Intrinsic Viscosity-molecular Weight Relationship of Poly (hexanediol adipate)

Abstract

In this work, a series of poly(Hexanediol adipate)(PHA) samples ($10^3 < M_n < 10^4$) with narrow molecular weight distribution were prepared by the polymerization between adilic acid and 1,6-hexandiol. The number average molecular weights (M_n) of the samples were measured by end-group analysis. Gel permeation chromatography (GPC) was used to determine the average molecular weights (M_n, M_v, M_w and M_z).The intrinsic viscosity of the samples in the tetrahydrofuran(THF) solution was determined at 298 K by the dilution extrapolation method and the one-point method, respectively. The relationship between the intrinsic viscosity and the molecular weight for PHA was studied by the Mark-Houwink-Sakurada (MHS) equation, and the parameters of equation were determined.

Keywords: One-point method; Poly(hexanediol adipate); intrinsic viscosity; molecular weight; Mark-Houwink-Sakurada.

1. INTRODUCTION

Poly(hexanediol adipate)(PHA) in different molecular weight has various differences in its properties. The PHA with an average molecular weight M_n less than 10^4 is usually used to synthesize polyurethane hot melt adhesives (PUR). Generally, the higher the molecular weight of PHA, the faster the crystallization rate of the synthesized PUR product[1,2].The crystallization rate of PUR has a significant effect on the bonding cure rate, so it is of great significance to determine the molecular weight of PHA efficiently and conveniently. There are many traditional methods to determine the molecular weight of polyester polyol, but only viscosity method to determine M_v can satisfy the requirements.

In this work, a series of PHA samples ($10^3 < M_n < 10^4$) with narrow molecular weight distribution were synthesized by polymerization between adilic acid and 1, 6-hexylene glycol. The intrinsic viscosity ($[\eta]$) of the samples dissolved in tetrahydrofuran (THF) were determined by the dilution extrapolation method and the one-point method, respectively. According to Mark-Houwink-Sakurada (MHS)[3,4,5] equation, the relationship between $[\eta]$ and the average molecular weights (M_n, M_v , M_w) for PHA was established, and the polydispersity correction on the PHA samples was made.

2. EXPERIMENTAL

2.1 Materials

Adilic acid (Shanghai Aladdin Bio-Chem Technology Co. LTD) , 1, 6-hexylene glycol (Shanghai Dibai Chemical Co. LTD) and THF (Shanghai chemistry Regent Co.) are all of analytical reagent.

2.2 Apparatus and Procedure

The synthesis of PHA samples consists of two steps: esterification and polymerization. The esterification reaction between adilic acid and 1,6-hexylene glycol was carried out in the temperature range of 433 ~ 453 K in a 250 ml three-neck flask equipped with thermometer, dephlegmator and blender. The reactor was heated with the oil jacket, and the reaction temperature was controlled automatically by adjusting the oil temperature which was maintained within ±0.5 K. In the second step, the polymerization was carried out under a reduced pressure (500-100 Pa) in the temperature range of 494 ~ 504 K for 2 ~ 4 h. When the acid value of the product is less than 1.0 mg KOH/g, the reaction is completed and a PHA sample was obtained.In this work, eight PHA samples with different molecular weights were obtained by different process conditions, and they are named as S1~S8.

2.3 Molecular Weight

In this work, the molecular weight of the PHA samples were determined by Gel-permeation Chromatography(GPC) (M_n: number average molecular weight; M_v: viscosity average molecular weight; M_w: weight-average molecular weight) and end-group analysis(M_n).

2.3.1 Gel-permeation Chromatography[6,7]

The PHA sample (0.02 g) was dissolved completely in THF at 303.15 K and left at room temperature for 24 h. A GPC equipment (Water-1515/2414) connected to a refractive index detector was used to determine the average molecular weights (M_n, M_v,

M_w) of the sample by Breeze 2 software. THF of chromatographic grade was used as eluent with a flow rate of 1 mL/min.

