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Chemoselective Polyamidation of 3,3′-Dihydroxybenzidine

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ABSTRACT: A chemoselective synthesis of poly(*o*-hydroxy-amide) as a polybenzoxazole precursor has been developed. The polycondensation was carried out by addition of isophthaloyl dichloride to a solution of 3,3′-dihydroxybenzidine and lithium chloride in *N*-methylpyrrolidinone and gave the selective *N*-acylated polymer, poly(*o*-hydroxy-amide) with an inherent viscosity of 0.7 dL g^{-1}. The structure of the polymer was characterized by IR, ^{1}H, and ^{13}C NMR spectroscopies. The model reaction was studied in detail to demonstrate the feasibility of the chemoselective polyamidation using benzoyl chloride and *o*-aminophenol.

KEY WORDS Chemoselective / Polyamidation / Poly(*o*-hydroxy-amide) / Isophthaloyl Dichloride / 3,3′-Dihydroxybenzidine /

Photosensitive polyimides (PSPIs) are widely used as protection and insulation layers of very large scale integrated circuit (VLSI), multi-chip modules for computers, telecommunications and thermal-heads because they simplify processing and do not need a photoresist used in the microlithography or a toxic etchant such as hydrazine.

Most PSPIs reported so far are a negative working type and need organic solvents as a developer.[1-3] However, the negative PSPIs tend to swell during development into the organic developer is an organic solvent, and it limits the pattern resolution. In order to overcome these problems, positive working PSPIs that can be developed with water-based solutions have been attracting great interest. Although, several groups[4-6] have reported resists consisting of poly(amic acid)s (PAAs) and *o*-diazonaphthoquinone (DNQ). However, dissolution rates of PAAs toward a 2.38% aqueous tetramethylammonium hydroxide (TMAH) solution are essentially too high to get sufficient dissolution contrast. Thus, the dissolution rates of PAAs have to be reduced by prebaking, or post exposure bake (PEB). Other DNQ sensitized approaches were made by introducing DNQ, and phenol moieties into PAA through sulfonic ester and ester linkages, respectively.[7,8] By controlling the contents of these groups to obtain good dissolution contrast, these PSPI-precursors have also been found to provide excellent positive images.

Khanna *et al.*[9] reported polyamides containing hydroxyl groups for a positive working DNQ sensitized photosensitive polymer system. Poly(*o*-hydroxy-amide) is a polybenzoxazole precursor, attracting increasing attention as an alkaline developable positive-type photosensitive polymer because of having an appropriate dissolution rate toward the 2.38% aqueous TMAH solution and no existence of phenol moiety after benzoxazole ring formation.

Poly(*o*-hydroxy-amide)s are generally prepared by polycondensation of bis(*o*-aminophenol)s with diacid dichlorides in the presence of base. Acylation of *o*-aminophenol might be expected to give either the *N*- or *O*-acyl products. The lithographic performance of photosensitive polymer is profoundly affected by the existence of *O*-acyl linkages. However, much attention has not been paid to the chemoselective polyamidation of bis(*o*-aminophenol)s.

The present paper describes a chemoselective synthesis of poly(*o*-hydroxy-amide) (PHA) from isophthaloyl dichloride with 3,3′-dihydroxybenzidine.

EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidinone (NMP) and *N*,*N*-dimethylacetamide (DMAc) were purified by vacuum distillation and stored over 4-A molecular sieves. *o*-Aminophenol, isophthaloyl dichloride and 3,3′-dihydroxybenzidine were purified by recrystallization. Other reagents and solvents were obtained commercially and used as received.

N-Benzoylbenzoxazoline-2-thione was prepared according to the reported procedure.[10]

Model compounds

The following model compounds were prepared from the corresponding acyl chlorides and *o*-hydroxy-amines.

2′-Hydroxybenzanilide (**1**). mp 170—171°C (from methanol). *Anal.* Calcd for $C_{13}H_{11}NO_2$: C, 73.23%; H, 5.20%; N, 6.57%. Found: C, 72.99%; H, 5.25%; N, 6.51%.

2-(Benzoylamino)phenyl Benzoate (**2**). mp 185—186°C (from ethanol). *Anal.* Calcd for $C_{20}H_{15}NO_3$: C, 75.70%; H, 4.76%; N, 4.41%. Found: C, 75.41%; H, 4.83%; N, 4.34%.

