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Characterization of Nitro-Substituted Polybenzimidazole Synthesized by the Reaction with Nitric Acid

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CHARACTERIZATION OF NITRO-SUBSTITUTED POLYBENZIMIDAZOLE SYNTHESIZED BY THE REACTION WITH NITRIC ACID

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ABSTRACT

Nitro-substituted poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole]s (PBIs) were synthesized by the reaction of PBI with nitric acid in sulfuric acid under various conditions. The number of nitro groups substituted on the aromatic ring of PBI per polymeric unit varied from 1.44 to 3.55 according to the reaction conditions. An increase in reaction temperature and concentration of the nitric acid increased the degree of substitution. The inherent viscosity of the substituted polymer increased as the reaction temperature decreased. When the reaction temperature was 30°C, the inherent viscosity of the polymer increased as the concentration of nitric acid increased. The nitro-substituted PBI exhibited polyelectrolyte behavior in formic acid. The nitro groups substituted on PBI were dissociated when the polymer was heated to 450°C, displaying exothermic be-

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havior, and the decomposition of polymer was proportional to its nitro group content. All nitro-substituted PBIs showed better solubilities in polar aprotic and acidic solvents, such as dimethylacetamide, dimethylsulfoxide, dimethylformamide, *N*-methylpyrrolidone, formic acid, sulfuric acid, and trifluoromethanesulfonic acid.

INTRODUCTION

Poly[2,2'-(*m*-phenylene-5,5'-bibenzimidazole] (PBI), which is commercially available primarily from Hoechst Celanese Corp., can be made into a fiber having excellent textile and tactile performance, since this polymer has high temperature stability, nonflammability, and high chemical resistance [1-4].

PBI has very limited solubility and well-known solvents for this polymer are dimethylacetamide (DMAc) and concentrated sulfuric acid. However, PBI does not show complete solubility in DMAc and the polymer can be separated into bulk fractions by varying the solution temperatures. The amount of polymer extracted increases along with the molecular weight of the fraction with increasing temperature. At the boiling point of the solvent, 75-80% of the polymer is solubilized. It has also been documented that solutions of PBI cannot be stored for long periods of time without "phasing out," i.e., a separation of the solution into two phases containing greater and lesser concentrations of PBI. Minor amounts of lithium chloride, zinc chloride, *N*-methylmorpholine, triethylamine, and triethanol amine act as stabilizers that prevent or retard "phasing out" [5]. Ammonium acetate can play a similar role as a stabilizer [6].

As described above, development of PBI for applications has been hindered by its difficult processibility due to limited solubility, and much effort is being devoted to increasing the solubility through modification of the polymer backbone and side chain. The modification of PBI by copolymerization and block copolymerization [7, 8] is a good example. Some work has also been performed by replacing the imidazole hydrogen by some aliphatic and aromatic substituents to produce a substituted PBI. *N*-Propanesulfonate PBI and *N*-benzylsulfonate PBI are water soluble [9]. Poly(methylbenzimidazole) and poly(dimethylbenzimidazolium) salt can be dissolved in dimethylsulfoxide (DMSO), *N*-methylpyrrolidone (NMP), dimethylformamide (DMF), and DMAc [10].

In this study the modification of PBI was tried by introducing nitro groups into the aromatic ring of benzimidazole by using nitric acid to increase the solubility of PBI. The thermal stability and viscosity behavior of modified PBI were also examined.

EXPERIMENTAL

Materials

PBI fiber produced by Hoechst Celanese Corp. was used. It is dark-brownish in color and its molecular weight is 20,000. The fibers were chopped and cleaned in a Soxhlet extraction apparatus using three kinds of solvents, carbon tetrachloride,

ethanol, and water, for 4 hours, respectively. After this treatment, the fibers were dried completely in a vacuum oven for 12 hours.

Reagents

Sulfuric acid (99.8%) and 60% nitric acid (GR grade) were used without further purification.

Nitration

PBI fibers (3.68 g; 1.0% of the weight of sulfuric acid) were suspended in 200 mL sulfuric acid and stirred for 2 hours. The amount of nitric acid added in the suspended mixture was controlled to 0.83, 2.5, 5.0, 7.5, 10.0, and 20.0% with respect to the volume of sulfuric acid. The addition of nitric acid was performed while stirring and cooling the flask in an ice bath. After 1 hour, the temperature was kept at either 30, 40, 60, 80, or 100°C for 2 hours. All procedures mentioned above were carried out under an atmosphere of nitrogen. After filtration of the insoluble residues, the solution was poured into ice water, and a precipitate was produced. The pH of the solution from which the precipitate was formed was controlled with a concentrated sodium hydroxide solution to 4–5. The final product was obtained after complete washing and drying in a vacuum oven for 12 hours.

