Intrinsic Viscosity–Number Average Molecular Weight Relationship for Poly(1,4-butylene adipate) diol

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ABSTRACT: The relationship between number average molecular weight (M_n) and intrinsic viscosity ([η]) was studied for poly(1,4-butylene adipate) diol (PBAD) in tetrahydrofuran, toluene, and ethyl acetate at 25°C. Thus, a series of PBAD samples were prepared by polymerization between 1,6-adipic acid and 1,4-butanediol. The values of M_n for the samples were determined by end-group analysis as well as by ebulliometry, and the average difference of M_n between the two analysis ways was about 2.69%. The Mark–Houwink–Sakurada equations for PBAD were obtained to relate [η] with M_n in the range of 1900–10,000. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1883–1887, 2010

Key words: end-group analysis; Mark–Houwink–Sakurada (MHS) equation; intrinsic viscosity; PBAD; molecular weight

INTRODUCTION

PBAD is a kind of polyester diols, which has different applications with different molecular weights. PBAD with high molecular weight can be used in various applications such as films and highly expanded foams,[1] whereas that with relative low molecular weight (<10,000) is the basic raw material of hot melt adhesive such as polyurethane.[2,3] For the latter, it has been discovered that the higher molecular weight, the faster setting speed of hot melt adhesive.[4] And the setting speed can affect the application of hot melt adhesive. Therefore, determining the molecular weight of PBAD effectively has obvious practical significance. However, the studies on PBAD with M_n less than 10,000 have not been reported.

There are many ways to determine molecular weight such as end-group analysis (M_n),[5] gel permeation chromatography (GPC) (M_n, M_w, and M_z),[1,6,7] H-NMR technique (M_n),[8] membrane osmometry (M_n),[9] light-scattering (M_w),[9] and viscometry method (M_v). But most of these ways are time consuming. Among them, the viscometry method is relatively quick and simple and requires easy-to-use apparatus, which only use a viscometer. The relationship between M_v and [η] can be described by Mark–Houwink–Sakurada (MHS) equation. In general, M_v is not experimentally accessible, and in most reports, different average molecular weights (M_n, M_w, and M_z), instead of viscosity–average molecular weight M_v, are substituted in MHS equation ignoring polydispersity effect.[10]

As far as we know, MHS coefficients for PBAD with M_n less than 10,000 have not been published. The objective of this work was to determine the MHS coefficients, a and K, for PBAD in the range of 1900–10,000. Here, M_n was used as the substitute of M_v to correlate to [η]. The molecular weights of the PBAD samples prepared in the laboratory were determined by end-group analysis and ebulliometry.[11] Intrinsic viscosities for the PBAD samples in tetrahydrofuran, toluene, and ethyl acetate at 25°C were determined in Ubbelohde viscometer.

EXPERIMENTAL

Materials

PBAD samples ($1900 \leq M_n \leq 10{,}000$) used in this work were prepared by reaction between 1,6-adipic acid and 1,4-butanediol at 140–220°C, followed by polymerization at 220–230°C and 0.67 mbar until the designed molecular weight was obtained.[1,12] Then, the products were extracted by precipitation fractionation[13] to obtain the samples with relative narrow molecular weight distributions. Tetrahydrofuran and distilled water were used as solvent and precipitator, respectively. The samples are white waxy solid at normal temperature and melt in the range of 40–60°C. Chemically pure-grade 1,4-butanediol and 1,6-adipic acid were purchased from Shanghai Chemistry Regent Co. (China). The others such as tetrahydrofuran, toluene, ethyl acetate, pyridine, acetic anhydride, and perchloric acid are analytical

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grade and were also purchased from Shanghai Chemistry Reagent Co. (China).

Charaterization

End-group analysis

Hydroxyl value analysis.[5] To determine hydroxyl value, the PBAD sample was first dissolved in acetic ether at 50°C. And then it was added to 5 mL acylating agent, which was prepared by 150 mL acetic anhydride and 35 mL ethyl acetate mixed solution with 2 mL perchloric acid as catalyst at 5°C. After 10–20 min, 10 mL pyridine + distilled water (volume ratio 1 : 3) mixed solution was added, and the sample was hydrolyzed for 5 min, followed by titration with 0.5 mol/L KOH in distilled water against a phenol red indicator.