2′,2″-Dihydroxyisophthalanilide (**3**). mp decomposition at 240°C (from methanol). *Anal.* Calcd for $C_{20}H_{16}N_2O_4$:

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C, 68.96%; H, 4.63%; N, 8.04%. Found: C, 68.66%; H, 4.55%; N, 7.91%.

5,5′-Bis{2-(benzoylamino)phenol} (**4**). mp 256°C. *Anal.* Calcd for $C_{26}H_{20}N_2O_4$: C, 73.53%; H, 4.75%; N, 6.60%. Found: C, 73.73%; H, 4.75%; N, 6.64%.

5,5′-Bis{2′-(benzoylamino)phenyl Benzoate} (**5**). mp 264°C. *Anal.* Calcd for $C_{40}H_{28}N_2O_6$: C, 75.94%; H, 4.46%; N, 4.43%. Found: C, 75.69%; H, 4.57%; N, 4.60%.

Model Reactions of the Benzoyl Derivative and o-Aminophenol.

Benzoyl derivative (1.0 mmol) was added to a solution of *o*-aminophenol (1.0 mmol) and base or inorganic salt (1.0 mmol) in NMP (2.0 mL) at room temperature. The solution was stirred for 2 h and poured into water (40 mL). The pH of mixture was controlled at 7.0 with addition of 1 M HCl. The precipitate was filtered off, washed with water, and dried.

Polymerization

PHA-1 was prepared from isophthaloyl dichloride and 3,3′-dihydroxybenzidine in the presence of pyridine (0.3 mL) in DMAc/cyclohexanone (2 : 1, 2.5 mL) according to the reported procedure.[11]

PHA-2: To a cooled solution of 3,3′-dihydroxybenzidine (0.216 g, 1.0 mmol) and lithium chloride (0.093 g, 2.2 mmol) in NMP (1.6 mL) was added isophthaloyl dichloride (0.203 g, 1.0 mmol) at below 0°C. This solution was stirred at room temperature for 24 h. The resulting polymer solution was diluted with NMP (2.0 mL), and the polymer was precipitated by pouring the solution into methanol (100 mL). After through washing with methanol and drying, the polymer weighed 0.326 g (94%). The inherent viscosity of the polymer in NMP was 0.70 dL g^{-1}, measured at a concentration of 0.5 g dL^{-1} at 30°C. IR (KBr): ν 3320, 1520 cm^{-1} (N–H), 1650 cm^{-1} (C=O, amide). *Anal.* Calcd for $(C_{20}H_{14}N_2O_4 \cdot 0.9H_2O)_n$: C, 66.27%; H, 4.14%; N, 7.73%. Found: C, 66.27%; H, 4.38%; N, 7.48%.

Measurement

Fourier Transform Infrared Absorption Spectroscopy (FT-IR). FT-IR spectra were recorded on a Horiba FT-210 FT-IR spectrophotometer under the following conditions: spectral width 4000—400 cm^{-1}, 10 accumulations, resolution 4 cm^{-1}, signal processed by H–G apodization. Samples were recorded as a potassium bromide pellet.

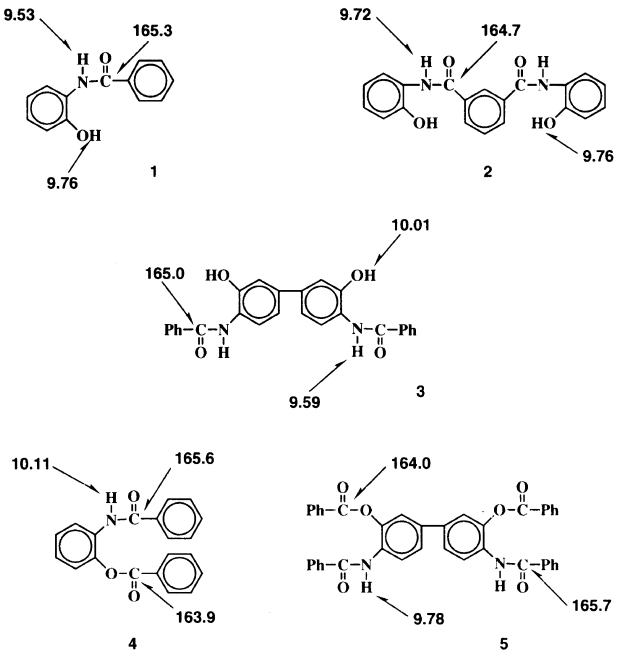
Nuclear Magnetic Resonance Measurements (NMR). NMR spectra were recorded on a JEOL EX270 (270 MHz) spectrometer in dimethyl sulfoxide (DMSO)-d_6 solution at ambient temperature.

