

Interactions of Organic Solvents with Aromatic Heterocyclic Polymers. I. *m*-Phenylene Polybenzimidazole

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Synopsis

A new method of interpreting gas-chromatographic (GC) data for determining solvents for thermally stable polymers has been developed. An equation is derived for molar Gibbs energy of sorption in terms of chromatographically measured parameters. The polymer used in this study is poly(5,5'-bibenzimidazole-2,2'-diyl-1,3-phenylene), or PBI. A battery of 40 compounds, including solvents and nonsolvents for PBI, was studied. This method involves determining molar heats of sorption and molar Gibbs energies of sorption at infinitely dilute surface coverage. Mathematical correlations between the measured thermodynamic quantities and the solvent polarizabilities and dipole moments were developed. From these correlations it was possible to explain the behavior of known solvents of PBI and predict new solvents for this polymer. The results of the interpretation of GC data were supported by quantitative solubility experiments.

INTRODUCTION

The gas chromatograph (GC) technique has become an important tool in the study of solvent-polymer interactions after the pioneering work of Smidsrød and Guillet.¹ Most of the studies reported were done above the glass transition temperature (T_g) of the polymers,^{2,3} because the slow diffusion of vapors in the glassy polymers impedes the establishment of equilibrium. Courval and Gray⁴ have suggested that the attainment of equilibrium in GC depends upon a kinetic parameter involving the thickness of the polymer layer, the carrier gas flow rate, and the diffusivity of the vapor in the polymer. This idea has been tested by Berens,⁵ who has studied solvents solubility in glassy poly(vinyl chloride).

In previous publications⁶⁻¹⁰ a new method of interpreting gas-chromatographic data in order to find suitable solvents for thermoplastic polymers was described. The method was successful in identifying solvents for this class of polymers, and it agreed well with thermodynamic arguments based on well-defined solubility criteria, such as weight fraction activity coefficient and the Flory-Huggins interaction parameter.

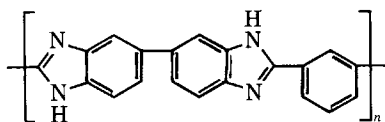
This article is the first of two investigating the solubility of aromatic heterocyclic polymers in organic solvents. Here, we test the method referred to earlier with a thermally stable polymer whose solvents previously were known. In the second article we apply the proven method to a polymer with no previously known organic solvents. In this work we use interpretations based on sorption theory and discuss solvent vapor sorption on the polymer at zero coverage.

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The utility of thermally stable aromatic heterocyclic polymers, such as poly(5,5'-bibenzimidazole-2,2'-diyl-1,3-phenylene), or PBI, has been limited because of their high glass transition temperatures and insolubility in most common organic solvents.^{11,12} In order to achieve solubility, many workers have resorted to structural changes by introducing pendent aromatic groups on the polymer backbone.¹³⁻¹⁵ Owing to the solubility of PBI in *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO), these solvents have been chosen in addition to a large battery of organic compounds to test the applicability of our new gas-chromatographic approach to the solubility study of this class of polymers. We chose GC as an experimental tool because a large number of potential solvents can be screened within a very short time and because the procedure is nondestructive and can be used with small amounts of polymers. The chemical structure of PBI is given below:



poly(5,5'-bibenzimidazole-2,2'-diyl-1,3-phenylene), PBI

THEORY

The retention volumes (V_g^0) of the solvents on PBI were calculated from retention times and other experimental data by a method previously described.⁶ Heats of sorption (ΔH_s) of solvent vapors on the polymer were calculated from V_g^0 values by the following relationship^{16,17}:

$$\frac{d(\ln V_g^0)}{d(1/T)} = \frac{-\Delta H_s}{R} \quad (1)$$

Below we describe a relation between molar Gibbs energy of sorption and specific volume.

