Preparation of Organo-Soluble Poly[(2,2′-*m*-phenylene)-5,5′-bibenzimidazole] with High Yield by Homogeneous Nitration Reaction

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ABSTRACT: To prepare organo-soluble poly[(2,2,′-*m*-phenylene)-5,5′-bibenzimidazole] (PBI) with high yield, a homogeneous nitration of PBI was attempted. Nitro-substituted PBI (NO$_2$-PBI) was synthesized through the homogeneous reaction of the PBI powder with nitric acid in sulfuric acid. The degree of substitution (DS) of this NO$_2$-PBI is higher than that of the NO$_2$-PBI prepared through the heterogeneous reaction of the PBI fiber. The viscosity of the NO$_2$-PBI prepared through the homogeneous reaction decreased with increasing amount of nitric acid added. The DS of the NO$_2$-PBI reached the maximum value of 2. The substitution efficiency of nitro groups decreased as the amount of nitric acid added increased. When a small quantity of nitric acid was added, the substitution of the sulfonic acid group was confirmed as well as that of the nitro group. The solubility of the NO$_2$-PBI depended strongly on the DS. The NO$_2$-PBI having the DS of about 2 was completely soluble in dimethylacetamide and almost soluble in *N*-methylpyrrolidone. At an elevated temperature, it was also soluble in other polar aprotic solvents such as dimethylformamide and dimethylsulfoxide. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 438–445, 2000

Key words: polybenzimidazole; nitro group; high yield; degree of substitution; solubility

INTRODUCTION

Poly[(2,2′-*m*-phenylene)-5,5′-bibenzimidazole] (PBI) is one of the most promising polymeric materials for high temperature applications. It has thermal and oxidative stabilities, nonflammability, and excellent chemical resistance. It has been widely used in the aerospace industry, where thermal stability is a primary requirement and is also used as a replacement for asbestos,[1] ion exchange resin, microporous adsorbent beads,[2] and in high temperature filtration fabrics.

In general, PBI has very poor solubility in most organic solvents. So, solvents for this polymer are only dimethylacetamide (DMAc) and concen-

trated sulfuric acid. However, PBI does not dissolve completely in these solvents and separates into bulk fractions upon decreasing solution temperature. PBI solution cannot be stored for long periods of time without phase separation into polymer rich and poor phases. Stabilizers, such as lithium chloride, zinc chloride, N-methylmorpholine, triethylamine, triethanol amine, and ammonium acetate, are used to prevent or retard this phase separation.[3,4] The applications of PBI as fibers and membranes are limited because the additional processes such as dissolution at high temperature and high pressure and successive filtration of insoluble residue are inevitable. For this reason, the improvement of solubility by modification of PBI has been an issue of intense interest. Random and block copolymerization are good examples.[5,6] The imidazole hydrogen in PBI was replaced by some aliphatic and aromatic substituents. N-benzylsulfonate PBI is water soluble.[7] Poly(methylbenzimidazole) and poly(dimethylbenzimidazolium) salt are soluble in dimethyl sulfoxide (DMSO), N-methylpyrrolidone (NMP), dimethylformamide (DMF), and DMAc.[8] PBI containing dibenzothiophenediyl or 5,5′-dioxodibenzothiophenediyl units has better solubility in polar aprotic solvents.[9]

In this study, to improve spinning tractability of PBI in various common organic solvents and miscibility with the other polymers, organo-soluble PBI with high yield was synthesized by introducing the nitro group through the reaction of PBI powder with nitric acid in homogeneous media. In addition, this NO_2-PBI was compared with NO_2-PBI prepared from heterogeneous reaction of PBI fiber. NO_2-PBIs having a wide range of degree of substitution (DS) were synthesized at various reaction conditions and the effects of the reaction condition on DS, molecular weight, and solubility were studied.

EXPERIMENTAL

Nitration

PBI powder, 1.84 g (Aldrich), was dissolved completely in 200 mL of sulfuric acid at room temperature. After nitric acid was added at 0°C, the solution was well stirred at the same temperature for 1 h. The solution was poured into ice water to produce a yellowish precipitate. The pH of the solution from which the precipitate was formed was adjusted to 5.0 with a concentrated sodium hydroxide solution, when the color of the precipitate turned dark brown. The final product was obtained after complete washing and drying in a vacuum oven for 12 h.

