Polybenzimidazole (PBI) Molecular Weight and Mark-Houwink Equation

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ABSTRACT: The molecular weight, and intrinsic viscosity of polybenzimidazole (PBI) and its phosphonylated derivatives are reported. The relationship between intrinsic viscosity $[\eta]$ and weight average molecular weight (M_w) for PBI has been established in H_2SO_4 and DMF-LiCl. The Mark Houwink constants K_w of 5.2×10^{-3} mL/g, α of 0.92 for H_2SO_4 solvent systems and, K_w of 3.2×10^{-2} mL/g, α of 0.754 for DMF-LiCl solvent system have been determined at $M_w < 65{,}000$. The intrinsic viscosity of PBI determined by the Huggins–Kraemer method was compared with a single point method, and found that both methods fit well for PBI in relatively low concentration solvent system, giving $\sim 99\%$ accuracy. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3436–3441, 2009

Key words: polybenzimidazole; molecular weight; intrinsic viscosity

INTRODUCTION

Polybenzimidazoles (PBI) are a class of polymeric materials possessing very high thermal stability, mechanical strength and chemical stability.[1–3] Poly(2,2′-*m*-phenylene-5,5′-bibenzimidazole) (PBI Scheme 1a), has been commercialized for use in applications such as heat-resistant fibers, and coating varnishes and other processes. PBI can also be functionalized to carry acidic functional groups (such as phosphonic acid and ester, Scheme 1b) forming thermally and chemically stable polyionomers for use as ion-exchange resins. The acid group modified PBIs are of interest for use as ion-exchange and membrane materials for PEM fuel cells operating at high temperature.[4–9]

We have found that the performance of films and membranes, based on PBI, depends largely on the molecular weight of the polymer. Thus, materials that are constructed from low molecular weight PBI are mechanically weak (e.g., exhibit a low tensile strength) and brittle. The increased interest in PBI products necessitates molecular weight characterization of not only the parent grade of the polymer but also the PBI derivatives. The solubility of aromatic PBIs is generally restricted to strong acids and polar aprotic solvents (such as, *N,N*-dimethyl formamide (DMF), *N,N*-dimethyl acetamide (DMAc), *N*-methyl pyrrolidinone (NMP)) preferably in combination with a lithium halide. The restricted solubility of these polymers somewhat complicates the molecular weight characterization techniques (demanding nature of the solvents). The molecular weight characterization of PBI has often been limited to single point inherent viscosity measurements.

In the 1980s, Kojima et al.[10,11] studied dilute solution properties of PBI in *N,N*-dimethyl acetamide by light scattering and intrinsic viscometry, and found that the characteristic parameters depend on molecular weight distribution. Recently, high molecular weight PBI (M_w = 199,200, inherent viscosity of 1.59 dL/g) in DMAc-4%LiCl solution was studied,[12,13] and results show that the polymer behaved like a polyelectrolyte in solution and conformation changes from a random coil, or wormlike chain to an "extended wormlike" at increasing concentrations.

It has to be stressed that any quantitative study that intends to correlate between molecular weight and inherent properties of a polymer should rather be made on species with very narrow molecular weight distribution. This is not an easy task when it comes to deal with PBI, since it is soluble in a very narrow range of solvents. The only way to narrow the molecular weight distribution of the selected specimen is mostly done, in this work, by an extraction procedure that yields a molecular weight distribution of <2. This is adequate for a variety of applications, but some correlation that is needed for processing the polymers is still missing.