Derivation of Molar Gibbs Energy of Sorption¹⁸

The specific retention volume corrected to 0°C is given by¹⁹

$$\begin{aligned} V_g^0 &= \frac{T_0 \text{ g solvent/g polymer}}{T \text{ g solvent/ml gas at } T} \\ &= \frac{T_0 \text{ g solvent}/(\text{g solvent} + \text{g polymer})}{T \text{ (g solvent)/ml gas at } T} \end{aligned}$$

Assuming very little solvent is present compared to polymer,

$$V_g^0 = \frac{T_0 w_1 RT}{T P_1 M_1} \quad (2)$$

$$= T_0 \frac{w_1 R}{P_1 M_1} \quad (3)$$

where w_1 is the weight fraction of solvent in polymer phase, P_1 is the partial

pressure of solvent, M_1 is the molecular weight of solvent, y_1 is the mole fraction of solvent in gas phase, P is the total pressure, R is the gas constant, and T_0 is the reference temperature, 273.15 K.

The change in chemical potential of a solvent from a temperature T and pressure P to the standard state in the polymer phase is given by

$$\mu_1^g - \mu_1^{0s} = RT \ln \left(\frac{f_1}{f_1^{0s}} \right) = RT \ln a_1^s \quad (4)$$

The change in chemical potential of a solvent from a temperature T and pressure P to the standard state in the gas phase is given by

$$\mu_1^g - \mu_1^{0g} = RT \ln \left(\frac{f_1^g}{f_1^{0g}} \right) = RT \ln a_1^g \quad (5)$$

At equilibrium, the chemical potentials of a solvent in the gas phase and in the polymer phase are equal. Hence, from eqs. (4) and (5) we obtain

$$\mu_1^{0s} - \mu_1^{0g} = RT \ln a_1^g - RT \ln a_1^s \quad (6)$$

But $-\Delta G_s = \mu_1^{0g} - \mu_1^{0s}$, so

$$-\Delta G_s = RT \ln \left(\frac{a_1^s}{a_1^g} \right) \quad (7)$$

where μ is the chemical potential, f is the fugacity, a is the activity, and ΔG_s is the molar Gibbs energy of sorption. Subscript 1 stands for solvent; superscripts s and g stand for polymer phase and gas phase, respectively.

We define activity coefficient in the polymer phase as

$$\Omega_1^s = \frac{f_1^s}{f_1^{0s}} \left(\frac{1}{w_1} \right) = \frac{a_1^s}{w_1} \quad (8)$$

We define standard state for the solvent in the gas phase as pure solvent at 1 atm and the temperature of interest, and in the polymer phase the solvent follows Henry's law. The standard state in the polymer phase is hypothetical for solvents which do not form solutions. To compare the thermodynamic interactions of solvents which do form solutions with solvents which do not form solutions, a common standard state was chosen. The choice of standard state eliminated the need to account for polymer specific surface area, which is difficult to estimate.

Now, if we define the Henry's law constant as

$$H_{1,2} = \lim_{w_1 \rightarrow 0} \frac{f_1^s}{w_1} \quad (9)$$

Then,

$$a_1^s = \frac{f_1^s}{f_1^{0s}} = \frac{f_1^s}{H_{1,2}} = w_1 \quad (10)$$

The gas phase activity becomes

$$a_1^g = \frac{f_1^g}{f_1^{0g}} = \frac{P_1}{P_1^0} = \frac{P_1}{1 \text{ atm}} \quad (11)$$

We approximate fugacity by partial pressure in eq. (11) because the gas phase

is at low pressure and high temperature. Inserting eqs. (10) and (11) into eq. (7), we get

$$-\Delta G_s = RT \ln \left(\frac{w_1}{P_1/1 \text{ atm}} \right) \quad (12)$$

Substituting for (P_1/w_1) from eq. (3), we get

$$-\Delta G_s = RT \ln \left(\frac{M_1 V_g^0}{T_0 R/1 \text{ atm}} \right) \quad (13)$$

In order to justify the use of eqs. (1) and (13) for the estimation of ΔH_s and ΔG_s , infinite dilution retention values were obtained by extrapolating retention times to zero peak height.^{4,6} Plots of $\ln V_g^0$ vs. $1/T$ were approximately linear, so that eq. (1) could be applied quite reliably to determine ΔH_s .