Thermogravimetry (TG). TG measurements were performed on a Seiko SSS 5000-TG/DTA 200 instrument at a heating rate of 10°C min^{-1}.

Viscosity Measurements. Viscosity measurements were carried out by using an Ostwald viscometer at 30°C.

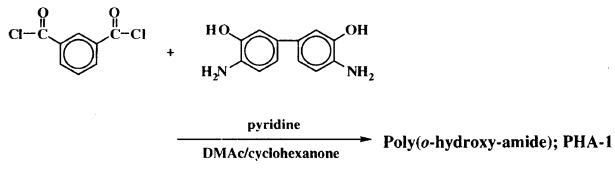
RESULTS AND DISCUSSION

The synthesis of PHA was reported by Kubota *et al.* from isophthaloyl dichloride and 3,3′-dihydroxybenzidine,[11] but the structure of polymer was confirmed merely by IR spectroscopy and elemental analysis. Thus, we synthesized a poly(*o*-hydroxy-amide) (PHA-1) with an inherent viscosity of 0.35 dL g^{-1} according to the reported procedure and its structure was characterized by ^1H and ^{13}C NMR spectroscopies. ^1H NMR spectra showed characteristic signals of amide, hydroxy groups and amide group of amide-ester unit at 9.81, 10.05 ppm and 10.50 ppm, respectively. These assignments will be discussed in the later section. Moreover, ^{13}C NMR spectra showed three signals of carbon nuclei in amide and amide-ester carbonyl groups at 165.0, 164.9, and 166.1 ppm. These findings indicated that the chemoselective polyamidation of 3,3′-dihydroxybenzidine was not achieved.



Chemical shifts (ppm): amino and hydroxy groups; ^1H-NMR, carbonyl carbon; ^{13}C-NMR (in DMSO-d_6).

Figure 1. Chemical shifts of model compounds.



To clarify the structure of products from model reactions and polymers, the following model compounds were prepared from the corresponding acid chlorides and *o*-aminophenol derivatives (Figure 1).

These peaks were assigned using the two dimensional H,H-COSY and H,H-NOESY spectra. The NOESY spectrum for 2′-hydroxybenzanilide (**1**) as a typical example is shown in Figure 2. Compound **1** shows the peaks at 9.53 and 9.76 ppm. Among them, only the former shows the correlation peaks with signals at 7.97 ppm, which are assigned to H_1 and H_5 in the benzene ring of the benzoyl groups. The NH proton is placed closer to the aromatic protons than the OH proton. Thus the peak at 9.53 ppm, which shows NOE with H_1 and H_5, is

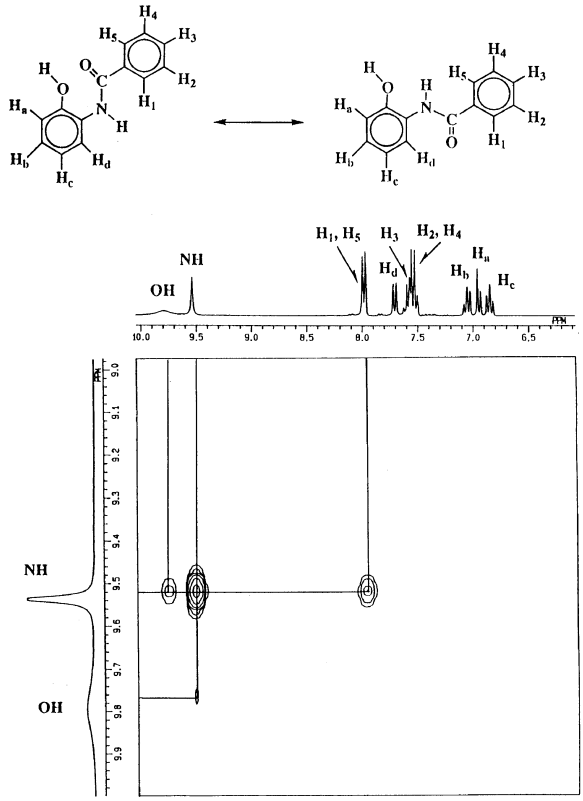
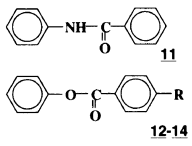