Characterization of Products

Infrared Spectroscopy. The products were powdered after nitration and mixed with KBr to make a pellet having a homogeneous mixture phase. The infrared absorption spectrum of the pellet was obtained on a Perkin-Elmer FT-IR spectrophotometer.

¹³C-CP/MAS NMR Spectroscopy. High resolution solid-state ¹³C-CP/MAS NMR spectra were obtained on a Bruker MSL-300 at a ¹³C resonance frequency of 75.47 MHz. Sample spinning at the magic angle was carried out at the rate of 4000 Hz.

Viscosity Measurement. The viscosity of the sample was measured in formic acid and DMAc at 30°C. The reduced viscosity (η_r) was determined in formic acid from the following equation in the 0.5 to 2.0 g/dL concentration range:

$$\eta_r = (\eta_{rel} - 1)/c$$

where η_{rel} is the relative viscosity and c is the concentration. The inherent viscosity (η_{inh}) was determined in DMAc at a concentration of 0.6 g/dL:

$$\eta_{inh} = \ln \eta_{rel}/c$$

Elementary Analysis. A Yanaco MT-2 with CHN corder was used to measure the carbon, hydrogen, and nitrogen contents in the polymer.

Thermogravimetric Analysis (TGA). A Perkin-Elmer TGA 7 was used under an atmosphere of flowing nitrogen gas at a heating rate of 10°C/min. The temperature was set from 30 to 700°C.

Differential Scanning Calorimetry (DSC). The thermal decomposition temperature and the exothermic heat were determined by using a Perkin-Elmer DSC 7 under an atmosphere of nitrogen flow from 30 to 500°C with the heating rate of 10°C/min.

Solubility Test. Twelve kinds of solvents were used for the solubility test. Polymer (0.1 g) in 10 mL solvent was stirred for 12 hours at 25°C.

RESULTS AND DISCUSSION

Reaction of PBI with Nitric Acid

Table 1 shows the reaction conditions for each sample. The reaction mixture became homogeneous at temperatures over 80°C. However, insoluble residue remained below 80°C, and in this case the residue was filtered. The higher the reaction temperature and the concentration of nitric acid, the smaller the amount of residue that remained. Sulfuric acid was used not only as a reaction medium but also as a catalyst for nitration and as a solvent for the resulting nitrated PBI. The PBI was not perfectly soluble in sulfuric acid, and excess amounts of nitric acid played a role in increasing the PBI dissolution as a powerful acidic solvent.

Figure 1 shows the IR spectra of PBI both before and after reaction with nitric acid. The peaks at about 1627 and 1562 cm^{-1} can be assigned to the C=N stretching band and N-H bending of the secondary aromatic amine, respectively [11]. PBI typically displays a sharp band near 1454 cm^{-1} , and this pattern is characteristic of the heterocyclic imidazole ring [12]. It should be noted that a shift of the N-H deformation from 1530 to 1562 cm^{-1} occurs after the stabilizing treatment, and strong absorptions at 1173 and 1210 cm^{-1} are consistent with the presence of aryl sulfonic acid groups [4]. New sharp peaks at 1517 and 1332 cm^{-1} are found in b) which indicate the presence of nitrobenzene [13, 14]. Therefore, it can be concluded

TABLE 1. Nitration Conditions for PBI

Sample code	Reaction temperature, °C	Nitric acid/sulfuric acid, v/v%
PBI	—	—
NP3005	30	5
NP4005	40	5
NP6005	60	5
NP8005	80	5
NP10010	100	10
NP10020	100	20
NP30s	30	0.83
NP303s	30	2.5
NP309s	30	7.5