EXPERIMENTAL

Apparatus, injection technique, and experimental procedure are described in a previous publication.⁶

PBI was coated on Fluoropak 80 from solution in DMF. A ratio of 5% w/w of polymer to Fluoropak 80 was prepared. The surface area of Fluoropak 80 used in this work is 1.3 m²/g. The coated Fluoropak was loaded into a 5-ft-long, 1/8-in.-outer diam stainless steel column. The column was preconditioned at 250°C with dry helium gas flow. The retention times of the solvents were extrapolated to zero sample size (or peak height) in all cases. This procedure allowed calculation of the heat of sorption in the linear portion of the isotherm.⁴ In order to obtain equilibrium thermodynamic data, the dependence of V_g^0 on the flow rate was investigated in a manner described earlier.⁶ Low flow rates within the range of 1 to 3 ml/min were used.

A maximum error of 5% was obtained in measuring V_g^0 . Such error reflects precision better than $\pm 5\%$ for ΔG_s and $\pm 10\%$ for ΔH_s .

RESULTS AND DISCUSSION

Heats and molar Gibbs energies of sorption for a variety of organic compounds (solvents) on PBI were calculated from retention data, and they are tabulated in Table I, together with solvent polarizabilities (α_1) and dipole moments (μ_1). We correlate ΔH_s and ΔG_s with solvent polarizabilities and dipole moments in an analogous manner to that done by us previously.

ΔH_s and ΔG_s were separately plotted against solvent polarizabilities, as in Figures 1 and 2. Lines that pass through the origin for the *n*-alkanes were established. These lines will be referred to as "reference lines," and they are represented mathematically by the following equations:

From Figure 1,

$$-\Delta H_s = 3.57\alpha \quad (14)$$

and from Figure 2,

$$-\Delta G_s = 1.04\alpha + b \quad (15)$$

where *b* is the intercept of the "reference line."

TABLE I
 Compounds Tested and their Thermodynamic and Physical Parameters

Code no.	Solvent	$-\Delta H_s$, kJ/mole	ΔG_s , kJ/mole (462.9 K)	Polarizability $\alpha \times 10^{24}/\text{cm}^3$	Dipole moment $\mu \times 10^{30}/\text{C m}$
1	<i>n</i> -Heptane	47.51	25.96	13.71	0
2	<i>n</i> -Octane	55.64	23.77	15.54	0
3	<i>n</i> -Nonane	64.17	22.21	17.42	0
4	<i>n</i> -Decane	70.01	19.79	19.30	0
5	<i>n</i> -Dodecane	82.21	16.15	23.00	0
6	<i>n</i> -Butyl bromide	60.11	—	—	—
7	Ethyl acetate	67.07	20.10	8.33	5.93
8	<i>n</i> -Propyl acetate	—	19.07	10.67	6.00
9	<i>n</i> -Butyl acetate	—	18.92	—	—
10	Acetaldehyde	64.42	15.19	4.49	9.07
11	<i>n</i> -Butyraldehyde	58.70	13.95	—	—
12	Acetone	73.63	12.57	6.43	9.30
13	Methyl ethyl ketone	63.95	12.57	8.24	—
14	Allyl alcohol	96.63	6.64	6.75	5.33
15	<i>n</i> -Propyl alcohol	93.33	—	6.90	5.64
16	<i>n</i> -Butyl alcohol	79.70	11.41	8.76	5.57
17	<i>n</i> -Pentyl alcohol	74.33	11.43	10.64	—
18	Ethyl alcohol	94.05	9.89	—	—
19	Nitromethane	80.20	8.01	4.95	11.93
20	Nitroethane	74.70	6.76	6.74	11.81
21	Nitropropane	78.25	7.87	8.48	12.01
22	Acrylonitrile	80.57	9.10	6.19	12.77
23	Methyl cyanide	71.89	9.90	4.40	13.21
24	Ethyl cyanide	77.65	9.31	—	—
25	1-Octene	—	25.09	15.36	1.13
26	Ethylenediamine	—	7.29	7.21	6.64
27	Diethylamine	44.06	16.96	9.62	3.07
28	Formamide	69.63	8.60	4.10	3.20
29	Dimethylformamide	—	N.P. ^a	7.84	11.34
30	Dimethylacetamide	—	N.P.	9.70	12.70
31	Tetramethylurea	93.66	4.68	13.04	13.06
32	1,2-Propanediamine	60.64	6.39	9.46	—
33	Di- <i>n</i> -propyl ether	—	24.66	12.57	3.43
34	Dimethyl sulfoxide	—	N.P.	9.61	13.20
35	Acetic anhydride	—	N.P.	8.81	9.34
36	Propionic anhydride	—	N.P.	12.50	—
37	<i>N</i> -Acetyethanolamine	—	5.73	10.22	14.17
38	<i>N</i> -Ethylacetamide	—	5.87	9.68	13.00
39	Formic acid	62.07	9.06	3.28	5.07
40	Acetic acid	67.93	7.41	5.12	5.80