The present work investigates the correlation between average weight molecular weight, M_w, and intrinsic viscosities, $[\eta]$, of PBI in concentrated sulfuric acid and DMF (containing 5 wt % lithium chloride). Concentration dependence of the single point methods of measuring $[\eta]$ of PBI is discussed in this

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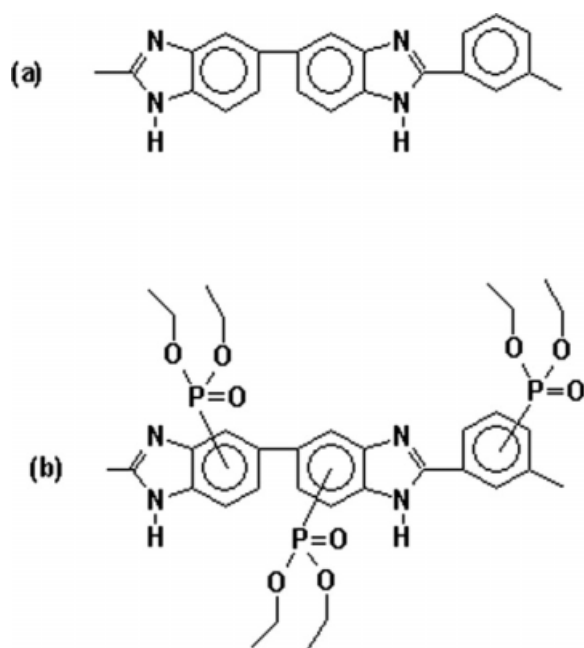
Scheme 1 Poly(2,2′-*m*-phenylene-5,5′-bibenzimidazole) (a) and its phosphonated derivative (b).

article. The impact on molecular weight after exposure the PBI to harsh synthetic condition is of concern. Thus, we selected a specific case of interest, the phosphonylation of PBI (where the polymer in exposed to extreme oxidative environment) to supplement this study. The use of the multi angle laser light scattering (MALLS) to measure the weight average molecular weight (M_w) of PBI combined with viscosity and gel permeation chromatography (GPC) is reported herein.

EXPERIMENTAL

Materials

Two PBI samples were obtained from Celanese, a high molecular weight (1.0 IV, 1099-85 Lott number 90454) and a lower molecular weight sample. *N,N*-dimethyl formamide (Fisher certified A.C.S.), dimethylsulfoxide (Fisher certified A.C.S.), methanol (Mallinckrodt HPLC) and 96% sulfuric acid (J.T. Baker A.C.S. reagent) were used without further purification. Lithium chloride (J.T. Baker A.C.S. Reagent) was dried in an oven at 120°C for 24 h before use, and 3,3′,4,4′, -tetra amino biphenyl) (Aldrich) was converted to freebase and recrystallized from water. Isophthalic acid (Aldrich 99%) was recrystallized from water before use. Diethyl phosphonyl PBI derivatives, PBIP$_{et}$, which are shown in Scheme 1 were synthesized in this laboratory, as described elsewhere.[4,14] In short, 1 : 10 : 10 eq. of PBI(M_w ~ 70,000) diethyl phosphite and benzoyl peroxide

were dissolved in DMAc, the solution was stirred (at 125°C) for 5 h before collecting the product.

Molecular weight determination

Weight average molecular weights of PBI and its derivatives were determined by MALLS measurements by a Wyatt Technology Dawn-DSP instrument, equipped with an Argon ion laser ($\lambda_o = 488$ nm) and an Optilab-DSP differential refractometer. The analyses were performed in batch-mode using calibration (pure toluene) and normalization (pure toluene/PSt 30k Da toluene solution) procedures recommended by the manufactory (Wyatt Technology). The data were analyzed by Zimm formalism and first order fitting. The molecular weight was calculated with ASTRA software (version 4.7). The measurements were performed in macro batch mode in 20 mL scintillation vials. Samples for MALLS measurements were prepared by dissolving PBI in 96% sulfuric acid at concentrations below 5×10^{-4} g/mL. The PBIP samples were characterized in methanol solution. The refractive index increments (dn/dc) were measured by an Optilab DSP. The dn/dc for PBI (in sulfuric acid), PBIP-DS$_{0.3}$ and PBIP-DS$_{3.0}$ (in methanol) at 30°C are 0.114, 0.112, and 0.106, respectively. Data acquisition and evaluation utilized Astra 4.20 and DNDC 5.00 software. MALLS measurements gave an apparent weight-average molar mass (M_w) using a Zimm plot. A typical Zimm plot of PBI polymer in H$_2$SO$_4$ solution is shown in Figure 1.