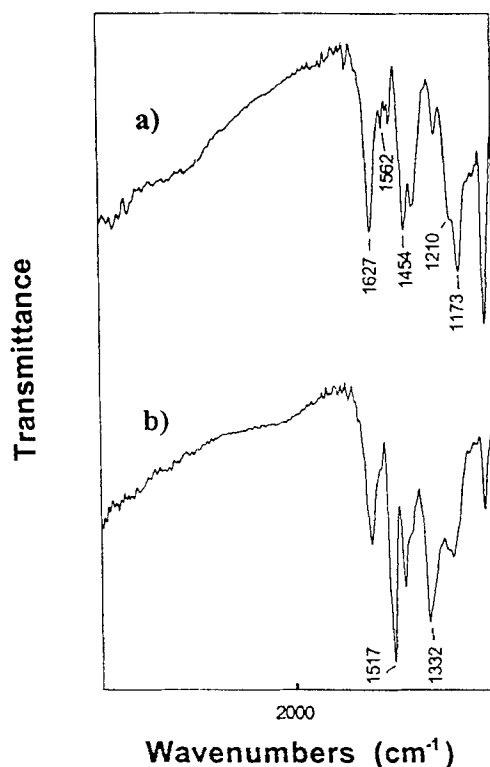
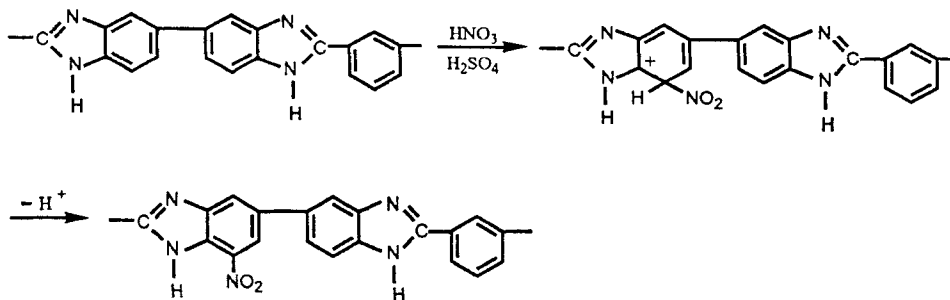


FIG. 1. Infrared spectra of (a) PBI and (b) PBI after reaction with nitric acid.

that new nitro groups were introduced to the aromatic rings of the polymer through the reaction of PBI with nitric acid (Scheme 1).

¹³C-CP/MAS NMR spectra are shown in Figs. 2 and 3. The spectrum of PBI consists of several lines that can be identified in the order of increasing magnetic field as the ones arising from the carbons of the imidazole rings attached to phenylene rings (151 ppm), the carbons connecting benzimidazole rings in the bibenzimidazole system (142 ppm), and the aromatic carbons bound to the nitrogen atoms



SCHEME 1. Nitration of PBI.

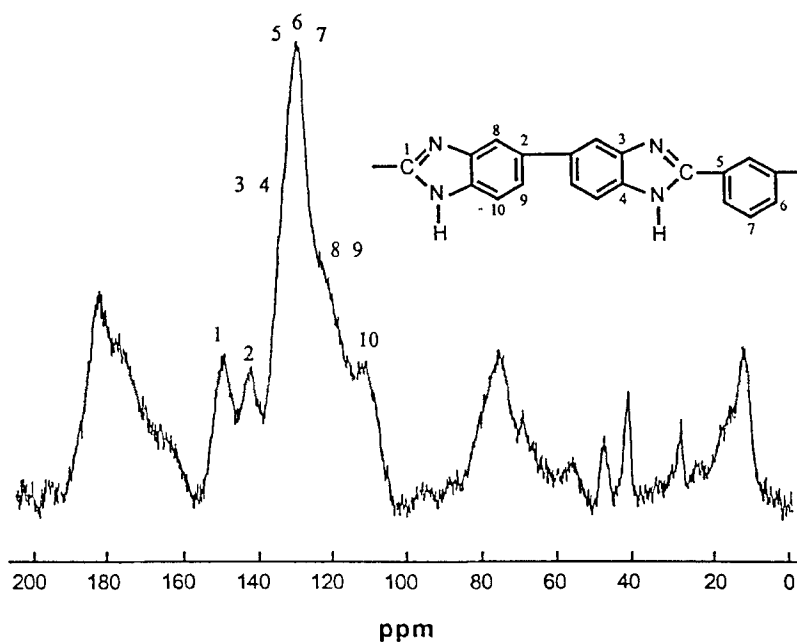


FIG. 2. ^{13}C -CP/MAS solid-state NMR spectrum of PBI.

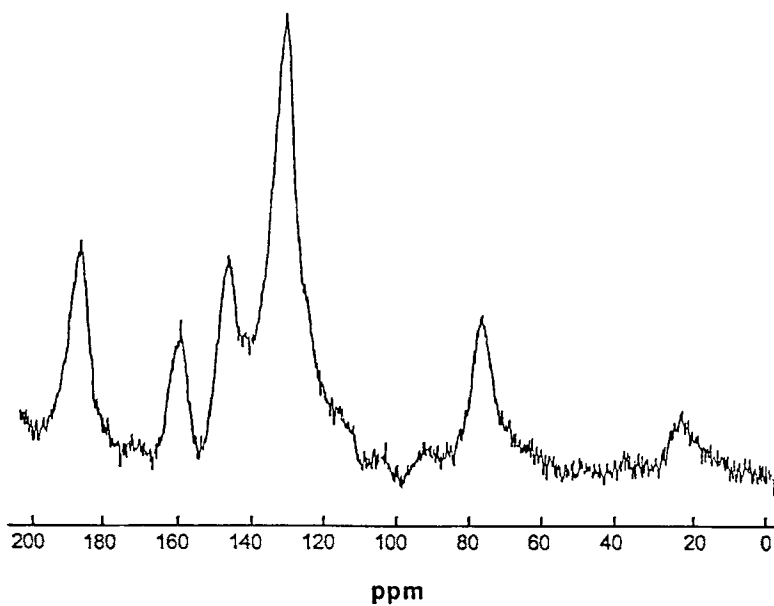


FIG. 3. ^{13}C -CP/MAS solid-state NMR spectrum of PBI after reaction with nitric acid.