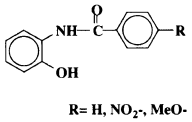
Figure 2. H,H-NOESY spectrum of 2′-hydroxybenzanilide.

assigned to the NH proton, and that at 9.76 ppm exhibiting no NOE, to the OH proton.

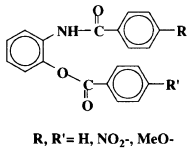
^{13}C NMR spectra of the ester-amide compound 2′-(*N*-benzoylamino)phenyl benzoate (**4**), 5,5′-bis{2′-(benzoylamino)phenyl benzoate} (**5**) shows two carbonyl signals at 163—166 ppm region, which are due to ester or amide carbonyl carbons. For example, **4** shows the signals at 163.9 and 165.5 ppm. The INADEQUATE technique to accomplish the assignment of these signals was used. However, clear information was not obtained because of quanternary carbons. Then, we tried to prepare 2′-(benzoylamino)phenyl 4-nitrobenzoate or 2′-{*N*-(4-nitrobenzoyl)amino}phenyl benzoate as a model compounds to compare the chemical shifts of ester or amide carbonyl groups with those of **4**. The reaction of **1** with *p*-nitrobenzoyl chloride in the presence of pyridine in tetrahydrofuran (THF) produced a mixture of 2′-{*N*-(4-nitrobenzoyl)amino}phenyl benzoate and 2′-(*N*-benzoylamino)phenyl 4-nitrobenzoate in the molar ratio of 7 : 2. The same products with the same molar ratio were obtained by the reaction of 2′-hydroxy-4-nitrobenzanilide with benzoyl chloride. These results might be explained by the intramolecular acyl exchange reaction of benzoyl and 4-nitrobenzoyl groups. Therefore, we selected *p*-nitro and methoxy substituted benzoyl groups as acyl groups which would not yield acyl exchange reaction due to the large difference of electron density on carbonyl carbons, and benzanilide and benzoate analogues, such as, 2′-hydroxy-4-nitorobenzanilide (**6**), 2′-hydroxy-4-methoxybenzanilide (**7**), 2′-(4-nitrobenzoylamino)phenyl 4-nitrobenzoate (**8**), 2′-(4-nitrobenzoylamino)phenyl 4-methoxybenzoate (**9**) and 2′-(4-methoxybenzoylamino)phenyl 4-methoxybenzoate (**10**) were prepared. The ^{13}C NMR carbonyl chemical



Model No.	R	Chemical shifts C=O
11	–	165.8
12	H	164.9
13	NO_2	163.4
14	MeO	164.4



Model No.	R	Chemical shifts Amide C=O
1	H	165.3
6	NO_2	163.9
7	MeO	165.1



Model No.	R	R'	Chemical shifts Ester C=O	Amide C=O
4	H	H	163.9	165.6
8	NO_2	NO_2	162.8	164.3
9	NO_2	MeO	163.8	164.2
10	MeO	MeO	163.8	165.1

Figure 3. Chemical shifts of model compounds.

Table I. Acylation of *o*-aminophenol with benzoyl derivatives[a]

Run No.	Additive	Conversion[b] %	*N*-Acylation[c] %	*N*,*O*-Acylation[c] %
1	None	99	92	8
2	Triethylamine	87	8	92
3	Pyridine	91	97	3
4[d]	None	95	97	3
5	LiCl	93	100	0
6	$CaCl_2$	91	100	0