The intrinsic viscosities of PBI samples were determined in two different solvents, using an Ubbelohde viscometer at 25 ± 0.05°C in a thermostated water bath (Cannon CT-200). Dried samples were dissolved with stirring in 96% sulfuric acid or DMF containing 5 wt % lithium chloride (DMF-LiCl). The solutions were filtered through a 0.2 μm PTFE filter (Millipore) directly into the viscometer. The viscometer was equilibrated for 15 min at each concentration. For each concentration (concentration varied from 0.001 to 0.01 g/mL), the measurements were repeated until
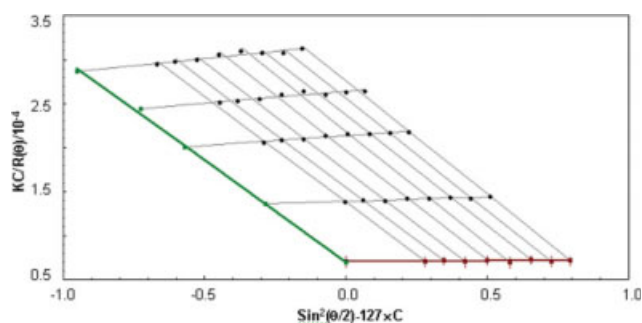

Figure 1 A typical light scattering Zimm plot of PBIP$_{Et}$ in H$_2$SO$_4$ solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the relative error of five successive measurements was less than 0.1% and an average value of flow times was recorded. The specific (η_{sp}) and reduced (η_r) viscosities were calculated at six different concentrations and converted to intrinsic viscosity [η] by extrapolation to infinite dilution using:

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C \tag{1}$$

$$\ln \eta_r/C = [\eta] + k''[\eta]^2 C \tag{2}$$

where k' and k'' are Huggins and Kraemer coefficients, respectively, and C is the concentration of the polymer solution.

The molecular weight distribution (M_w/M_n) of PBI and derivatives was determined by gel permeation chromatography (GPC) at 85°C with a Waters 410 differential refractometer detector using PMMA standards for calibration. N,N-dimethyl formamide containing lithium bromide (5 wt %) was used as the eluent. Since the number average molecular weight (M_n) of PBI cannot be correctly measured or estimated by using PMMA calibration, the M_n was calculated from the molecular weight distribution.

The Nuclear magnetic resonance (NMR) measurements were performed on a Bruker Avance Instrument (300 mHz) in d[6]-DMSO at room temperature. Elemental analyses were measured by Galbraith Laboratory.

PBI preparation

Table I displays all the PBI specimens that are included in this study. Two commercial samples of PBI-4 and PBI-7 (Celanese) were fractionated by extraction with DMF at 152°C (reflux) for 2 h. The insoluble portion was then removed and collected by centrifugation, the precipitant was then washed with DMF. This material was then extracted with DMSO at 180°C for 1 h. The remaining insoluble material was then removed by centrifugation. The polymer extracts were isolated by the addition of a large excess of methanol and collection of the precipitated polymer by vacuum filtration. The precipitant was washed with fresh methanol and dried under vacuum at 100°C for 24 h. The DMSO extract (PBI-8) yielded a higher molecular weight PBI (M_w = 70,800) than the DMF extract (PBI-5, M_w = 35,800) that exhibits a darker brown color and could be dissolved in polar aprotic solvents at an ambient temperature. PBI-8 was used for the preparation of two phosphonylated PBI samples with degrees of substitution of $\sim$ 0.33 and three, designated as PBIP$_{et}$0.3 and PBIP$_{et}$3.0, respectively, in Table I. The second Celanese sample, PBI-4 (was found to be of M_w = 31,400), was almost completely soluble in refluxing DMF. Different molecular weight fractions could be obtained by addition of methanol to DMF solutions until turbidity appeared and the precipitant could be collected by centrifugation. The precipitates were washed with fresh methanol and dried under vacuum at 100°C for 24 h. Two specimens were obtained this way: PBI-1 with the lowest molecular weight (M_w = 13,200) and PBI-6 (M_w = 45,600). PBI-2 and PBI-3 are mixtures of PBI-1 and PBI-5 with a ratio of 50 : 50 and 70 : 30, respectively. PBI-9 has been synthesized in our laboratory from 3,3,4,4,-tetra amino biphenyl (TAB) and isophthalic acid in polyphosphoric acid by the method described by Iwakura et al.[3] The isophthalic acid was recrystallized from water, and 3,3',-Diaminobenzidine (tetrahydrochloride dehydrate) was converted to free-base and recrystallized from water. In short, an 8.0 wt % solid solution of isopthatlic acid and TAB in polyphosphoric acid was heated for 5 h at 200°C in a 500 mL round bottom flask, using mechanical stirring. The polymer obtained was a brown resinous mass,