(134 ppm). The three remaining lines (129, 120, and 111 ppm) have been assigned to the protonated carbons of PBI with a contribution of the nonprotonated carbons of the phenylene ring to the line centered at 129 ppm [15]. In Fig. 3 the peak at about 111 ppm disappears, which means that carbons at the 10 position have a slightly different environment compared with the carbons in the original PBI. In the case of substituted benzenes, *m*-carbon atoms remain almost unaffected by any kind of substituent. Electron-withdrawing groups decrease the *p*-electron densities in *o*- and *p*-positions. Thus, a deshielding is observed. In nitrobenzene an intramolecular electric field intensity of the nitro group increases, and σ -electron densities at the *o*- and *o'*-positions are reduced [16]. Therefore, dominated deshielding effects appear in the substituted carbon and *p*-carbon in the aromatic ring. As a result, deshielding of the peak at 111 ppm implies that the carbons at the 8 or 10 position were probably substituted on new nitro groups.

Degree of Substitution of Nitro Groups

Carbon, hydrogen and nitrogen contents of each sample are listed in Table 2. In any case the absolute carbon content should not vary. Hence N/C (%) was considered to be a barometer in estimating the degree of nitration. If one nitro group per repeat unit of polymer is substituted, N/C (%) is found to be 29.18. If two, N/C (%) becomes 35.01. In case of three and four nitro substituents, 40.82 and 46.65 of N/C (%) are obtained, respectively. In most cases of samples, N/C (%) varied from 31 to 34, which means that one or two nitro substituents attached to the aromatic rings in one polymeric repeat unit. However, under severe conditions, which were a considerably higher reaction temperature and higher concentration of nitric acid, N/C (%) reached a value over 35. In practice, N/C (%) of NP10010 and 10020 were 38.58 and 44.05, respectively.

TABLE 2. Elemental Analysis Results of PBI and Nitro-Substituted PBIs

Sample code	Carbon, %	Hydrogen, %	Nitrogen, %	N/C, %
PBI	59.27	4.89	13.99	23.60
NP3005	50.86	3.81	16.83	33.09
NP4005	48.53	4.06	15.85	32.66
NP6005	46.88	3.62	15.78	33.66
NP8005	44.81	3.41	15.53	34.66
NP30s	52.08	3.40	16.54	31.76
NP303s	49.93	3.67	16.22	32.49
NP309s	44.72	3.66	15.17	33.92
NP10010	42.85	2.80	16.53	38.58
NP10020	39.52	2.48	17.54	44.05
$C_{20}H_{12}N_4$	—	—	—	23.33
$C_{20}H_{11}N_5O_2$	—	—	—	29.18
$C_{20}H_{10}N_6O_4$	—	—	—	35.01
$C_{20}H_9N_7O_6$	—	—	—	40.82
$C_{20}H_8N_8O_8$	—	—	—	46.65

Table 3 shows the degree of substitution obtained from elemental analysis results. At the same concentration of nitric acid the degree of substitution increased as the reaction temperature increased, and at the same reaction temperature (30°C) the degree of substitution similarly increased as the concentration of nitric acid increased. Under severe conditions the maximum degree of substitution was obtained, and NP10020 yielded 3.55. On the other hand, a relatively low value of 1.44 was obtained from NP30s produced under the mildest condition.

Viscosity of Nitro-Substituted PBI

Table 4 shows the inherent viscosity (η_{inh}) of nitro-substituted PBIs measured in the DMAc solution at 30°C. Generally, PBI cannot be dissolved in DMAc completely, but all the nitro-substituted PBIs were dissolved in DMAc perfectly. Therefore, the viscosity measurement could be well accomplished. The nitro-substituted PBIs had a viscosity range of 0.05 to 0.89 dL/g. Nitro groups substituted at aromatic rings in the polymer chain may hinder the strong intermolecular hydrogen bonding which results in limited solubility. The intermolecular hydrogen bonding weakened by the nitro groups increases the mobility of polymer chains in the solution. However, considering that the insoluble residue filtered after nitration is thought to have a high molecular weight, under severe reaction conditions the chain-scission of the polymer may occur increasingly. For this reason, the viscosity of nitro-substituted PBI is considered to be lower than that of the original PBI. In Table 4, η_{inh} decreases as the reaction temperature of each sample increases. This seems to be mainly ascribable to polymer chain cleavage at a reaction temperature over 80°C. On the other hand, η_{inh} increased as the amount of nitric acid added increased (Fig. 4). Such a trend can be explained by the fact that the insoluble residue decreased and the chain-scission of polymer did not occur seriously at a low temperature, i.e., 30°C, in spite of the increase of the amount of nitric acid. From these results it is obvious that the nitration of PBI with little chain-scission can be achieved at a low temperature and a high concentration of nitric acid.