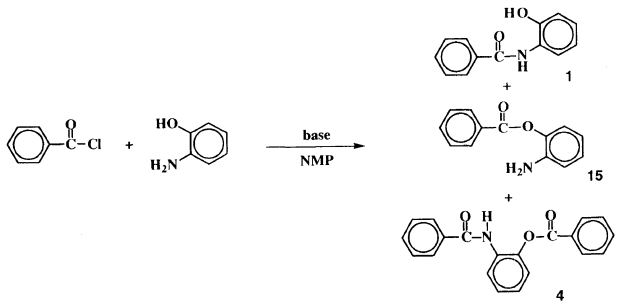
[a] Reactions of benzoyl chloride (1 mmol) and *o*-aminophenol (1 mmol) were carried out at room temperature in 2 mL of NMP for 2 h in the presence of 1 mmol of additive. [b] Conversion of acyl derivatives to amide and ester. [c] Composition was determined by ^1H NMR. [d] *N*-Benzoylbenzoxazoline-2-thione was used instead of benzoyl chloride.

shifts of these compounds are listed in Figure 3. The resonance for amide carbonyl of benzanilide (**11**) is observed at 165.8 ppm. On the other hand, phenyl benzoate (**12**) shows the resonance of ester carbonyl at 164.9 ppm. Furthermore, the resonance for ester carbonyl of *p*-nitrophenylester (**13**) is shifted to upper field compared to that for ester carbonyl of *p*-methoxyphenylester (**14**). The similar chemical shifts were observed in the hydroxy-amides compounds, **1**, **6**, and **7**. Based on these findings, chemical shifts for ester and amide carbonyls of compounds, **4**, **8**, **9**, and **10** are assigned as shown in Figure 3. So, the carbonyl peaks of **4** at 163.9 and 165.6 ppm were assigned to ester and amide carbonyl carbons, respectively. Similarly, ester and amide carbonyls of **5** were assigned as shown in Figure 1.

Model Reaction

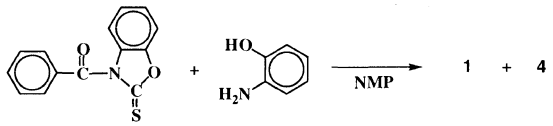
To achieve the chemoselective polyamidation of 3,3′-dihydroxybenzidine and isophthalic acid derivative, first,

model reactions were carried out using benzoyl chloride and *o*-aminophenol in the presence of various base in NMP at room temperature (Table I, run 1—3).



The above reaction might be expected to give the following three products, such as compounds **1**, **4** and 2′-aminophenyl benzoate (**15**). Compound **15** should not be obtained because of intramolecular rearrangement of compound **15** to the more thermodynamically stable isomer, compound **1**.[12] Actually, we cannot observe the formation of **15** for all reactions. The basicity of base strongly affected the ratio of products **1** and **4**. Compound **1** was predominantly obtained in the absence of base or in the presence of pyridine ($pK_a = 5.4$). On the other hand, the reaction in the presence of triethylamine ($pK_a = 9.8$) gave compound **4**, preferentially. This result would be explained by the formation of phenolate ion which is a stronger nucleophile than phenol and aniline.

It is generally accepted that the lower the selectivity lead the greater the reactivity. The reactivity of active esters and amides towards nucleophiles is lower than that of acid chlorides. In the previous paper,[13] we reported the synthesis of chemoselective polyamides from dicarboxylic acids and diamines having various functional groups, where *N*,*N*′-isophthaloyldibenzoxazoline-2-thione was used as an active amide. Thus, chemoselective amidation of 3,3′-dihydroxybenzidine should be expected. The reaction of *N*-benzoylbenzoxazoline-2-thione as an active amide with *o*-aminophenol was performed in NMP at room temperature (Table I, run 4), giving compound **1** (97%) and compound **4** (3%). A perfect chemoselective amidation could not be achieved.



The reaction of *N*-benzoylbenzoxazoline-2-thione and *p*-aminophenol produces the selective *N*-acylated product, 4′-hydroxybenzanilide quantitatively.[13] Thus, an intramolecular hydrogen bond between the amino and hydroxy group of *o*-aminophenol which enhances a nucleophilicity of phenol group and tends to decrease that of amino group, would be considered to play an important role on the selective acylation of *o*-aminophenol.