PBI fiber (Hochest-Celanese), not perfectly soluble in sulfuric acid, was suspended in sulfuric acid and stirred for 2 h. After nitric acid was added at 0°C, the solution was well stirred at the same temperature for 1 h and kept at 30°C for 2 h. All procedures were performed under nitrogen. After filtration of insoluble residues, the solution was poured into ice water to produce a precipitate. The subsequent workup was the same as that used for the PBI powder.

Characterization of Product

Infrared Spectroscopy

The products were mixed with KBr to make a pellet having a homogeneous mixture phase. The infrared absorption spectrum of the pellet was obtained on a Nicolet Magna-IR spectrophotometer at the resolution of 4 cm^{-1}.

Elemental Analysis

A Vario EL elemental analyzer (Elementar Co.) with CHNS corder was used to measure the carbon, hydrogen, and nitrogen contents in the polymers.

Viscosity Measurement

The viscosity was measured in a Ubbelohde viscometer at 25°C. The inherent viscosity (η_{inh}) was determined in sulfuric acid at a concentration of 0.4 g/dL from the following equation:

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

where η_{rel} is the relative viscosity and c is the concentration of the solution.

Solubility Test

DMAc was used for the solubility test. Polymer (1.0 g) was dissolved in 100 mL of the solvent for 12 h at a fixed temperature and the weight of insoluble residue was measured. The solubility was obtained from the following equation:

$$\text{Solubility } (\%) = \frac{1 - W}{W_o} \times 100$$

Table I   Reaction Condition for the Nitration of PBI

Sample	Nitric Acid (g)/ Sulfuric Acid (mL)	Reaction Temperature (°C)	PBI Used
1	1.03[a]/200	0°C (1 h), 30°C (2 h)	Fiber
2	2.05[a]/200	0°C (1 h), 30°C (2 h)	Fiber
3	3.08[a]/200	0°C (1 h), 30°C (2 h)	Fiber
4	8.20[a]/200	0°C (1 h), 30°C (2 h)	Fiber
5	2.05[a]/200	0°C (1 h), 30°C (2 h)	Powder
6	4.10[a]/200	0°C (1 h), 30°C (2 h)	Powder
7	8.20[a]/200	0°C (1 h), 30°C (2 h)	Powder
8	0.10[b]/200	0°C (1 h)	Powder
9	0.21[b]/200	0°C (1 h)	Powder
10	0.41[a]/200	0°C (1 h)	Powder
11	1.03[a]/200	0°C (1 h)	Powder
12	2.05[a]/200	0°C (1 h)	Powder
13	4.10[a]/200	0°C (1 h)	Powder
14	1.03[a]/100	0°C (1 h)	Powder
15	1.03[a]/300	0°C (1 h)	Powder

[a] 60% nitric acid was used.
[b] 1 N nitric acid was used.

where W_o is the initial weight of polymer and W is the weight of undissolved polymer.

RESULTS AND DISCUSSION

The nitration of PBI fiber was divided into two steps. One was addition of nitric acid at 0°C and the other was the reaction for the further dissolution, which was performed at 30°C. In this study, one of the nitration processes of PBI powder included the further dissolution step at 30°C in order to compare with the results from the nitration of PBI fiber even though it is a completely homogeneous reaction. The other nitration process of PBI powder was performed at 0°C without the further dissolution. The reaction condition for the nitration is summarized in Table I.

Carbon, hydrogen, and nitrogen contents of each sample are listed in Table II. DS was calcu-