TABLE 3. Degree of Nitro-Substitution of Each Sample

Sample code	Degree of substitution
PBI	0
NP3005	1.67
NP4005	1.60
NP6005	1.77
NP8005	1.94
NP10010	2.61
NP10020	3.55
NP30s	1.44
NP303s	1.57
NP309s	1.81

TABLE 4. Inherent Viscosity of Nitro-Substituted PBIs Measured in DMAc at 30°C

Sample code	$\ln \eta_r/0.6, \text{ dL/g}$
NP3005 ^a	0.8363
NP4005 ^a	0.6773
NP6005 ^a	0.7348
NP8005 ^a	0.2340
NP10010 ^a	0.1046
NP10020 ^a	0.0512
NP30s	0.5928
NP303s	0.6320
NP309s	0.8943

^aNitrated at a concentration of 5% nitric acid (with respect to the volume of sulfuric acid).

Figures 5 and 6 show the variation of reduced viscosity (η_{sp}/c) of NP3005, NP4005, NP6005, and NP8005 with their concentrations, respectively. The increase of η_{sp}/c with decreasing polymer concentration suggested that nitrated PBI would reveal typical polyelectrolyte behavior due to the dissociation of proton counterions from formic acid and also due to the expansion of the polymer chain owing to the net charge increase of the polymer backbone. Such behavior is also found in polyimidazoles that are not modified [17]. Similarly, poly(dimethylbenzimidazolium) salt shows the same behavior due to the above-mentioned reasons.

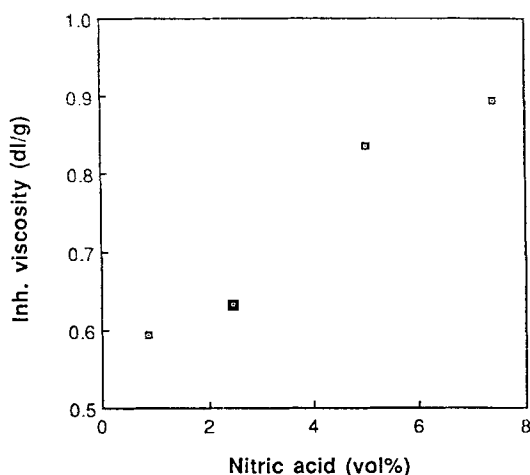


FIG. 4. Inherent viscosity ($c = 0.6 \text{ g/dL}$; in DMAc at 30°C) of PBI nitrated at 30°C as a function of the concentration of nitric acid added.

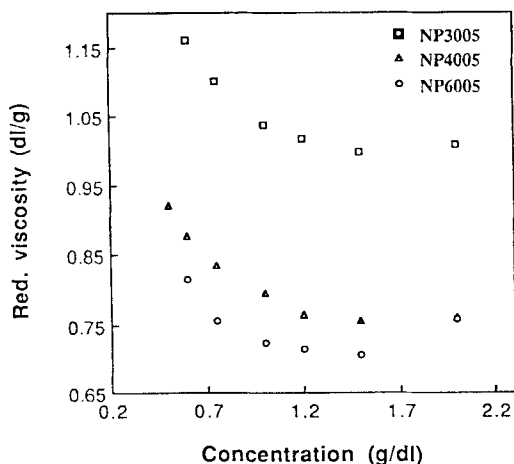


FIG. 5. Reduced viscosity of nitrated PBIs measured in formic acid at 30°C.

Thermal Properties of the Nitro-Substituted PBI

Thermal properties of the polymer was evaluated by thermogravimetry (Table 5). It is well known that PBI is special because of its dramatically excellent thermal stability, and in practice the weight loss of PBI was only 22.1% after heating to 700°C. Its initial weight loss occurred below 120°C and this was due to a loss of water, since PBI is known as a hygroscopic polymer. Except for the loss of water, the polymer barely decomposed up to 500°C. However, in the case of nitro-substituted PBI, 35–50% decomposition was observed from the results of TGA, a 13–28% larger value compared with that of PBI. We can find from Fig. 7 that NP6005 first decomposed at about 350–450°C. In the case of NP10020 the decomposition temperature range was broader, and the weight loss in this temperature range was larger than that of NP6005.