Inorganic salts such as lithium chloride and calcium chloride are known to improve the solubility of polyamides because of weakening or completely removing the inter- and intramolecular hydrogen bonds of amide

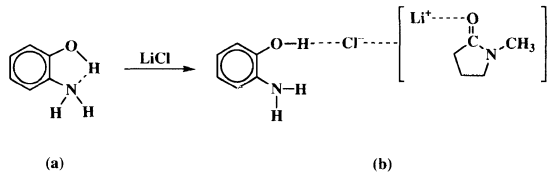
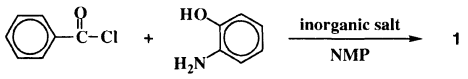


Figure 4. Model of *o*-aminophenol-lithium chloride complex.

units. Therefore, model reactions using inorganic salts were carried out in the absence of base (Table I, run 5—6). Lithium chloride (LiCl) and calcium chloride worked effectively to achieve the chemoselective amidation.



The details of interaction between LiCl and polar groups such as amide, hydroxy and amino group had not been revealed, though a great deal of academic research of them were reported.[14,15] One can imagine that the intramolecular hydrogen bond between the hydroxy and amino groups would activate the hydroxy group by increasing the nucleophilicity of its oxygen atom, and deactivate the amino group by decreasing the nucleophilicity of its nitrogen atom (Figure 4 (a)). On the other hand, LiCl will form ion pairs in polar aprotic solvents such as, $[Li \cdot x\text{NMP}]^+Cl^-$ ion pairs. These ion pairs produce strong bonds with amide and cellulose molecules which result in the dissolution of those molecules. Based on these considerations, we investigated the effect of LiCl on the chemoselective reaction by ^{1}H NMR. Hydrogen bonding can be detected because it usually produce a chemical shift to a lower field. In the spectrum of *o*-aminophenol and LiCl in DMSO-d_6 comparing with that of *o*-aminophenol, ^{1}H chemical shifts of hydroxy and amino groups shifted 0.5 and 0.02 ppm lower compared with those of functional groups in the absence of LiCl, respectively. In the spectra for *m*- and *p*- aminophenol with LiCl, similar ^{1}H chemical shifts were also observed. These results suggest that ion pairs strongly interact with the hydroxy groups of *o*-aminophenol.

According to these findings, intermolecular hydrogen bonds between ion pairs and the hydroxy groups of *o*-aminophenol are formed in NMP, and the nucleophilicity of the hydroxy groups is increased. At the same time, the reactivity of the amino groups is also enhanced due to the disappearance of the intramolecular hydrogen bond. Free amino groups would have higher nucleophilicity than hydrogen-bonded hydroxy groups. Then, the chemoselective amidation resulted, as shown schematically in Figure 4 (b).

Polymer Synthesis

On the basis of model reactions, the chemoselective polyamidation was carried out. PHA-2 with an inherent viscosity of 0.70 dL g^{-1} was prepared from isophthaloyl dichloride and 3,3′-dihydroxybenzidine in the presence of lithium chloride by mixing the two monomers at room temperature.

