s*-triazine were obtained in the high-pressure reaction of *o*-aminophenol with benzonitrile.

It is interesting to note that the condensation of *o*-aminophenol with benzonitrile was actually accelerated by the application of high pressure, despite the fact that the total number of molecules remained unchanged from the initial state to the final one. Since ammonia is a supercritical fluid under 150–450 MPa above 180 °C,[32] it is thought that the ammonia formed as the byproduct probably acted as the solvent for the product of 2-phenylbenzoxazole, which reduced the total volume of molecules from the initial state to the final one, and hence the reaction equilibrium readily shifted to the direction yielding 2-phenylbenzoxazole at a reasonable reaction rate.

Table 1 summarizes the results of the high-pressure synthesis of 2-substituted benzoxazoles from *o*-aminophenol and various nitriles. It is obvious that these reactions were accelerated by the application of high pressure. 2-*p*-Tolylbenzoxazole was obtained under 200–350 MPa at 180 °C, whereas the syntheses of 2-*o*-tolylbenzoxazole and 2-undecylbenzoxazole required higher reaction temperature (270–300 °C) under 360–540 MPa owing to the steric hindrance and low reactivity of the aliphatic nitrile, respectively.

It is known that the formation of benzoxazoles from *o*-aminophenol and nitriles was effected by use of acid catalysts. Hoelljes and Wagner reported that the reaction of *o*-aminophenol with benzonitrile proceeded slowly; however, it was promoted by the presence of hydrogen chloride, which was introduced as *o*-aminophenol hydrochloride.[28] Hence, we investigated the high-pressure synthesis of 2-substituted benzoxazoles from various nitriles and *o*-aminophenol hydrochloride (eq 4).



(4)

The condensation of *o*-aminophenol hydrochloride with benzonitrile was carried out under a high pressure of 150–500 MPa at a high temperature, affording 2-phenylbenzoxazole with the elimination of ammonium chloride. Figure 1 shows the effect of applied pressure and reaction temperature on the yield of 2-phenylbenzoxazole formed by the reaction for 15 h. Although the yield of the benzoxazole increased with increasing reaction temperature, a notable decrease in the yield was observed as the applied pressure increased for the reaction. That is, this reaction was actually depressed by the application of higher pressure. This is a marked contrast to the above-mentioned reaction where the parent *o*-aminophenol was used in place of its hydrochloride. In addition, higher reaction temperature above 200 °C was essential to produce 2-phenylbenzoxazole. The results may be explained as follows. The condensation proceeded in an equilibrium process where both the total number and total volume of the molecules probably did not decrease from the initial state to the final one (necessary to facilitate high-pressure condensation), and for a melt diffusion-limited process, the yield of the product thereby decreased with increasing pressure.

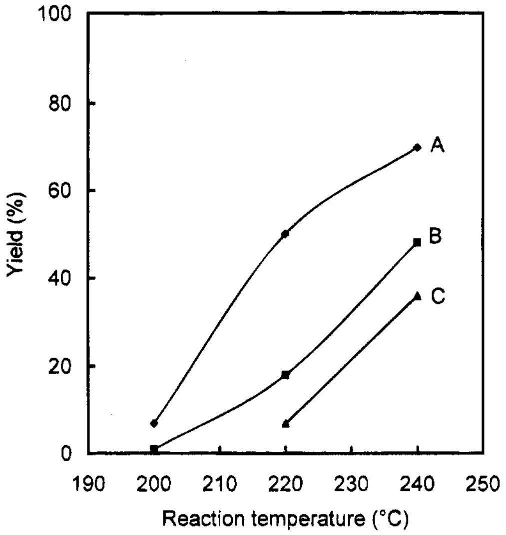


Figure 1. Effects of applied pressure and reaction temperature on the yield of 2-phenylbenzoxazole synthesized by the reaction of *o*-aminophenol hydrochloride and benzonitrile for 15 h: (A) 150, (B) 350, and (C) 500 MPa.

The results of the reaction of high-pressure synthesis of 2-substituted benzoxazoles from *o*-aminophenol hydrochloride and various nitriles are summarized also in Table 1. They clearly indicated again that this reaction was depressed under high pressure and required higher reaction temperature, compared with the condensation using the parent *o*-aminophenol mentioned above.

High-Pressure Polymer Synthesis. The model reaction was extended to the high-pressure synthesis of aliphatic poly(benzoxazoles). The high-pressure polycondensation of AHB with a series of aliphatic dinitriles having 6–10 methylene units was carried out in the absence of both solvent and catalyst in a Teflon capsule by using a piston–cylinder type hot-pressing apparatus. For the polycondensation, a 5 mol % excess of the aliphatic dinitrile versus AHB or AHB–HCl was used intentionally to compensate for possible loss of the liquid dinitriles, though stoichiometric balance is normally a key factor for obtaining high-molecular-weight condensation polymers.