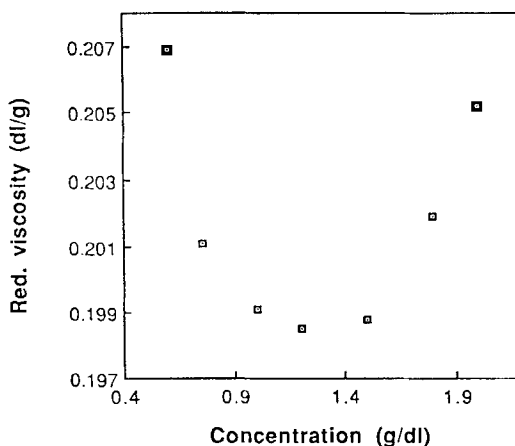


FIG. 6. Reduced viscosity of NP8005 measured in formic acid at 30°C.

TABLE 5. Thermogravimetric Analysis Results of PBI and Nitro-Substituted PBIs from 30 to 700°C

Sample code	Total weight loss at 700°C, %
PBI	22.10
NP3005	39.42
NP4005	39.00
NP6005	39.60
NP8005	40.67
NP10010	45.40
NP10020	51.33
NP30s	35.65
NP303s	38.23
NP309s	40.83

N-Propanesulfonate PBI and *N*-benzylsulfonate PBI show about 35 and 25% weight losses, respectively, after heating up to 700°C under the conditions where moisture in the polymers is eliminated thoroughly [9]. Both polymers also show a first decomposition temperature which is much lower than that of the unmodified PBI. In the case of PBI containing dibenzothiophene units, 50% decomposition is observed at 565°C [18]. Hu et al. [10] reported that the TGA thermogram of poly(*N*₁-methylbenzimidazole) showed about an 8% weight loss between 180 and 500°C due to the loss of a methyl group. Furthermore poly(dimethylbenzimidazoli-

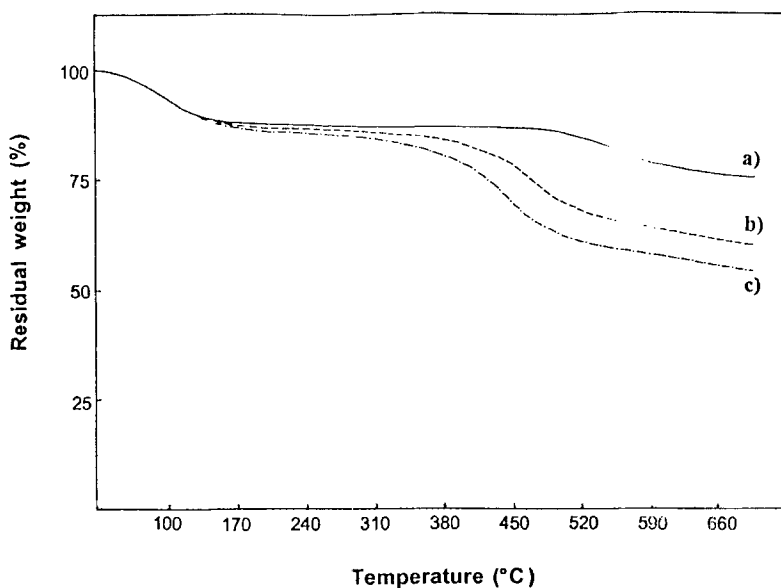


FIG. 7. TGA thermograms of (a) PBI, (b) NP6005, and (c) NP10020.

um)iodide shows a two-stage loss between 180 and 400°C and the total weight loss reaches 35%, which might be attributed to the two different counterions contained in the polymer. PBIs containing azo groups are stable in air up to 400°C, and a 10% weight loss is observed between 400 and 420°C. The differential thermal analysis curves of these polymers exhibit interesting features. No appreciable change is observed up to 380°C. In the 380–415°C region, all polymers show strong exothermic peaks. Such a behavior suggests that the first step in the thermal degradation of these polymers might be the elimination of the azo group, probably as molecular nitrogen [19]. The first step in the thermal decomposition of certain aromatic polymers prepared by oxidative coupling of primary amines occurs in a loss of nitrogen [20]. A similar observation was also noted by Riordan and Blair [21] in the thermal degradation of azopolyamides.