^a N.P. = No peak or very broad peak.

The vertical difference from a polar solvent point to the relevant reference line is the contribution to ΔH_s and ΔG_s from polar and hydrogen bonding interactions. These differences, which are represented by ΔH_{ad} and ΔG_{ad} , were plotted against the dipole moments of the solvents. Linear relationships were observed in both cases (Figs. 3 and 4). The lines were fitted to the points for solvents exhibiting only dipole-dipole interactions. The least mean-squares method employed for these fits yielded very small and insignificant values for

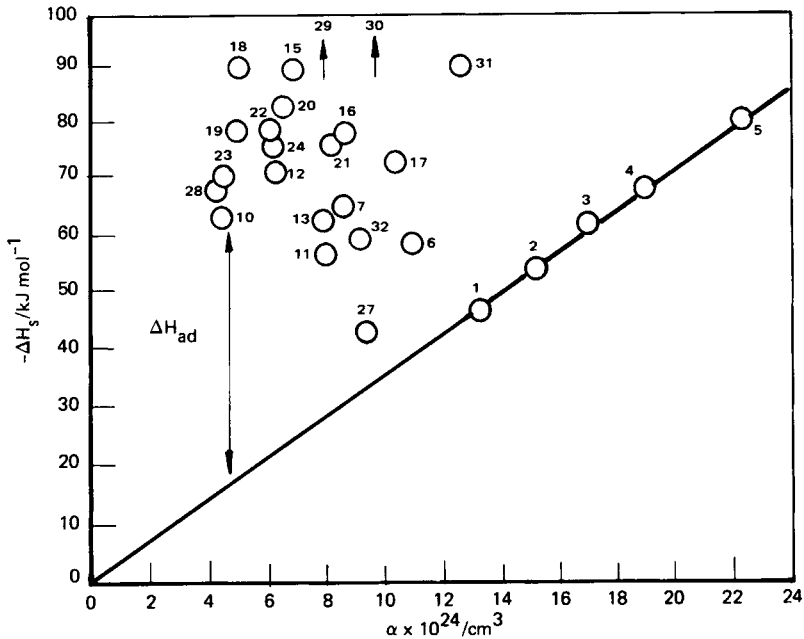


Fig. 1. Heat of sorption vs. polarizability of solvent.

the intercepts, which were ignored. These lines are represented mathematically by the following equations:

From Figure 3,

$$-\Delta H_{ad} = 4.23\mu \quad (16)$$

and from Figure 4,

$$-\Delta G_{ad} = 1.97\mu \quad (17)$$

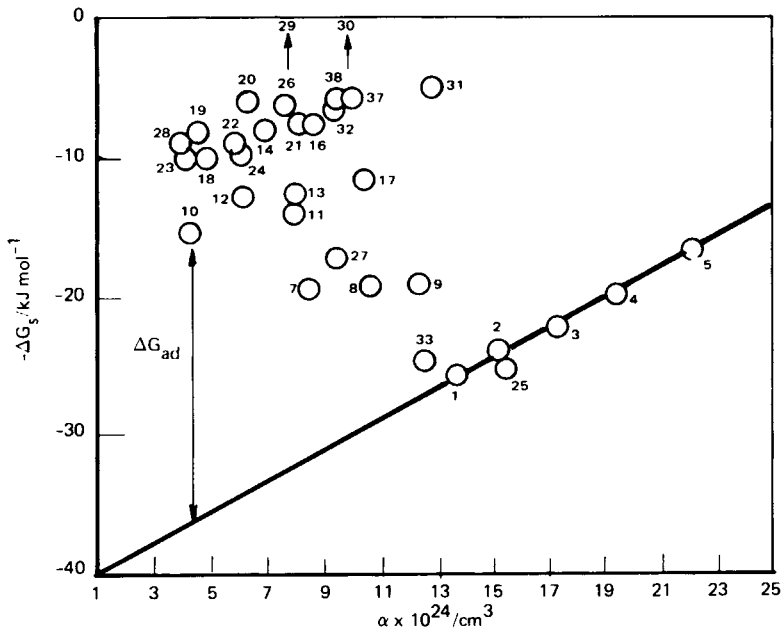


Fig. 2. Gibbs energy of sorption vs. polarizability of solvent.

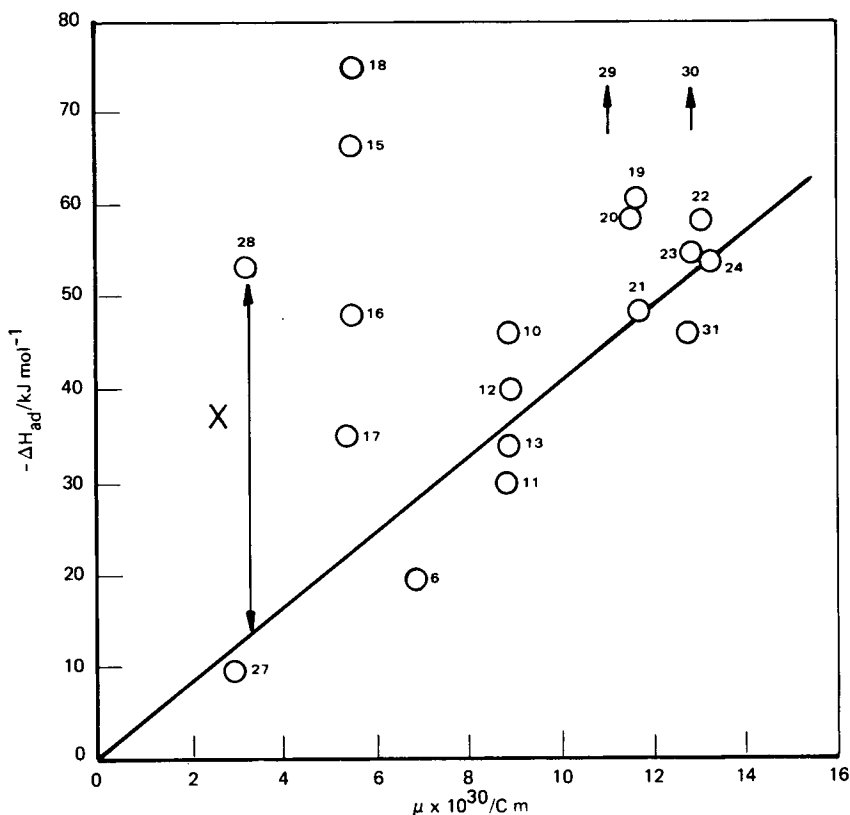


Fig. 3. ΔH_{ad} vs. dipole moment of solvent.