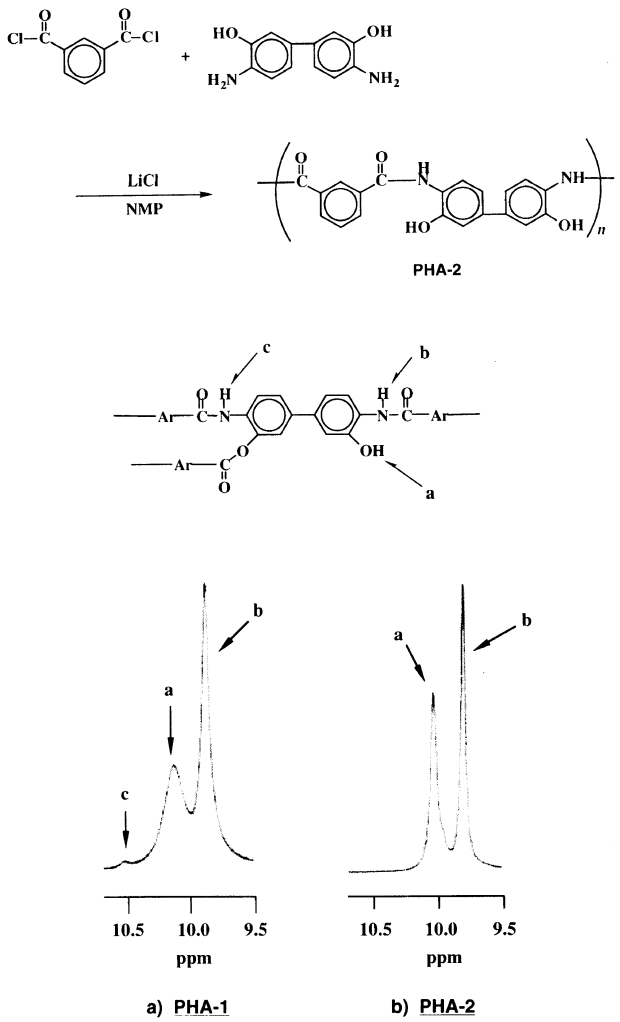


Figure 5. ^{1}H NMR spectra of PHA-1 and -2.

Characterization of Polymers

The IR spectra of PHA-1 and -2 were consistent with those of model compounds and known analogues. PHA-1 showed characteristic N–H, amide I, amide II, and ester carbonyl bands in the range of 3410—3320, 1650—1640, 1520—1510 and 1745—1735 cm^{-1} (shoulder), respectively. On the other hand, the ester carbonyl absorption was not observed in PHA-2.

The microstructure of polymers was determined by NMR spectroscopies. C-H COSY, H-H COSY and H,H-NOESY experiments were supported to confirm the assignment for the proton and carbon signals in the ^{1}H and ^{13}C spectra. ^{1}H NMR spectra of PHA-1 and -2 exhibited two large peaks at 9.81 and 10.05 ppm which are due to hydroxy and amide protons. Furthermore, the small extra peak of NH proton due to the amide-ester structure was observed in the spectrum of PHA-1 (Figure 5). To assign these signals, we measured NOESY spectrum of PHA-2 (Figure 6). The signal at 9.81 ppm is correlated with signals at 8.21 and 8.62 ppm, which are assignable to H_4 and H_6 in the benzene ring of the isophthaloyl groups. On the other hand, the signal at 10.05 ppm is not connected with another signal. Hence, the signals at 9.81 and 10.05 ppm can be assigned to the NH and OH protons, respectively. This relationship between NH and OH protons, such as the existence of OH signal in lower field comparison to that of NH signal,

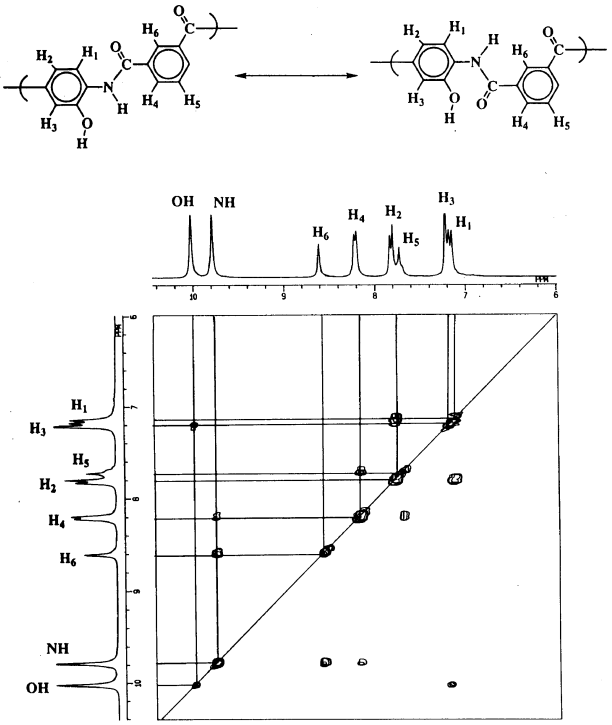


Figure 6. H,H-NOESY spectrum of PHA-2.

Peaks	a	b	c	d	e	f
Reference value*)	125.7	116.9	122.5	136.2	113.3	148.0
Observed value	125.5	117.4	124.1	137.6	114.2	149.4

Peaks	g	h	i	j	k
Reference value	164.7	130.5	128.7	134.6	126.7
Observed value	165.0	130.5	128.8	135.0	126.7

*) On the basis of assignments for model compounds.