The polymerization proceeded with the elimination of ammonia under 150–500 MPa at 230–300 °C for 5–40 h, giving poly(benzoxazoles) in the form of a light brown solid. When the reaction capsule was opened, ammonia gas was liberated which was detected by the characteristic strong order, leaving the polymer pellet.

The formation of poly(benzoxazoles) was confirmed by means of IR spectroscopy, with the disappearance of absorption bands at around 3400 cm^{-1} due .to both amino and hydroxyl groups of AHB and at about 2245 cm^{-1} based on the nitrile group of aliphatic dinitriles and the appearance of an absorption at around 1620 cm^{-1} due to the benzoxazole C=N moiety. The elemental analysis values of the polymers generally agreed well with the calculated values for the proposed poly(benzoxazole) structures except for some deviation of the carbon analysis.

Table 2 shows the effect of reaction temperature on inherent viscosity of the polymer having 8 methylene units formed by the polymerization at 300 MPa for 15 h. The inherent viscosity increased with increasing

Table 2. High-Pressure Synthesis of Aliphatic Poly(benzoxazole) Having 8 Methylene Units from AHB and Decanedinitrile

polymerization conditions			polymer
pressure, MPa	temp, °C	time, h	η_{inh},[a] dL·g^{-1}
300	230	15	0.13
300	250	15	0.18
300	270	15	0.19
300	300	15	0.14
0.1	250	15	0.13
150	250	15	0.12
300	250	15	0.18
520	250	15	0.17

[a] Measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C.

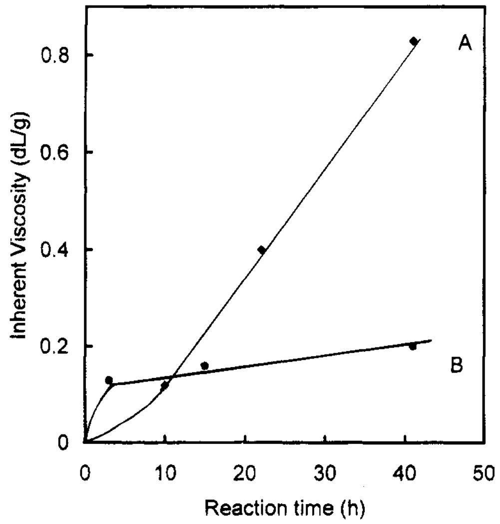


Figure 2. Time dependence of the inherent viscosity of the poly(benzoxazole) having 10 methylene units formed by polymerization from AHB: (A) the polymer formed under 0.1 MPa at 250 °C; (B) the polymer formed under 350 MPa at 250 °C.

temperature in the range from 230 to 270 °C; however, temperatures higher than that tended to lower the viscosity. This is probably due to the instability of the AHB monomer at 300 °C for a long time, and hence the polymers synthesized at that temperature were more colored with lower inherent viscosity. The results were consistent with those for the melt polycondensation of AHB with aliphatic dinitriles under ordinary pressure.[9]

Figure 2 depicts the reaction time dependence on inherent viscosity of the polymer with 10 methylene units. In the case of the polycondensation under ordinary pressure, the viscosity value increased steadily with increasing reaction time. On the other hand, although the polycondensation under high pressure at an initial stage proceeded faster than that under ordinary pressure, the progress of the high-pressure polymerization was depressed at a later stage, giving the polymer with a low inherent viscosity of 0.2 dL·g^{-1} even after the polymerization for 40 h.

Table 2 also exhibits the effect of applied pressure on inherent viscosity of the polymer with 8 methylene units formed by the polymerization at 250 °C for 15 h. Regardless of applied pressure in the range of 150–500 MPa, no appreciable difference in the inherent viscosity of the polymer (around 0.15 dL·g^{-1}) was observed. It is obvious that the pressure effect on the polycondensation was quite different from that of the model reaction. As mentioned above, the ammonia formed by the reaction probably acted as a solvent for 2-substituted benzoxazoles. On the contrary, the poly(benzoxazole) thus formed did not dissolve in the ammonia byproduct, and hence the polycondensation was not accelerated by the application of high pressure.