Using eqs. (14)–(17), ΔH_s and ΔG_s can be estimated mathematically from solvent parameters by the following semiempirical equations:

$$-\Delta H_s = 3.57\alpha + 4.23\mu \quad (18)$$

and

$$-\Delta G_s = 1.04\alpha + 1.97\mu + b \quad (19)$$

However, from Figures 3 and 4 it can clearly be observed that the points for solvents with hydrogen bond-forming tendency fall above the lines represented by eqs. (18) and (19). The vertical distances from these points to the point of their intersection with the line are measures of specific interactions. Therefore, for solvents with specific interactions,

$$-\Delta H_s = 3.57\alpha + 4.23\mu + X \quad (20)$$

and

$$-\Delta G_s = 1.04\alpha + 1.97\mu + X' + b \quad (21)$$

The terms X and X' represent the magnitudes of specific interaction contributions to ΔH_s and ΔG_s , respectively.

The magnitude of the specific interaction can be estimated either graphically from Figures 3 and 4 or mathematically from the difference between the exper-

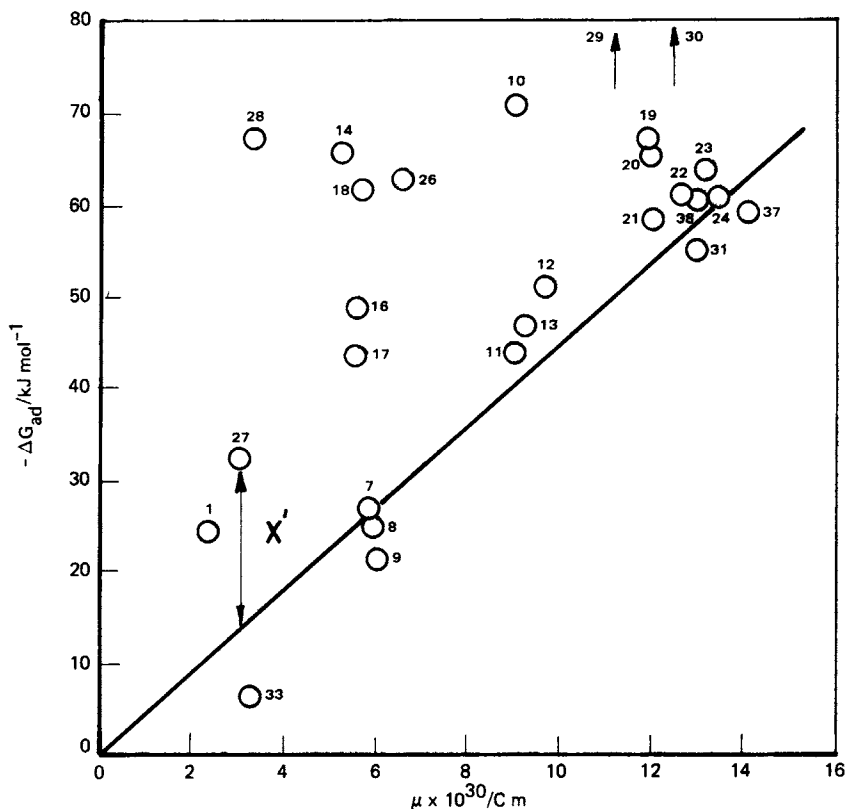


Fig. 4. ΔG_{ad} vs. dipole moment of solvent.

imental ΔH_s and ΔG_s values and those estimated from eqs. (18) and (19), respectively. When comparing the graphic and the mathematical interpretation of ΔH_s and ΔG_s , no significant change in the analysis of the interaction trends between the solvents and the polymer was observed. We therefore favor use of ΔG_s over ΔH_s for the reason that it can be estimated from a single temperature measurement of the retention volume [see eq. (13)].