The hydroxyl value determined by end-group analysis can be calculated using eq. (1):

$$H = (V_0 - V) \cdot C_{\mathrm{KOH}} \times 56.1/m \quad (1)$$

where H (mg/g) is the hydroxyl value of sample, V_0 (mL) is the volume of KOH solution consumed in blank assay, V (mL) is the volume of KOH solution consumed by sample, C_{KOH} (M) is the concentration of KOH solution, m (g) is the mass of sample.

Acid number analysis. To determine the acid number, the sample was first dissolved in toluene + ethanol mixed solution (volume rate 2 : 1), followed by titration with 0.1 mol/L KOH in distilled water against a phenol red indicator.

The acid number can be calculated by eq. (2).

$$H' = (V' - V'_0) \cdot C'_{\mathrm{KOH}} \times 56.1/m \quad (2)$$

where H' (mg/g) is the acid number of sample, V'_0 (mL) is the volume of KOH solution consumed in blank assay, V' (mL) is the volume of KOH solution consumed by sample, C'_{KOH} (M) is the concentration of KOH solution, m (g) is the mass of sample.

Ebulliometry

Ebulliometry is a very simple method used to determine the molecular weight of a polymer if the molecular weight is not higher than 40,000 and if a suitable solvent is found. In this article, the number average molecular weights for the PBAD samples were below 10,000. According to ebulliometry, eq. (3) is applied.

$$\left(\frac{\Delta T}{C}\right)_{C\to 0} = \frac{K_b}{\rho M_n} \quad (3)$$

where ΔT (K) is the temperature difference of solvent and solution, C (g/mL) is the concentration of solution, K_b is the ebullioscopic constant, ρ (g/cm^3) is the density of solvent, M_n is the number average molecular weight of the samples.

Temperature differences of solvent and solution were determined under normal pressure. The increment of sample added to solvent each time is 0.2 g in 25 mL solvent. The solvent used here was toluene.

TABLE I
The Hydroxyl Value, the Acid Number and the Molecular Weight Determined by End-Group Analysis for Each PBAD Sample

Sample	H (mg/g)	H' (mg/g)	M_n^1 (g/mol)
1	55.74	0.42	1998
2	38.44	0.24	2901
3	27.86	0.56	3948
4	18.4	0.36	5980
5	14.25	0.15	7792
6	11.01	0.21	9996

Intrinsic viscosity determination

Intrinsic viscosities of the PBAD samples in tetrahydrofuran, toluene, and ethyl acetate at 25°C were determined in Ubbelohde viscometer of the diltion type by extrapolation to zero concentration of specific viscosity measurement obtained at four different concentration levels. The capillary diameter of Ubbelohde viscometer was 0.4–0.5 mm and the solution concentrations were lower than 1% (w/V). The corrections for kinetic energy and shear were negligible in these conditions.

Solubility determination

The solubility of PBAD sample was measured by the isothermal method.[14] A 150-mL flask was used to determine the solubility; the temperature was controlled to be constant (fluctuates within 0.05 K) through a thermostated bath. The dissolution of the solute was examined by the laser beam penetrating the vessel. The masses of the samples and solvents were weighed using an analytical balance (Mettler H542 balance) with an accuracy of (±0.0001 g).

RESULT AND DISCUSSION

Molecular weight

The hydroxyl values (H) and the acid numbers (H') of the PBAD samples determined by end-group analysis are displayed in Table I.

The molecular weight of the PBAD sample can be calculated using eq. (4)[15]:

$$M_n = 56.1 \times 2 \times 1000/(H + H') \quad (4)$$

where M_n is the number average molecular weight.

TABLE II
The Intercept and the Molecular Weight Determined by Ebulliometry for Each PBAD Sample

Sample	Intercept	M_n^2 (g/mol)	M_n^1 (g/mol)	Error%
1	1.95	1983	1998	0.75
2	1.27	3058	2901	5.41
3	0.95	4086	3948	3.50
4	0.63	6125	5980	2.42
5	0.49	7923	7792	1.68
6	0.38	10,236	9996	2.40

The values of M_n for the PBAD samples are also displayed in Table I.

According to the values of ΔT for different concentrations of the PBAD samples measured by ebullioscopy, the plots of C versus $\Delta T/C$ are obtained and they are almost linear. The intercepts of the lines are obtained by extrapolation to zero concentration and listed in Table II. In this way, the values of M_n for the samples are calculated from eq. (3) in which $K_b = 3.33$ K Kg mol^{-1}.[16] The results are also listed in Table II.