Table II   Elemental Analysis of PBI and NO$_2$-PBIs

| Sample	C (%)	H (%)	N (%)	S (%)	N/C	S/C
PBI	72.06	4.66	16.50	—	0.2389	—
1	49.93	3.67	16.22	—	0.3249	—
2	50.86	3.81	16.83	—	0.3309	—
3	44.72	3.66	15.17	—	0.3392	—
4	44.72	3.64	15.25	—	0.3401	—
5	53.24	3.48	18.69	1.08	0.3511	0.0203
6	50.27	3.45	17.61	2.14	0.3503	0.0426
7	44.81	3.18	15.70	4.76	0.3505	0.1062
8	59.64	4.81	15.12	2.67	0.2536	0.0448
9	60.01	4.83	15.95	2.88	0.2657	0.0480
10	58.59	4.31	17.83	1.55	0.3043	0.0265
11	55.83	3.78	19.36	0.32	0.3467	0.0057
12	55.62	3.69	19.36	0.36	0.3480	0.0065
13	55.78	3.70	19.45	0.18	0.3488	0.0032
14	53.59	3.61	18.02	0.62	0.3363	0.0015
15	53.10	3.59	18.22	0.44	0.3431	0.0083
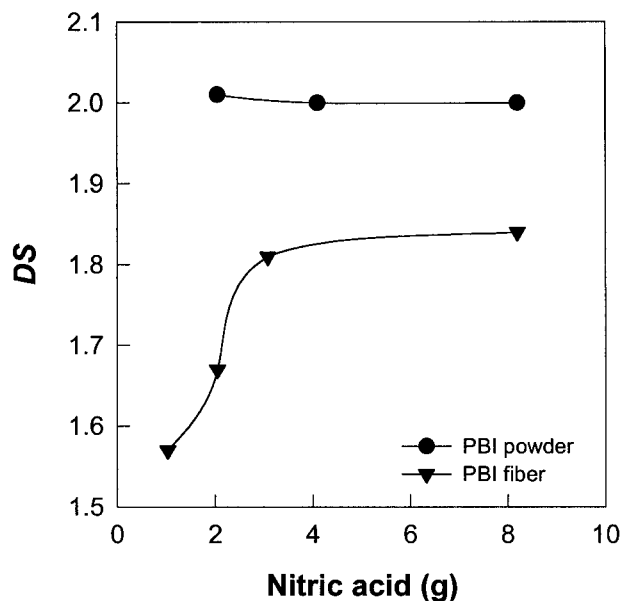
Figure 1 Degree of substitution of NO$_2$-PBI with the amount of nitric acid. Reaction condition: 1st, 0°C for 1 h; 2nd, 30°C for 2 h.

lated from N/C (%) value obtained from elemental analysis. If one nitro group is substituted by repeat unit, N/C (%) is 29.18. If two, N/C (%) becomes 35.01. In most sample cases, N/C (%) varied from 31 to 34, indicating that one or two nitro substituents attached in one polymeric repeat unit. Figure 1 shows the DS of NO$_2$-PBI prepared through further dissolution procedure at 30°C for 2 h. The NO$_2$-PBI produced from PBI powder has higher DS than that from PBI fiber. This is mainly because the nitration of PBI powder was homogeneous that the substitution of nitro groups was more favored. In the case of the NO$_2$-PBI produced from PBI powder, the DS did not increase over 2 despite a large amount of added nitric acid. It might be considered that the number of the attachable site of the nitro groups in the repeating unit of PBI is limited to 2 when the reaction temperature is lower than 30°C.

The viscosity of the NO$_2$-PBI produced from PBI fiber is lower than that of the original PBI fiber because of two possibilities. One is that the insoluble residue containing higher molecular weight polymer was filtered off after nitration and the other is that chain-scission may occur during nitration. The viscosity of the NO$_2$-PBI produced from PBI fiber was increased as the amount of nitric acid added was increased as shown in Figure 2. Such a trend can be explained by the fact that the high molecular weight polymer in the insoluble residue dissolved as nitric acid was added due to increased solvation power although chain-scission might occur. On the contrary, in the case of the NO$_2$-PBI produced from PBI powder, there was no insoluble residue in the reaction and the acid-induced degradation occurred dominantly as the amount of nitric acid increased. Thus, the molecular weight of the NO$_2$-PBI produced from PBI powder decreased with increasing amount of nitric acid.