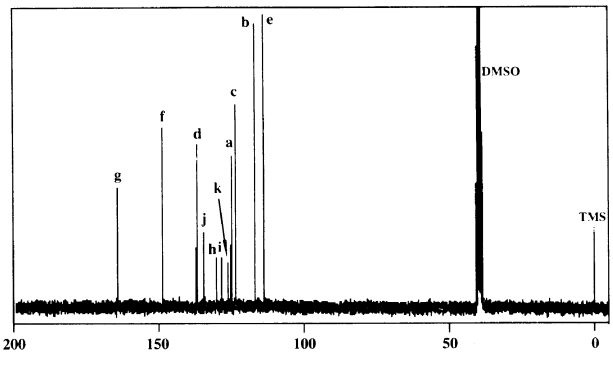


Figure 7. ^{13}C NMR spectrum of PHA-2.

was similar to the results of model compounds.

The ^{13}C NMR spectrum of PHA-2 is presented in Figure 7. All peaks were assigned on the basis of chemical shifts for model compounds. The signal of carbon nucleus in amide carbonyl group for PHA-2 appeared at 165.0 ppm. On the other hand, in the spectrum for PHA-1, two small extra signals of carbon nuclei in amide and ester carbonyl groups derived from *N,O*-acylation (3—4%) appeared at 164.9 and 166.1 ppm, respectively (Figure 8). Furthermore, no peaks at around 170 ppm

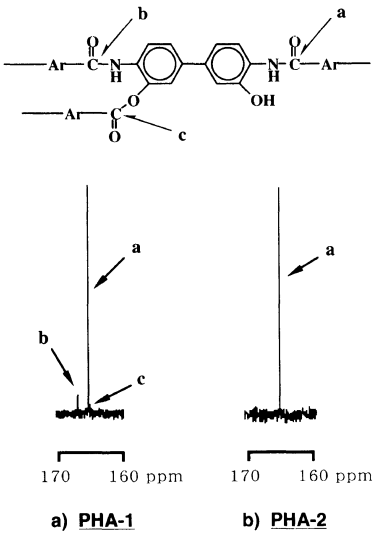


Figure 8. ^{13}C NMR spectra of PHA-1 and -2 (carbonyl region).

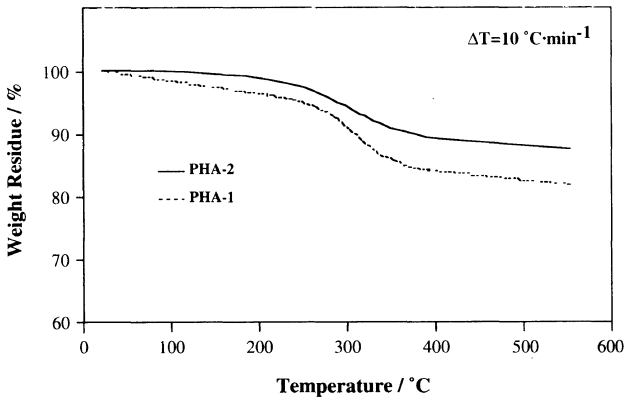


Figure 9. TG traces of PHA-1 and -2 under nitrogen.

due to the carboxy end groups of polymer were observed. These findings clearly indicate that the polycondensation of isophthaloyl chloride and 3,3′-dihydroxy-benzidine in the presence of lithium chloride produced the desired PHA.

The polymers were light brown solids. The thermal stability of the polymers (PHA-1 (dashed line) and PHA-2 (solid line)) was examined by thermogravimetry (TG) (Figure 9). The rapid weight loss for both polymers, observed at 200—400°C in the TG trace. In this range, weight losses of PHA-1 and PHA-2 were 13.4% and 11.0% respectively. The value of PHA-2 is in good agreement with the value of weight loss (10.4%) calculated from the elimination of water due to the oxazole ring formation. The PHA-1 also showed gradually weight loss before dehydration. The excess weight loss of PHA-1 comparison with that of PHA-2 was attributed to the elimination of ester group.

CONCLUSIONS

We have demonstrated that the chemoselective synthesis of PHA can be achieved by the polycondensation of isophthaloyl dichloride with 3,3′-dihydroxybenzidine in the presence of lithium chloride.

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