Table 3 summarizes the results of the high-pressure synthesis of aliphatic poly(benzoxazoles) having 6–10 methylene units. A series of poly(benzoxazoles) with inherent viscosities of 0.16–0.20 dL·g^{-1}, indicative of low molecular weights, were obtained by the high-pressure polycondensation using AHB monomer, whereas the polycondensation under ordinary pressure afforded the poly(benzoxazoles) with somewhat higher viscosity values of 0.2–0.4 dL·g^{-1}.[9]

Next, the polycondensation of AHB–HCl with aliphatic dinitriles was conducted under 200–350 MPa at 270–320 °C for 15–40 h, affording aliphatic poly(benzoxazoles) contaminated with the byproduct of ammonium chloride as white pellets. This was evidenced by means of TG of the products. Curve A in Figure 3 shows the TG curve of the product prepared by the high-pressure polycondensation of AHB–HCl with dodecanedinitrile. The initial weight loss occurred at around 250 °C, followed by gradual weight loss at a 250–400 °C temperature range due to sublimation of the ammonium chloride. Further rapid weight loss was observed at 400–450 °C due to thermal decomposition of the poly(benzoxazole). Therefore, to remove the ammonium chloride, the polymerization products were washed thoroughly with water after the white pellets were crushed. The polymers thus purified showed no weight loss up to 400 °C both in nitrogen and in air, as shown in curves B and C in Figure 3.

Figure 4 shows the reaction temperature dependence on inherent viscosity of the poly(benzoxazole) having 10 methylene units. Under ordinary pressure (curve A), the inherent viscosity of the polymer increased with increasing temperature up to 270 °C. When the polymerization temperature was 300 °C, however, the viscos-

Table 3. High-Pressure Synthesis of Aliphatic Poly(benzoxazoles)

monomers		polymzn[a]		polymer	
bis(aminophenol)	dinitrile, m	pressure, MPa	temp, °C	η_{inh},[b] dL·g^{-1}	T_{m},[c] °C
AHB	6	250	270	0.17	281
AHB	7	250	270	0.20	282
AHB	8	300	250	0.18	259
AHB	9	300	270	0.16	202
AHB	10	270	250	0.16	218
AHB-HCl	6	200	300	0.23	274
AHB-HCl	7	250	320	0.35	261
AHB-HCl	8	250	300	0.64	244
AHB-HCl	9	300	280	0.51	193
AHB-HCl	10	200	290	0.43	219

[a] The polymerization was carried out for 15 h. [b] Measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C. [c] Determined by DSC at a heating rate of 20 °C·min^{-1} in nitrogen.

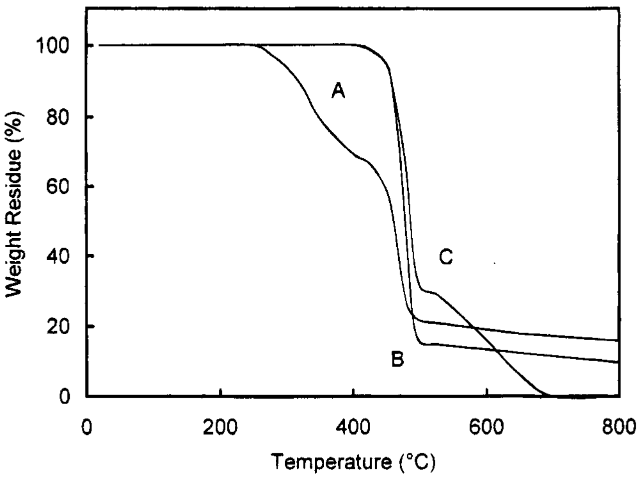


Figure 3. TG curves of the poly(benzoxazole) having 10 methylene units, formed by polymerization from AHB−HCl under 200 MPa at 290 °C for 15 h, at a heating rate of 10 °C·min^{-1}; (A) the as-prepared polymer containing ammonium chloride measured in nitrogen, and the purified polymer measured (B) in nitrogen and (C) in air.

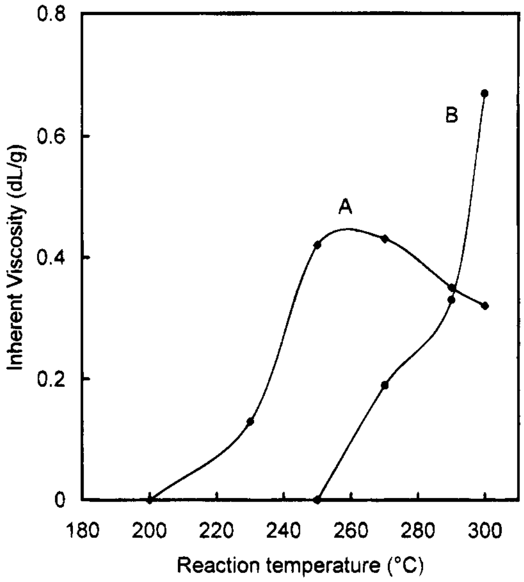


Figure 4. Temperature dependence of the inherent viscosity of the poly(benzoxazole) having 10 methylene units formed by polymerization from AHB−HCl: (A) the polymer formed under 0.1 MPa for 15 h; (B) the polymer formed under 300 MPa for 15 h.