From the results in Figures 1 and 2, the DS of the NO$_2$-PBI from PBI powder reached the maximum value of 2 when a small quantity of nitric acid was added whereas its viscosity dropped with increasing amount of nitric acid added. Moreover, PBI powder dissolved clearly in sulfuric acid without insoluble residue. Therefore, it is clear that the preparation of the NO$_2$-PBI from PBI powder does not require the addition of large amount of nitric acid for the sufficient substitution and the subsequent procedure of increasing reaction temperature for further dissolution. The next discussion involves the NO$_2$-PBI prepared from PBI powder at 0°C for 1 h without further reaction at 30°C. The amount of nitric acid added was controlled from 0.1 g (sample 8) to 4.1 g (sample 13). Figure 3 shows the change of viscosity and DS with the amount of nitric acid added. The viscosity of NO$_2$-PBI was decreasing as increasing amount of nitric acid was added. In con-
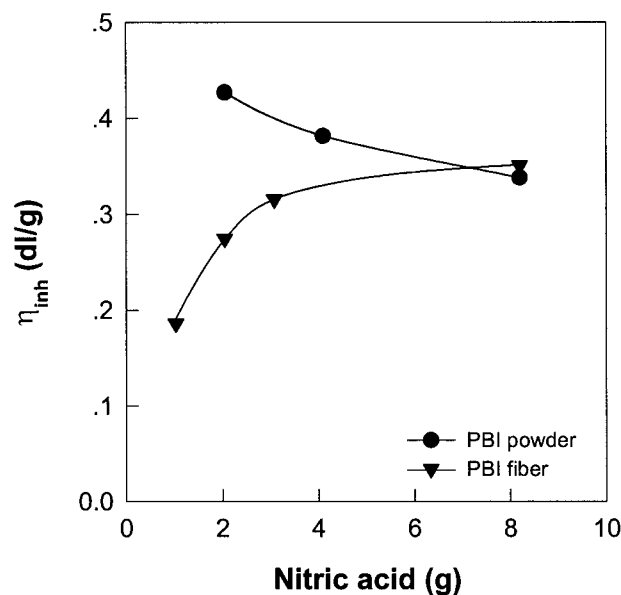
Figure 2 Inherent viscosity of NO$_2$-PBI with amount of nitric acid. Reaction condition: 1st, 0°C for 1 h; 2nd, 30°C for 2 h.
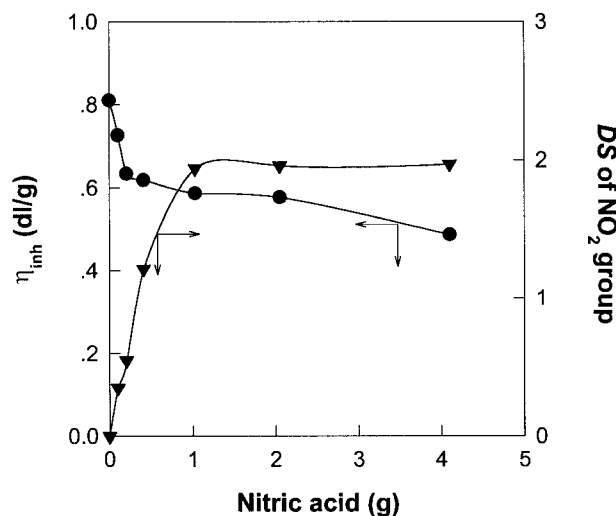
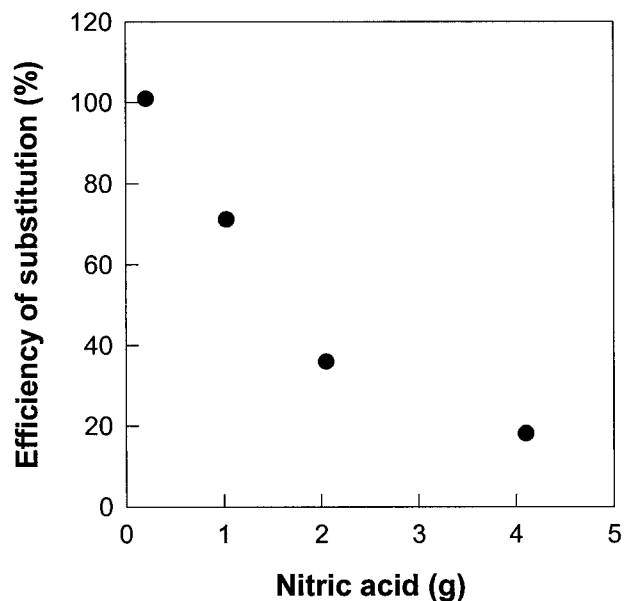**Figure 3** Degree of substitution of nitro group and inherent viscosity of NO_2-PBI prepared at 0°C for 1 h with the amount of nitric acid needed.