TABLE I
M_w, M_n, Molecular Weight Distribution and Intrinsic Viscosity of PBI Samples

Sample	M_w[a]	M_w/M_n[b]	M_n[c]	[η]$_{DMF-LiCl}$ (mL/g)	[η]$_{H_2SO_4}$ (mL/g)
PBI1	13,200	1.5	8,800	41.2	32.2
PBI2	19,800	1.8	11,000	53.5	45.5
PBI3	25,000	1.7	14,700	70.2	55.6
PBI4	31,400	2.0	15,700	85.5	78.5
PBI5	35,800	1.5	23,900	94.4	89.8
PBI6	45,600	1.5	30,400	103.8	95.4
PBI7	49,500	2.0	24,750	106.5	107.4
PBI8	70,800	1.9	37,300	116.5	117.8
PBI9[d]	73,300	2.5	29,300	N/A	126.2
PBIP$_{Et}$0.3	79,900	1.9	39,950	N/A	N/A
PBIP$_{Et}$3.0	142,000	1.9	74,700	N/A	N/A

[a] M_w determined by light scattering measurement.
[b] M_w/M_n determined by GPC measurement.
[c] M_n calculated from the M_w/M_n.
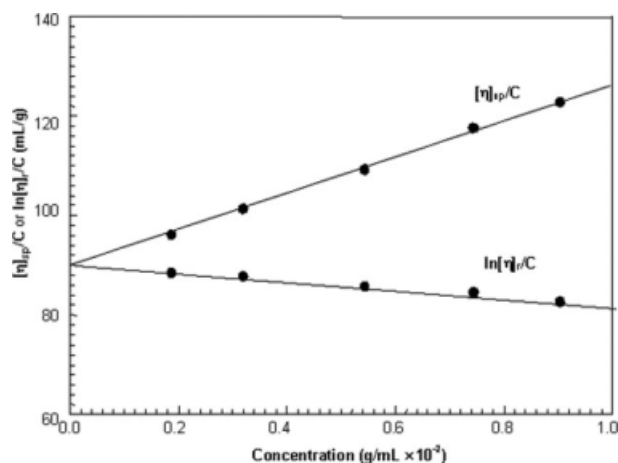[d] Synthesized in this lab.

Figure 2 A typical Huggins-Kraemer dual extrapolation plot for PBI ($M_w = 35,800$) in 96% sulfuric acid at 25°C.

similar to the commercial products. It is soluble in DMAc, and DMSO at elevated temperature and DMF/LiCl at ambient temperature.