The deviations ($(M_{n2} - M_{n1})/M_{n1}$) of M_n between the two analysis ways are shown in Table II, and the maximal value is 5.41% and the average one is 2.69%, which means the number average molecular weights determined by end-group analysis and those by ebullioscopy are consistent. So, the number average molecular weight can be determined by end-group analysis, and the values (M_{nexp}) are used in the correlation establishment in the following section. Moreover, compared to H-NMR technique and GPC technique mentioned before, these two ways both require technique easy-to-use apparatus.

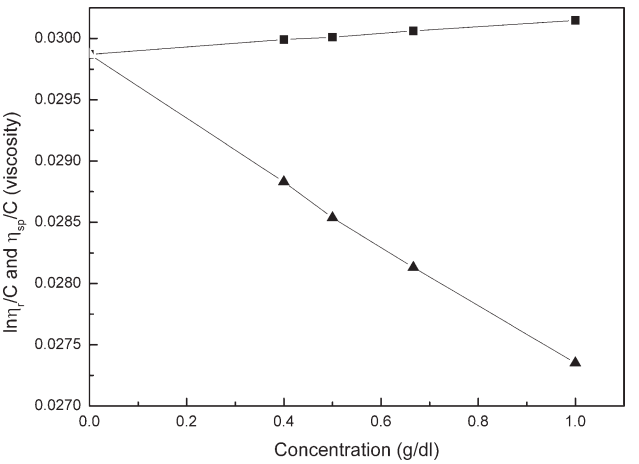

Figure 1 Intrinsic viscosity for PBAD where $M_n = 9996$: (■) ηsp/C, (▲) lnηr/C.

Intrinsic viscosity

Relative viscosities (η_r) are measured using a Ubbelohde viscometer. Stock solution (1 g/dL) is diluted by pure solvent to generate a range of concentrations down to 0.4 g/dL. The viscometer is maintained at 25 ± 0.1°C using a circulating water bath. In the usual fashion, relative viscosities is defined as the efflux time of the polymer solution divided by that of the pure solvent; the specific viscosity (η_{sp}) is

TABLE III
Intrinsic Viscosity Determined in Tetrahydrofuran, Toluene and Ethyl Acetate at 25°C for Each PBAD Sample and M_{nexp} vs. M_{ncal}

Sample	Actual M_n	log M_n	[η] (dL/g)	log [η]	Calculated M_n	Error%
Tetrahydrofuran						
1	1998	3.300595	0.00972	−2.01233	1965	1.65
2	2901	3.462548	0.01277	−1.89381	2935	1.17
3	3948	3.596377	0.01586	−1.7997	4037	2.25
4	5980	3.776701	0.02125	−1.67264	6207	3.8
5	7792	3.891649	0.02383	−1.62288	7347	5.71
6	9996	3.999826	0.02987	−1.52476	10241	2.45
Toluene						
1	1998	3.300595	0.00927	−2.03292	2031	1.65
2	2901	3.462548	0.01145	−1.94119	2871	1
3	3948	3.596377	0.01436	−1.84285	4162	5.42
4	5980	3.776701	0.01726	−1.76296	5626	5.92
5	7792	3.891649	0.02052	−1.68782	7472	4.1
6	9996	3.999826	0.02547	−1.59397	10648	6.52
Acetic ether						
1	1998	3.300595	0.01387	−1.85792	2081	4.15
2	2901	3.462548	0.01597	−1.7967	2700	6.88
3	3948	3.596377	0.0199	−1.70115	4060	2.84
4	5980	3.776701	0.02543	−1.59465	6393	6.91
5	7792	3.891649	0.02769	−1.55768	7486	3.93
6	9996	3.999826	0.03254	−1.48758	10093	0.97

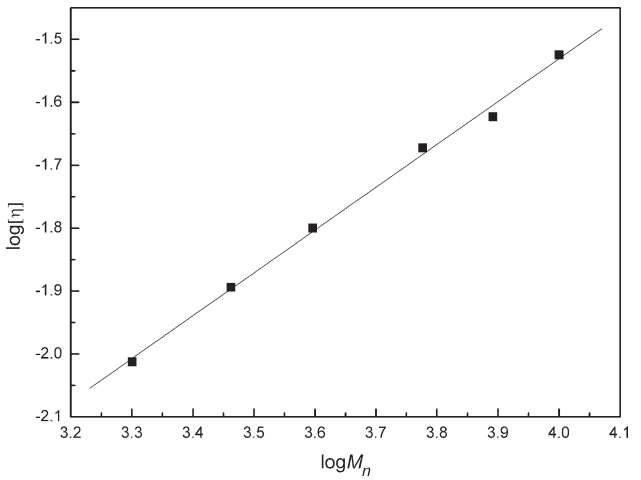

Figure 2 Relation of log [η] and log M_n for PBAD samples in tetrahydrofuran at 25°C.