Figure 4 Change in the substitution efficiency with the amount of nitric acid needed.

trast, the DS increased up to 2. Further increase of the DS over 2 was not found as increasing amount of nitric acid was added. If nitric acid is consumed only to substitution reaction and 1 nitro group is substituted to PBI repeating unit, 0.34 g of nitric acid is needed in our experiment. Thus, extra amount of nitric acid over 0.68 g participates no more in substitution reaction, theoretically. However, the role of nitric acid is considered as substitution and chain-scission and so, an amount of nitric acid higher than 0.68 g may be needed to achieve the maximum DS, 2. From Figure 3, 1.0 g of nitric acid was sufficient to reach the DS of 2 in this experiment.

For the detailed examination of the role of nitric acid, the substitution efficiency of nitric acid was obtained from the following equation:

$$\text{Efficiency of substitution } (\%) = \frac{M_s}{M_o} \times 100$$

where M_s is the molar quantity of nitric acid participating in the substitution, which was calculated from DS and M_o is the number of moles of nitric acid added. The nitric acid in which the amount was less than 0.4 g was consumed mostly in substitution reaction and its substitution efficiency was about 100%, as shown in Figure 4. In this case, the degradation of polymer by nitric acid was limited to a low level. However, as the amount of nitric acid was increased, the substitu-
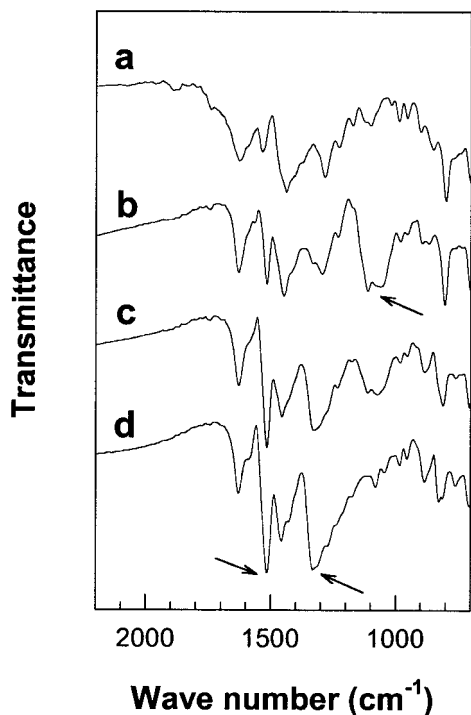
tion efficiency significantly fell off to 20%, indicating that extra amount of nitric acid which did not take part in the substitution reaction increased, resulting in the severe degradation. In nitration process, sulfuric acid is used as a solvent and a catalyst. However, excess amount of sulfuric acid gave rise to the chemical degradation, which is revealed in Figure 5. The viscosity of NO_2-PBI
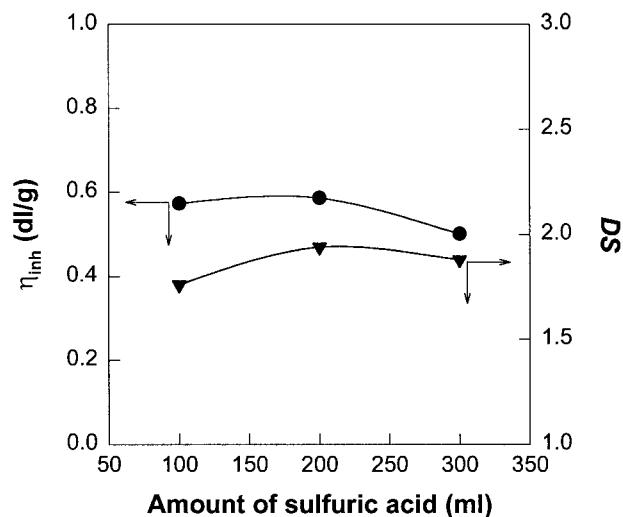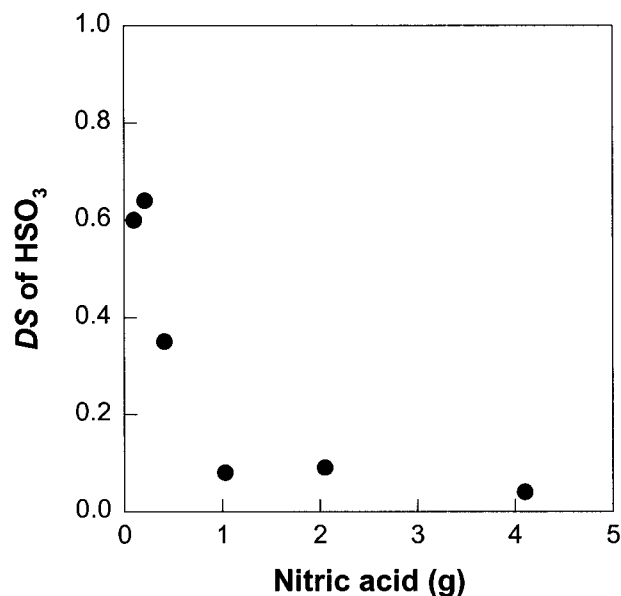