RESULTS AND DISCUSSION

Table I gives the M_w, M_n and molecular weight distribution of PBI and PBIP. The molecular weight of the series PBI 1–8 were found to be in the range of $M_w \sim 13,200$–70,800 and $M_n \sim 8,800$–37,300, respectively. The molecular weight distributions of the PBI specimens were found to be in the range of 1.5–2.0, where the high value (~ 2) belongs to the original commercial samples, PBI-7 and PBI-4, and their extracts exhibit lower values as expected. PBI-8 ($M_w = 70,800$) forms a hard mass when dry, and unlike the lower molecular weight materials, dissolves only partially in the polar aprotic solvents at room temperature. This polymer, however, is soluble in DMAc, NMP and DMSO upon heating and remains dissolved when the solution is cooled back to ambient temperature. All the PBI specimens dissolved completely in DMF when lithium chloride was added. The MALLS measurements present the opportunity to assess the second virial coefficient, A_2, of the PBI's solutions. The A_2 of PBI in the sulfuric acid is $\sim 1.85 \times 10^{-5}$ mol mL g^{-2}, and A_2 of phosphonylated derivative of PBI, (i.e., PBIP) in the methanol, is $\sim 1.14 \times 10^{-3}$ mol mL g^{-2}. The positive values of the A_2 suggests that H_2SO_4 (96%) is a "reasonable" solvent for such a highly extended relatively rigid polymer chain, while indicating that methanol, a nonsolvent for PBI, is a good solvent for PBIP. The later is primarily due to strong interaction between the phosphoryl groups —C-P(= O), which is a strong Lewis base, and hydroxyls of the methanol. The observed differences of A_2 for PBI and PBIP is significant, but the A_2 data here is limited, and we

are not ready at this stage of the study to speculate more on the nature of the interactions between the polymer and surrounding medium; especially, much more data is needed to analyze the multifaceted of a highly concentrated inorganic acid, such as H_2SO_4, as a nondestructive solvent to organic polymers.

Intrinsic viscosities of each PBI sample in both sulfuric acid (96%) and DMF-LiCl are shown in Table I. A typical Huggins-Kraemer plot for PBI in sulfuric acid is shown in Figure 2. Intrinsic viscosity values in the range of 32.1–117.8 mL/g were obtained for PBI in sulfuric acid, and of 41.2–116.5 mL/g for $PBI_{DMF-LiCl}$.

Plots of a log [η] versus log M_w of PBI in sulfuric acid and DMF-LiCl (Fig. 3) yield linear relationships for $M_w < 65,000$. Mark-Houwink constants that were obtained from the slope and intercept of each plot to be: $a = 0.93$ and $K_w = 4.7 \times 10^{-3}$ mL/g for sulfuric acid (96%), and $a = 0.75$ and $K = 3.2 \times 10^{-2}$ mL/g for DMF-LiCl. Note that at the high end of these plots, the higher molecular weight data (PBI-8) seems to diverge downward, similar divergence was reported by Kojima et al.[11] for PBI-DMA solutions. The constants a and K_w are dependent on the molecular weight range and molecular weight distribution.[11] Choe et al. found $a = 0.73287$ and $K_w = 1.35326 \times 10^{-4}$ for broad molecular weight distribution ($M_w/M_n > 2.5$) and M_w (>150,000)of PBI.[15,16] Values of $a > 0.7$ are generally the case for highly extended or relatively rigid chains, such as PBI in good solvents. Helminiak et al.,[17] who reported a value of $a = 0.63$ for PBI-DMAc (at 30°C) claimed that addition of lithium chloride to DMAc solutions improves solubility and promotes chain expansion. This has been attributed to coordination of lithium chloride with the benzimidazole moiety and subsequent chain expansion by electrostatic repulsion.[18,19] The fact is that benzimidazole polymers can form salts with strong acids has been
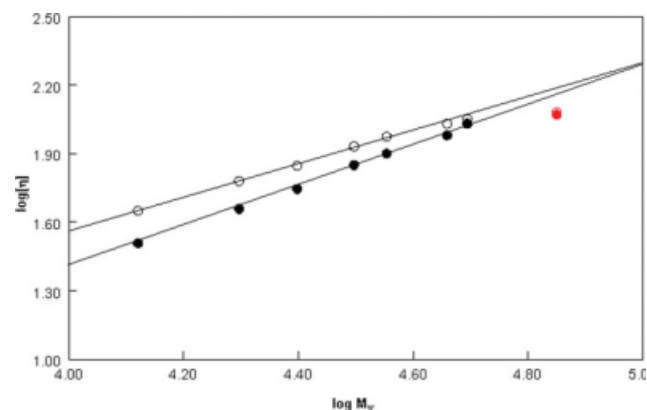