Solvents with the tendency of forming hydrogen bonds with the polymers showed strong dependence of retention time on sample size. The retention time at zero sample size was calculated by extrapolating the linear plots of sample size against retention time of the solvent.

At 462.9 K, DMAc, DMF, DMSO, formamide, *N*-ethylacetamide, acetic anhydride, and propionic anhydride had relatively long holdup times in the column, and their peaks were broad and diffuse and were difficult to distinguish from a slight drift of the recorder baseline. Therefore, the retention times for these solvents were not measured owing to the great uncertainty in the peak profile. At higher column temperature the peaks of the above solvents were still diffuse but to a lesser extent. This behavior suggests that absorption (rather than adsorption) of the solvents into the coated polymer film is most probable. DMF and DMAc are known solvents for PBI and possess low ΔG_s values. Therefore, their points fall well above the reference line in Figure 4. However, their ΔG_s values were not measured owing to the uncertainty in their retention values caused by the highly diffuse peaks.

Similar situations to those of DMF and DMAc were encountered with DMSO, acetic anhydride, and propionic anhydride. It is anticipated that these compounds would have values of ΔG_s similar in magnitude to those of DMF and DMAc. The low ΔG_s values suggest that these compounds might be good solvents for PBI. ΔH_s for DMF, DMAc, DMSO, acetic anhydride, propionic anhydride, and some amines were not calculated because of the experimental difficulties mentioned above, but the results of the retention times indicate very large values of ΔH_s for these compounds. In terms of eqs. (20) and (21), these compounds possess large values of X and X' (see Figs. 3 and 4). Other compounds with large X and X' values such as formamide, acids, and alcohols demonstrated limited or no ability to dissolve PBI. In some cases, this is probably due to the replacement of interchain interactions in the polymer by equally strong or stronger chain-solvent-chain interactions and in other cases may be due to either weak specific interaction with the polymer or steric effects. A good example of the former type of interaction and that which results in dissolution is the interaction between the nonsolvent formamide and PBI and the solvent dimethylformamide and PBI. In the case of formamide, a bridgelike formation due to chain-solvent-chain bonding could result in limited swelling but a hindered dissolution of the polymer. However, with dimethylformamide such bridge formation cannot exist because of the lack of sufficient hydrogen bonding sites on this solvent. This argument is demonstrated schematically and in a simplified manner in Figure 5.

Alcohols and organic acids are not commonly known solvents for PBI; however, they give large values of X and X' , indicating their potential as solvents for the polymer. Owing to their potential as commercially attractive solvents, experiments were conducted to examine the solubility of PBI in them.²⁰ These experiments involved placing the polymer in a known volume of solvent for 12 hr at 90°C. Constant volume was always maintained during the experiment by regular additions of liquid. After 12 hr, the solution was filtered, and the weight of residual polymer was measured. The percentage weight loss of polymer was calculated, and it will be used here as a quantitative measure of the effectiveness of the liquids tested in dissolving PBI (see Table II). The data listed in Table II were found to be reproducible to within $\pm 5\%$ by weight. Approximately 18% weight loss of polymer was observed in the case of butyl alcohol. 2-(2-Ethoxyethoxy)ethanol was not chromatogrammed in this study, but its potential solubility to PBI was tested by the above method. About 29% polymer weight loss was observed with this alcohol. Acetic acid was also tested by this method, and approximately 39% polymer weight loss was observed. (This clearly indicates that, of the solvents studied, acetic acid is a better solvent for PBI than other compounds with large values of X and X' (with the exception of DMAc and DMF).