The DSC thermograms of nitro-substituted PBI revealed strong exotherms as shown in Fig. 8, and the onset temperatures and the areas of these exothermic peaks are listed in Table 6. Figure 9 shows the IR spectra of NP309s before and after heating to the temperature where the exotherm ended. The characteristic signals of

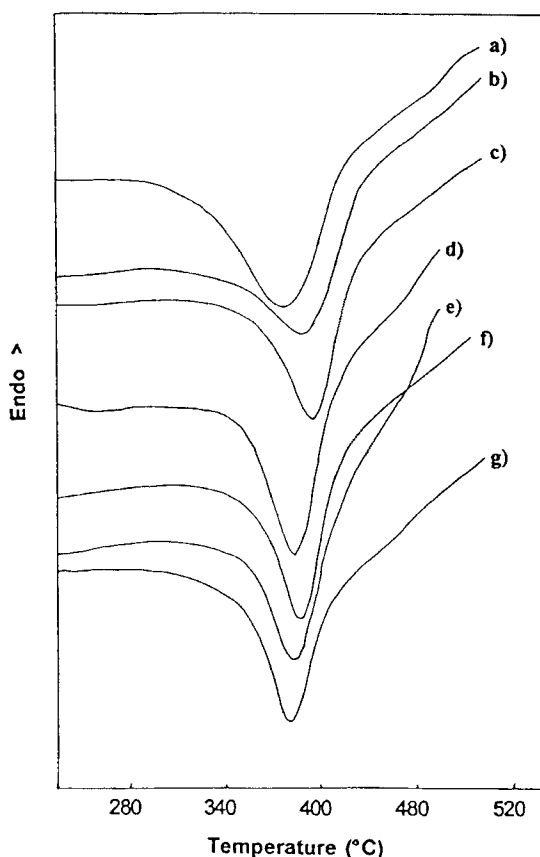


FIG. 8. DSC thermograms of nitro-substituted PBIs: (a) NP8005, (b) NP30s, (c) NP303s, (d) NP4005, (e) NP6005, (f) NP309s, (g) NP3005.

TABLE 6. Differential Scanning Calorimetric Results of Nitro-Substituted Derivatives of PBI

Sample code	Exotherm peak onset, °C	Peak temperature, °C	Peak area, kJ/g
NP3005	351.15	379.35	1.31
NP4005	350.05	382.81	1.23
NP6005	352.14	376.71	1.35
NP8005	319.14	377.78	1.51
NP30s	340.93	392.08	1.14
NP303s	356.88	394.74	1.19
NP309s	351.70	386.76	1.47

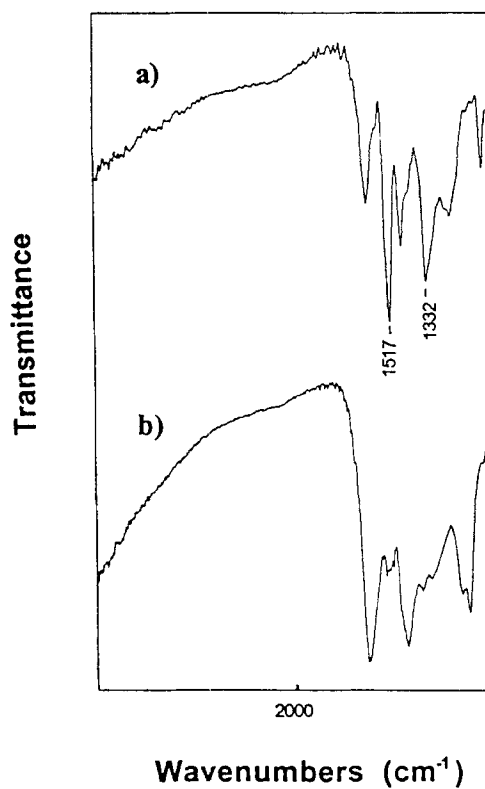


FIG. 9. Infrared spectra of NP309s: (a) before heating, (b) after heating to 500°C.

nitrobenzene at 1517 and 1332 cm^{-1} almost disappeared, and each intensity decreased to a much smaller scale. From the above results, it is considered that the exotherm behavior of the nitro-substituted PBI can be assigned to the dissociation of nitro groups from about 300 to 450°C and the maximum peak temperature exists between 375 and 395°C. The peak broadness and sharpness are related to peak area, which is implicated in the energy of exothermic activation. Finally, the peak area of each sample increased with an increase in the degree of substitution. This result supports the idea that the decomposition of nitro groups occurred in the above temperature range. Therefore, it is quite evident that the first step in the decomposition curves exhibited in the TGA thermograms of nitro-substituted PBI can be ascribed to a loss of nitro groups. Figure 10 confirms this. An almost linear relationship was obtained between the degree of substitution and the total decomposition (%) of the nitro-substituted PBI. Except for the decomposition of nitro groups, nitro-substituted PBI showed behaviors similar to those of PBI in thermal degradation.