$\eta_r - 1$. Data for ln η_r/C and η_{sp}/C are plotted and the data regressed (e.g., see Fig. 1), providing the intrinsic viscosity as the intercept.[7]

The values of [η] for the PBAD samples determined in tetrahydrofuran, toluene, and ethyl acetate at 25°C in Ubbelohde viscometer are listed in Table III. For the same PBAD sample, the value of [η] in ethyl acetate is maximal. For the same solvent, the value of [η] increases with the increase of M_n.

Correlation establishment

The intrinsic viscosity is related to the molecular weight according to Mark–Houwink–Sakurada equation[17–19]:

$$[\eta] = k\, M_v^{\alpha} \tag{5}$$

where [η] is the intrinsic viscosity in dL g^{-1}, M_v is the viscosity-average molecular weight, and k and a are coefficients for given solute–solvent system and temperature. For PBAD with relativity lower molecular weight (1900–10,000), M_n is used as the substitute of M_v in eq. (5), then eq. (6) is obtained.

$$[\eta] = K M_n^{a} \tag{6}$$

where the exponent a is the same as that in eq. (5), and the coefficient K is different from k in eq. (5).

Eq. (6) is taken a double-logarithm plot for the two sides, and the values of log [η] and log M_n are also shown in Table III, where M_n values are determined by end-group analysis. Figures 2–4 show the plots of log [η] versus log M_n, which are close to straight lines. The values of r^2 are 0.998, 0.997, and 0.996, respectively. According the lines, the slopes and the intercepts represent the coefficients a and K, respectively.

From the three figures above, the coefficients K and a are obtained. The values of a determined in tetrahydrofuran, toluene, and ethyl acetate are 0.68,

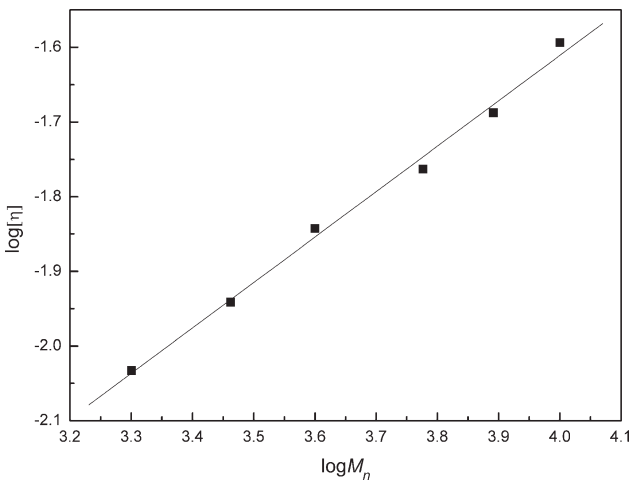

Figure 3 Relation of log [η] and log M_n for PBAD samples in toluene at 25°C.

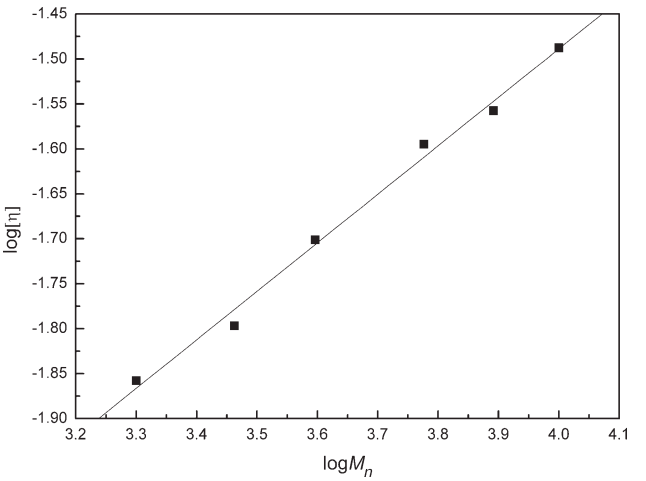

Figure 4 Relation of log [η] and log M_n for PBAD samples in ethyl acetate at 25°C.