CONCLUSIONS

It has been demonstrated in this work that the approach developed by us⁶⁻¹⁰ for predicting solvents for molten polymers can be extended, with some modifications, to estimate solvents and determine strength of interaction between aromatic heterocyclic polymers and candidate solvents. The application of our approach to this work has helped us to isolate and select several solvents from

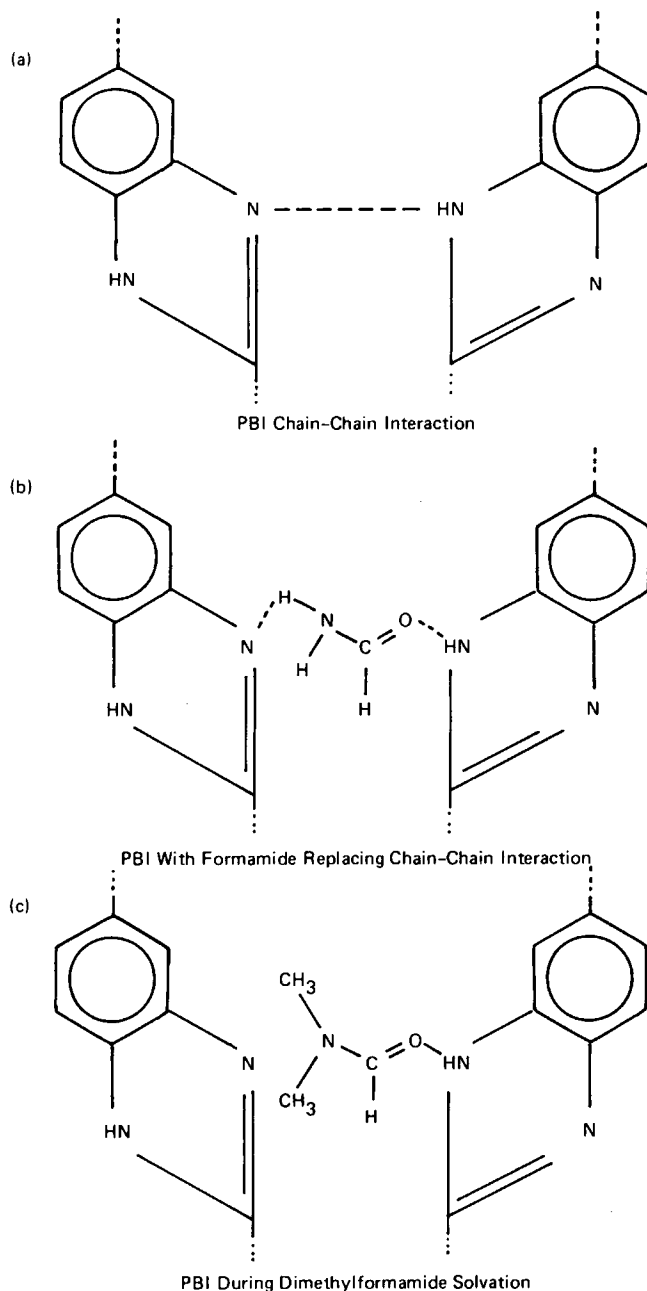


Fig. 5. Chain-chain and chain-solvent interaction for PBI.

a large battery of unknowns. The main feature of this work lies in determining the magnitude of the specific interaction (X and X') between the solvent molecules and the polymeric surface. Compounds with large X and X' values can be grouped as potentially strong candidates for dissolving the polymer.

Alcohols and organic acids that are not commonly known solvents for PBI were identified as potential solvents by this method. Quantitative evaluations of these

TABLE II
Comparison of Solubilities with X' and X

Compound	Solubility of PBI, wt %	X , kJ/mole	X' , kJ/mole
Butyl alcohol	18.3	26.0	9.6
2-(2-Ethoxyethoxy)ethanol	28.7	—	—
Acetic acid	38.5	26.5	28.8
Dimethylformamide	∞	∞	∞
Dimethylacetamide	∞	∞	∞

compounds as solvents for PBI has confirmed the reliability of the solvent prediction approach described in this work.

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