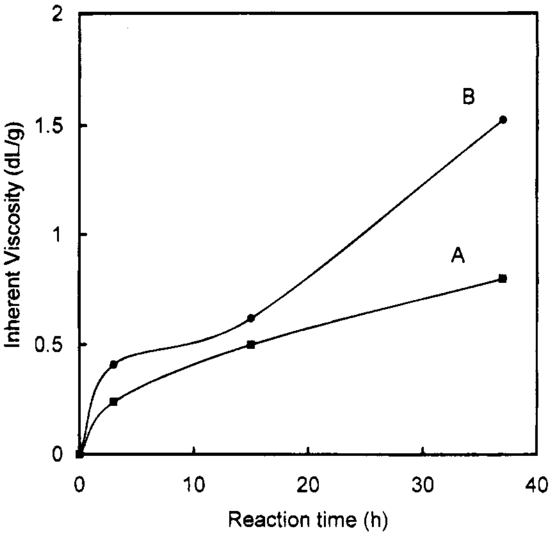


Figure 5. Time dependence of the inherent viscosity of the poly(benzoxazole) having 10 methylene units formed by polymerization from AHB−HCl: (A) the polymer formed under 0.1 MPa at 250 °C; (B) the polymer formed under 300 MPa at 300 °C.

ity value decreased appreciably, probably due to evaporation of the dinitrile monomer during the polymerization, thus losing the stoichiometric monomer balance necessary for high-molecular-weight polymer formation. In the case of the high-pressure polycondensation under 300 MPa (curve B), the polymerization did not occur below 250 °C, and the inherent viscosity increased with increasing temperature, reaching 0.7 dL·g^{-1} for the polymerization at 300 °C. This indicated that a higher reaction temperature was required for the high-pressure polycondensation using AHB−HCl, leading to the formation of high-molecular-weight polymer. The high polymer formation is presumably because the dinitrile monomer was held in the closed reaction vessel at a high temperature, maintaining the monomer stoichiometry. The results of the high-pressure polycondensation using AHB−HCl resembled those of the model reaction with use of *o*-aminophenol hydrochloride with respect to the reaction temperature. The polycondensation and the model reaction both under 300 MPa did not occur below the critical temperatures of 250 and 200 °C, respectively. Above these temperatures, the inherent viscosities of the poly(benzoxazoles) as well as the yield of the benzoxazole compounds increased with increasing reaction temperature.

Figure 5 depicts the reaction time dependence on inherent viscosity of the polymer with 10 methylene units starting from AHB−HCl. As shown in curve A, the increase in inherent viscosity of the polymer formed under ordinary pressure at 250 °C was gradual in the 3−38 h time range, and the final viscosity value was 0.83 dL·g^{-1}. On the other hand, in the case of the high-pressure polymerization under 300 MPa at 300 °C (curve B), the inherent viscosity increased remarkably with increasing reaction time, reaching as high as 1.5 dL·g^{-1} after 38 h. The results are very important, strongly suggesting that the application of high pressure actually promoted the polycondensation and further representing the best effect of high pressure in forming high-molecular-weight poly(benzoxazoles) from AHB−HCl. This is in marked contrast to the results of the high-pressure polycondensation using the parent AHB monomer mentioned above.

Table 3 also summarized the results of the high-pressure synthesis of a series of aliphatic poly(benzoxazoles) by the polycondensation with use of AHB−HCl. The polymers thus obtained had inherent viscosities of 0.2−0.6 dL·g^{-1}, indicative of moderately high molecular weights, compared with the polymers obtained from the parent AHB monomer. These viscosity values were somewhat lower than those of the poly(benzoxazoles) prepared by the polycondensation using AHB−HCl under orindary pressure (0.4−0.7 dL·g^{-1}),[9] though the polymerization conditions were different from each other. From these results, it was concluded that the high-pressure polycondensation using AHB−HCl, which was carried out in the closed reaction vessel and was hence accompanied by no evaporation of the dinitrile monomers, was a useful method for the ready preparation of the aliphatic poly(benzoxazoles) having reasonable molecular weights. Furthermore, this is probably attributed in part to the higher purity and higher stability in air of the AHB−HCl monomer, compared