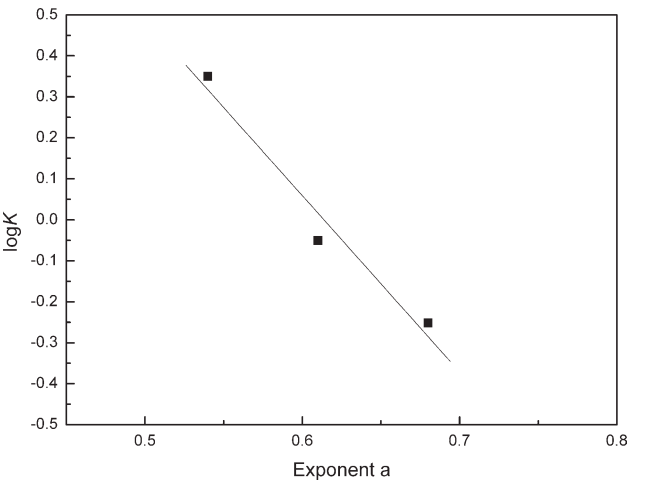

Figure 5 The value of log K versus exponent a.

TABLE IV
The Mass of PBAD Samples Soluble in 50 mL Tetrahydrofuran, Toluene and Ethyl Acetate at 25°C and 30°C

T (°C)	m^a (g)	m^b (g)	m^c (g)
25	0.63	0.60	0.46
30	0.78	0.75	0.68

[a] Tetrahydrofuran.
[b] Toluene.
[c] Ethyl acetate.

0.61, and 0.54, respectively. K values are 0.56×10^{-4}, 0.89×10^{-4} , and 2.24×10^{-4}, respectively.

The following coefficients for MHS equation are proposed for PBAD in the M_n range of 1900–10,000:

$$[\eta] = 0.56 \times 10^{-4} M_n^{0.68} \quad \text{(tetrahydrofuran)} \quad (7)$$

$$[\eta] = 0.89 \times 10^{-4} M_n^{0.61} \quad \text{(toluene)} \quad (8)$$

$$[\eta] = 2.24 \times 10^{-4} M_n^{0.54} \quad \text{(ethyl acetate)} \quad (9)$$

Table III lists the calculated molecular weights (M_{ncal}) using eqs. (7)–(9) and the differences between M_{nexp} and M_{ncal}. The maximal difference is 6.91% and the average one is 3.74%. Compared the values of a and K, just as reported in some literatures,[8,9] the plot (Fig. 5) of log K versus exponent a is linear almost and inversely related. A high value (>0.5) of exponent a indicates that the secondary forces between the polymer and the solvent molecule are strong, in other words, a better solvent. The exponent a changes with the quality of solvent.[9,20] According to the values of a above, tetrahydrofuran, toluene, and ethyl acetate are all good solvents for PBAD, and tetrahydrofuran is the best one. So, we can predict the solubility of PBAD in tetrahydrofuran will be higher than that in toluene and ethyl acetate.

Solubility determination

The solubilities of PBAD sample with M_n of 5980 in tetrahydrofuran, toluene and ethyl acetate are measured at 25°C and 30°C. The results (Table IV) represent the solubility of PBAD in tetrahydrofuran is higher and the solubility in ethyl acetate is lower, which is consistent with the values of a.

CONCLUSIONS

Poly(1,4-butylene adipate) diols with number average molecular weights (1900–10,000) were synthesized. The number average molecular weights of the samples were determined by end-group analysis and by ebulliometry, and the values of M_n determined by these two methods were almost consistent. Then, the correlations between number average molecular weight and intrinsic viscosity in tetrahydrofuran, toluene, and ethyl acetate at 25°C for PBAD were established as follows:

$$[\eta] = 0.56 \times 10^{-4} M_n^{0.68} \quad \text{(tetrahydrofuran)}$$

$$[\eta] = 0.89 \times 10^{-4} M_n^{0.61} \quad \text{(toluene)}$$

$$[\eta] = 2.24 \times 10^{-4} M_n^{0.54} \quad \text{(ethyl acetate)}$$

The average deviation between M_{nexp} and M_{ncal} was about 3.74%. According to the values of a (>0.5), tetrahydrofuran, toluene, and ethyl acetate are all good solvents for PBAD.

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