Figure 5 Effect of the amount of sulfuric acid on degree of substitution and inherent viscosity of NO_2-PBI prepared at 0°C for 1 h.

began to decrease as the amount of sulfuric acid increased over 200 mL. The DS increased slightly as the amount of sulfuric acid increased.

Figure 6 illustrates the IR spectra of the PBI powder and the NO_2-PBIs prepared from the PBI powder. The peaks at about 1627 and 1530 cm^{-1} are assigned to the C=N stretching and the N—H bending of the secondary amine, respectively.[10] PBI typically displays a sharp band near 1454 cm^{-1} which is the characteristics of the heterocyclic imidazole ring.[11] New sharp peaks at 1517 and 1332 cm^{-1} indicate the presence of nitrobenzene.[12] The intensities of these peaks of sample 13 were much stronger than those of sample 8 because of the higher DS. Compared with the PBI fiber, the PBI powder used in this study is not acid-treated for the stabilization so that the peak of aryl sulfonic acid does not exit. It is quite noteworthy that the strong absorption at 1100 cm^{-1}, which is consistent with the presence of aryl sulfonic acid group, appears in the spectra of samples 8 and 10. This peak disappeared in the spectrum of sample 13. In nitration reaction, the mixture of nitric acid, and the concentrated sulfuric acid generates the nitronium ion, NO_2^+, and this


Figure 7 Degree of substitution of sulfonic acid group of NO_2-PBI prepared at 0°C for 1 h.

is the active electrophilic species. Its formation results from protonation of nitric acid by sulfuric acid acting as a proton donor. When the small quantity of nitric acid is added, it is all consumed to the substitution reaction. After the substitution, the unsubstituted phenylene ring may be acid-treated freely by H^+ and HSO_4^-. On the other hand, when a large amount of nitric acid is added, the phenylene rings in PBI are substituted fully by nitro groups, so that there is no room for the substitution of sulfonic acid groups. Moreover, an extra amount of nitric acid which is not involved in the substitution reaction reacts first with sulfuric acid to make $_2^+$ and H_2O to hinder the reaction of PBI with sulfuric acid. For this reason, NO_2-PBI with higher DS exhibits no aryl sulfonic acid peak in the IR spectrum. The DS of sulfonic acid group, which was calculated from the S/C value in the elemental analysis (Table II), supports the above discussion clearly. The DS of sulfonic acid group decreased as the amount of nitric acid increased as shown in Figure 7. Almost no substitution of the sulfonic acid group occurred when an excess amount of nitric acid over 1 g was added.

In Figure 8, the dependence of the solubility of the NO_2-PBI on the DS is presented. On the whole, the solubility was improved outstandingly as the DS was increased over 1. In contrast, the solubility of the NO_2-PBI having the DS lower

Figure 6 IR spectra of PBI and NO_2-PBIs prepared at 0°C for 1 h. The amount of nitric acid added: control (a), 0.10 g (b), 0.41 g (c), and 4.1 g (d).