Solubility of Nitro-Substituted PBI

Development for applications of PBI have been hindered by difficult processibility due to its limited solubility. The N—H hydrogen on PBI is less reactive compared to the monomer because of interchain hydrogen bonding. The limited solubility of PBI has been attributed to interchain hydrogen bonding as well as to the polarity of the imidazole ring. The work done by Hu et al. [10] includes the substitution of N—H hydrogen by a methyl group to reduce the hydrogen bonding and increase the basicity of the imidazole ring. Poly(dimethylbenzimidazolium) salt has an extended solubility in DMAc, DMF, DMSO, and NMP. Gieselman and Reynolds [9] reported that water-soluble PBI was synthesized by *N*-propanesulfonation and *N*-benzylsulfonation. PBIs containing azo groups also showed an increased solubility. According to Srinivasan et al. [18], PBIs containing dibenzothio-

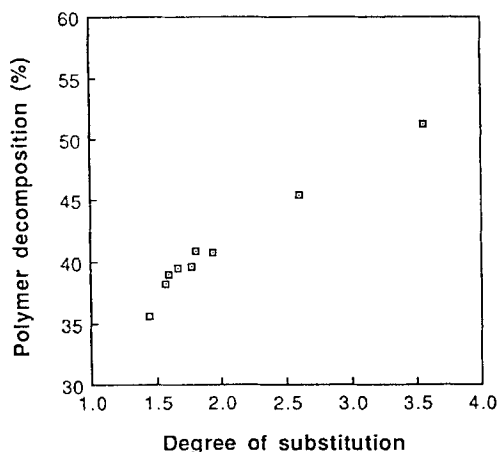


FIG. 10. Polymer decomposition (%) vs degree of substitution of nitro-substituted PBI.

phenediyl or 5,5'-dioxodibenzothiophenediyl units have better solubility in polar aprotic solvents.

Solvents with a low molar Gibb's energy of sorption, ΔG , may be good solvents for PBI [22]. DMF and DMAc are known to be solvents for PBI and possess a low Gibb's energy value.

In connection with the above viewpoint, solvents for the solubility test were selected considering their polarizabilities, dipole moments, and hydrogen-bond-forming abilities, which contribute to Gibb's energy. PBI did not fully dissolve in DMAc, DMF, and DMSO as shown in Table 7. The ability to dissolve PBI depends on the replacement of the interaction in the polymer by equally strong or stronger solvent-chain interactions. Hydrogen-bond-forming ability plays a most important role in the solvation of PBI, but the hydrogen-bond-forming ability of DMF is not stronger than that of polymer chains. Solvent molecules can attach to the surface of the polymer, but they cannot penetrate into the interface enough to solvate the polymer molecules since they cannot overcome the chain-chain interaction due to hydrogen bonding. A similarity can be found in the case of DMAc and DMSO. It is important for PBI solvation that the chain-chain interaction should be decreased. In the case of nitro-substituted PBI, it is dissolved in polar aprotic solvents. Newly substituted nitro groups have a high electron density which may cause repulsion of polymer chains to a decrease in chain-chain interactions. Moreover, nitro groups have enough dipole moments to help the solvent molecule approach the polymer by dipole-dipole interaction. In the case of nitro-substituted PBI, all polymer chains become more easily solvated and are dissolved in polar aprotic solvents for these reasons. However, in the case of formamide, a bridge-like formation due to chain-solvent-chain bonding results in limited swelling and hindered dissolution of the polymer. On the other hand, with DMAc such a bridge formation cannot exist because of the lack of sufficient hydrogen bonding sites on this solvent.

TABLE 7. Solubility of PBI and NP6005 in Various Solvents

Solvent	PBI	NP6005
<i>N,N'</i> -Dimethylacetamide	PS ^a	S ^b
<i>N,N'</i> -Dimethylformamide	I ^c	S
Formamide	I	I
Dimethylsulfoxide	I	S
1-Methylpyrrolidin-2-one	I	S
Nitrobenzene	I	I
Sulfuric acid	PS	S
Formic acid	I	S
Methanesulfonic acid	I	I
Trifluoromethanesulfonic acid	I	S

^aPS, partially soluble.

^bS, soluble.

^cI, insoluble.

CONCLUSIONS

Nitro-substituted PBIs were synthesized by reaction with nitric acid in sulfuric acid under various conditions, and their viscosity behaviors, thermal properties and solubilities were investigated. A higher inherent viscosity was displayed by the product obtained under a lower reaction temperature. The viscosity of the polymer produced increased with an increase in the concentration of nitric acid at a low temperature of 30°C. A higher degree of substitution was obtained under conditions where the reaction temperature and the concentration of nitric acid were increased. Nitro-substituted PBIs showed a characteristic exothermic peak due to the loss of nitro groups. They also showed better solubilities in polar aprotic and acidic solvents.

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