Figure 3 Mark-Houwink plot for PBI in 96% sulfuric acid ($K_w = 4.7 \times 10^{-3}$ mL/g, $a = 0.93$, $R^2 = 0.992$) (●) and in DMF-5% LiCl ($K_w = 3.2 \times 10^{-2}$ mL/g, $a = 0.754$, $R^2 = 0.995$) (○). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observed by Aharoni et al.[20,21] A much higher value $a = 1.10$ was reported for the other highly rigid polymer, poly(2,5-benzimidazole) (ABPBI) in concentrated sulfuric acid.[22] The results obtained in the present study suggest that sulfuric acid [$a = 0.92$] expands the PBI chain to a greater extent than DMF-LiCl [$a = 0.75$]. The PBI-9 synthesized in our laboratory exhibits a higher intrinsic viscosity (126.2 mL/g in H_2SO_4). The M_w of 73,960 is calculated for PBI-9 using a and K_w that is determined in Figure 3. However, a M_w of 190,000 can be obtained if using Choe et al.'s expression, since the PBI-9 has a higher molecular weight distribution ~ 2.5, where some fractions reached M_w $\sim 170,000$, as detected by GPC and this value is comparable with that reported[13]

In the present study, the intrinsic viscosity [η] was obtained by measuring the specimen viscosity in at least four different concentrations with extrapolation of the Huggins -Kraemer plot to infinite dilution. The method is time consuming, especially working with high concentrations of sulfuric acid as a solvent. Several equations had been developed in which only one specific solution concentration is used to estimate the intrinsic viscosity of a polymer solution. The single point method[23–25] uses the specific η_{sp}, and relative viscosity η_{rel}, at only one concentration to obtain [η]. Chuah et al.[26] examined the intrinsic viscosity, [η], that had been obtained for poly(trimethylene terephthalate) in HFIPA by single point equations and reported that the equations worked fairly well in estimating [η] for PTT within $\pm 3\%$ accuracy. Thus, we calculated PBI in H_2SO_4 and DMF-LiCl by using the single point method according to the following equations:

$$[\eta] = \frac{(\eta_{sp} + 3 \ln \eta_{rel})}{4c} \qquad (3)$$

$$[\eta] = \frac{\eta_{sp} + \ln \eta_{rel})}{2c} \qquad (4)$$

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_{rel})}}{c} \qquad (5)$$

Comparison of the intrinsic viscosities of PBI in the H_2SO_4 and DMF obtained from Huggins-Kraemer plots and the 'single point' methods given by eqs. (3)–(5),[23–25] are shown in Table II. The data suggests that estimating [η] of PBI by using 'single point' calculation fits quite well with more than 99% accuracy recorded at relatively low concentrations (the concentrations have specific viscosity $\eta_{sp} < 0.2$). In the case of relatively higher concentrations, for the higher molecular weight PBI, the estimation of [η] using these methods still gives reasonable values, within $\sim 3\%$.

TABLE II
Comparison of Calculated $[\eta]_{DMF}$ and $[\eta]_{H_2SO_4}$[a]