than 0.5 was not better than that of the PBI itself even at higher temperature, i.e., 80°C. At room temperature, the NO_2-PBI with the DS around 2 was completely soluble in DMAc and considerably in NMP but almost insoluble in DMF and DMSO. The dominant enhancement of solubility of the NO_2-PBI was found when the 0.41 g of nitric acid was added, which may arise from the fact that the solubility in DMSO increases in condition that both the nitro group and sulfonic acid group is substituted in PBI. At 80°C, NO_2-PBIs having DS over 1 were completely soluble in the solvents. The limited solubility of PBI is attributed to the interchain hydrogen bonding as well as the polarity of the imidazole ring as illustrated in Figure 9. The work done by Hu et al.[8] includes the substitution of N—H hydrogen by a methyl group to reduce the hydrogen bonding and to increase the basicity of the imidazole ring. The ability to dissolve PBI depends on the replacement of the interaction in the polymer by equally strong or stronger solvent–chain interactions. However, the hydrogen bonding ability between DMAc and PBI is not stronger than that of PBI molecules themselves. It is important that the chain–chain interaction should be hindered for the solvation of PBI. The nitro groups substituted to the phenylene ring in PBI have strong repulsive force that the PBI chains are hard to associate with
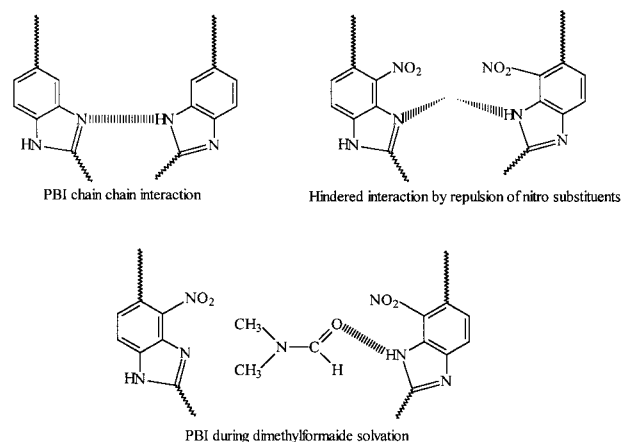

Figure 9 Chain–chain interaction and solvation of PBI in DMAc.

themselves. Consequently, the DS of the nitro group is the major factor governing the solubility of the NO_2-PBI.

CONCLUSIONS

The NO_2-PBI prepared from the PBI powder through the homogeneous reaction showed higher DS than that prepared from the PBI fiber through the heterogeneous reaction. The viscosity of the NO_2-PBI prepared from the PBI powder decreased with amount of nitric acid added in contrast with that prepared from the PBI fiber. The nitration of the PBI powder was well accomplished at 0°C for 1 h. The DS of the NO_2-PBI reached the maximum value of 2. When a small quantity of nitric acid was added, it was consumed mostly to the substitution reaction, whereas when a relatively large amount of nitric acid was added, the efficiency of the substitution was lowered and the chemical degradation occurred seriously. The nitration of PBI was accompanied by the substitution of the sulfonic acid group when the small quantity of nitric acid was added. In contrast, PBI was not acid treated when a relatively large amount of nitric acid was added. The solubility of PBI was improved significantly when the DS of nitro group was over 1. It was concluded that this nitration method is an effective tool for preparing organo-soluble PBI with high DS to a high yield. In the near future, we will report on the spinning of the NO_2-PBI and the solution blend with other high performance polymers.[13,14]
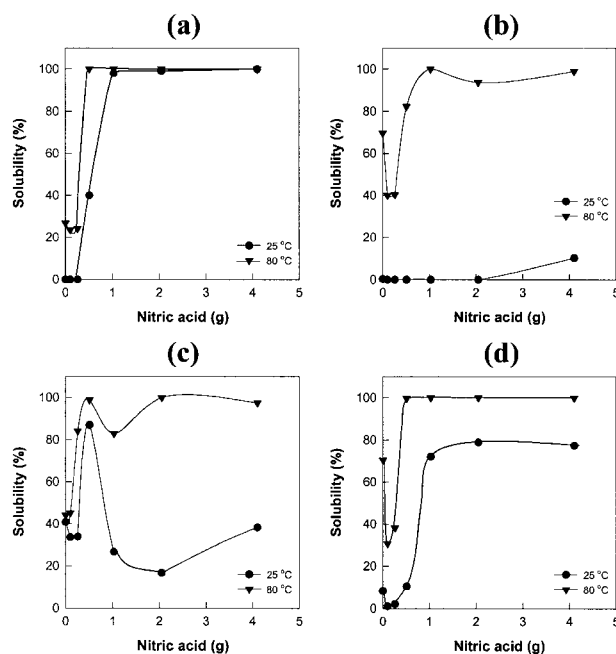
Figure 8 Degree of NO_2-PBI at 25 and 80 °C in DMAc (a), DMF (b), DMSO (c), and NMP (d) with the amount of nitric acid added.

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