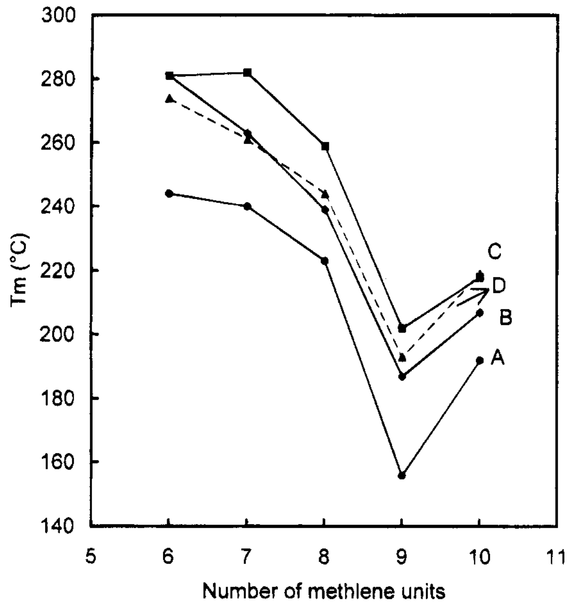


Figure 6. Effect of the number of methylene units on T_m of the aliphatic poly(benzoxazoles): (A) the polymer formed from AHB under 0.1 MPa, (B) the polymer formed from AHB−HCl under 0.1 MPa, (C) the polymer formed from AHB under 250−300 MPa; (D) the polymer formed from AHB−HCl under 200−300 MPa.

with the parent AHB. This was supported by the evidence that the poly(benzoxazoles) obtained from AHB−HCl were lighter in color, that is, pale yellowish brown.

Properties of Polymers. An interesting melting behavior was observed for the aliphatic poly(benzoxazoles) prepared by the different methods. Figure 6 shows the effect of a number of methylene units on the polymer melting temperature (T_m) of the aliphatic poly(benzoxazoles), which exhibited a well-known odd−even effect. Unexpectedly, the poly(benzoxazole) having 7 methylene units had a higher T_m than the value predicted by this relationship. The polymer might have a special crystalline structure, compared with the other poly(benzoxazoles),[9] though the crystalline structure is unclear yet at present.

In general, the polymers formed under high pressure (curves C and D) had higher T_m values than those formed under ordinary pressure (curves A and B). This is probably because the thickness of crystals of the former polymers through high-pressure crystallization of the molten polymers during the polymerization was larger than that of the latter polymers. From the X-ray diffraction study, all the aliphatic poly(benzoxazoles) prepared under both ordinary-pressure and high-pressure conditions had high crystallinity; however, no appreciable difference in crystallinity was observed between the high-pressure polymerized polymers and the polymers prepared under ordinary pressure. It is interesting to note that the high-pressure polymerized polymers from AHB had the highest T_m values among them (curve C), despite the fact that they had the lowest inherent viscosities. Naturally, the T_m values of the aliphatic poly(benzoxazoles) obtained under high pressure were higher than those of the poly(benzoxazoles) prepared by the two-step silylation method reported previously.[8]

Conclusions

As a model compound study, 2-phenylbenzoxazole was synthesized readily from *o*-aminophenol and benzonitrile without use of both solvent and catalyst and with the elimination of ammonia under 150−400 MPa at 180−190 °C. This reaction was accelerated under high pressure, probably due to the byproduct ammonia acting as the solvent. The condensation of *o*-aminophenol hydrochloride with benzonitrile was also successful, affording 2-phenylbenzoxazole along with the formation of ammonium chloride. However, this reaction was retarded by the application of high pressure. The high-pressure polycondensation of AHB with aliphatic dinitriles proceeded under 150−500 MPa at 230−300 °C, affording highly crystalline poly(benzoxazoles) with inherent viscosities of about 0.2 dL·g^{-1}. When the polycondensation of AHB−HCl with the dinitriles was carried out under 200−350 MPa at a high temperature of 270−320 °C, poly(benzoxazoles) with higher inherent viscosities up to 0.6 dL·g^{-1} were obtained. Thus the high-pressure effect in forming high-molecular-weight poly(benzoxazoles) from AHB−HCl is very important from a practical viewpoint and the finding will be applied to the synthesis of other heterocyclic polymers with high molecular weights.

Acknowledgment. The authors gratefully acknowledge the support for this work by a Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials, Design, Preparation, and Control from the Ministry of Education, Science and Culture of Japan (No. 4205041).

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MA9460652