η_{sp}	H-K plot	Solomon[25]	Kuwahra[23]	Rao and Yassen[24]
		$[\eta]_{DMF}$		
0.090	53.5	53.2	53.0	53.6
0.126		53.5	53.3	
0.179		53.2	52.9	
0.250		53.3	52.8	
0.250	94.4	95.0	94.2	97.0
0.395		96.3	95.2	
0.533		94.3	93.0	
0.719		94.7	93.2	
0.177	103.8	104.0	103.4	105.6
0.255		105.3	104.5	
0.377		105.9	104.8	
0.548		105.4	104.0	
0.157	116.5	116.8	116.1	118.3
0.187		117.6	116.9	
0.269		115.9	114.9	
0.582		116.3	114.6	
		$[\eta]_{H_2SO_4}$		
0.141	32.2	32.4	32.2	32.7
0.163		32.3	32.1	
0.203		32.3	32.1	
0.262		32.0	31.7	
0.180	89.8	91.0	90.4	92.3
0.323		92.3	91.2	
0.594		93.0	91.7	
0.876		94.4	92.8	
0.189	107.4	106.1	105.4	107.8
0.351		105.9	104.8	
0.498		105.2	103.8	
0.619		103.5	102.0	
0.139	156.2	157.6	156.8	159.4
0.304		156.9	155.4	
0.460		159.4	160.8	

[a] With extrapolated values from the Huggins and Kremer equations.

The phosphonylated derivatives, $PBIP_{et}3$ and PBI-$P_{et}0.3$, were synthesized using PBI-8. The $PBIP_{et}3$ contains three phosphonyl groups per one PBI repeat unit, while $PBIP_{et}0.3$ only one phosphonyl group per three PBI repeat units (Scheme 1). The degrees of substitution were estimated by ^{1}H-NMR and elemental analysis. The ratio of carbon bound aromatic protons to the methyl protons of the diethyl phosphonyl groups were obtained from the ^{1}H-NMR. Integration of protons of the two PBIP specimens confirms a DS of ~ 0.33 and a DS of ~ 3 for $PBIP_{et}0.3$ and $PBIP_{et}3$, respectively. Molecular weights of the PBIP derivatives should increase accordingly as degree of substitution increases, whenever substitution occurs, a proton is replaced with $PO(OC_2H_5)_2$ (137 Da), unless severe degradation take place. The theoretical increase in molecular weight after substitution can be determined by the formula: $M_n = (R + 136DS)DP_n$, where R is the molecular weight of the repeat unit of

PBI (308), DS is the degree of substitution and DP_n is the degree of polymerization. The M_n calculated from the above formula for PBIP$_{et}$0.3 and PBIP$_{et}$3 are 42,700 and 86,600, respectively, (it is assumed that the polymer backbone consists of PBI substitutes with diethyl phosphonyl groups only, and the DP_n of the original PBI-8 is 120). Compared to the experimental values 39,950 (PBIP$_{et}$0.3) and 74,700 (PBIP$_{et}$3.0) seems indicate that slight degradation occurred during phosphonylation, despite the fact that the reaction had been conducted at a harsh condition (five times excess peroxide at 120°C for 5 h).

CONCLUSIONS

This study reveals that a linear relationship exists between the molecular weight and intrinsic viscosity of PBI solutions. Useful working plots have been established for specimens with M_w up to $\sim 65,000$ and molecular weight distribution of ~ 2.0 or less. At higher molecular weight and distributions the relationship might diverge from linearity. And further studies and more experimental data have to be collected for clarifying this zone. The values of Mark-Houwink constant, α, in sulfuric acid and DMF-LiCl, was determined to be 0.93 and 0.75, respectively, suggesting that PBI in these solvents is a highly extended relatively rigid chain. The thorough analysis of viscosity data confirms that estimating [η] of PBI by using the single point method is feasible. Thus, with a single relatively low concentration (specific viscosity η$_{sp}$ < 0.2), [η] with more than 99% accuracy may be recorded. In the case of relatively high concentrations and high molecular weight of PBI, the estimation of [η] using these methods still gives reasonable values within error margin $\sim 3\%$. The correlation among molecular weight, degree substitution and degree of polymerization of PBI derivatives is given by the formula, $M_n = (R + 136DS)DP_n$. This formula shows an increase in molecular weight consistent with a significant amount of substitution. In the specific case of interest where highly oxidative environment is applied the PBI exhibits sturdiness and resistance to degradation. A more detailed study on this subject is currently underway.

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