2.3.2 End-group Analysis[8]

End group analysis is suitable for determining the molecular weight of a polymer having a M_n value in the range of 500 to 20,000, and is performed by measuring the acid and hydroxyl values of the sample as follows.

Determination of acid value The acid value (A_v) is defined as the mass(mg) of potassium hydroxide consumed to neutralize the carboxyl groups per gram of sample. The operation procedure of the measurement process is the same as the literature[9,10] and described briefly as follows: the sample was first dissolved in 30 ml of toluene-ethanol (2:1 V/V) mixed solution, followed by titration with 0.1 mol/L standard KOH-ethanol solution against phenolphthalein indicator. The volume of the KOH-ethanol solution consumed was recorded. Repeat the titration experiment three times and take the average to reduce the experimental error. The acid value is calculated as follows:

$$A_V(\text{mgKOH/g}) = \frac{M_{\text{KOH}} \times c_{\text{KOH}} \times (V_s - V_0)}{m_s} \qquad (1)$$

Where M_{KOH} (56.1g/mol) is the molar mass of KOH, C_{KOH} is the concentration of KOH-ethanol solution, V_s(mL) is the volume of KOH-ethanol solution consumed by titration, V_0(mL) is the volume of KOH-ethanol solution consumed in the blank experiment, m_s (g) is the mass of sample.

Determination of hydroxyl value The hydroxyl value of PHA is determined by acetic anhydride-perchloric acid method[9,10]. The hydroxyl group in the sample is acylated with acetic anhydride, and the excess acetic anhydride is hydrolyzed to acetic acid, and the acetic acid is titrated with KOH-ethanol solution. The hydroxyl value(Q_{v}) of the sample is calculated as follows:

$$Q_{\mathrm{V}}(\mathrm{mgKOH/g}) = \frac{M_{\mathrm{KOH}} \times c_{\mathrm{KOH}} \times (V_{\mathrm{s}} - V_0)}{m_{\mathrm{s}}} \quad (2)$$

The number average molecular weight The number average molecular weight (M_{n}) of the sample can be calculated by the following equation[11]:

$$M_{\mathrm{n}} = \frac{M_{\mathrm{KOH}} \times 2 \times 1000}{A_{\mathrm{V}} + Q_{\mathrm{V}}} \quad (3)$$

2.4 Determination of intrinsic viscosity

2.4.1 Dilution extrapolation method

The intrinsic viscosity of the PHA sample dissolved in THF at 298K was determined in the Ubbelohde viscometer by extrapolation to zero concentration of specific viscosity measurements obtained at four different concentration levels viscometer(capillary diameter: 0.4-0.5mm) and the relationship between the viscosity and the solution concentration was analyzed by dilution extrapolation method.

The specific viscosity (η_{sp}) and the relative viscosity (η_{r}) are defined as follows:

$$\eta_{\mathrm{sp}}=\frac{\eta-\eta_0}{\eta_0}=\frac{t-t_0}{t_0}=\eta_{\mathrm{r}}-1 \qquad (4)$$

where η and η_0 are the viscosity of the polymer solution and the pure solvent, respectively; t and t_0 are the outflow time of the above two, respectively.

At a certain temperature, the Huggins equation[12] (or the Kraemer equation[13]) can be used to describe the relationship between η_{sp} (or η_{r}) and the concentration of the polymer solution as follows :

$$\frac{\eta_{\mathrm{sp}}}{C}=[\eta]+\mathrm{k}[\eta]^2C \qquad (5)$$

$$\frac{\ln\eta_{\mathrm{r}}}{C}=[\eta]-\beta[\eta]^2C \qquad (6)$$

where k and β are constants related to temperature and solvent, C(g/dL) is the concentration of the polymer solution,

The relationship between $[\eta]$ and η_{sp} (or η_{r}) is defined as follows:

$$[\eta]=\lim_{c\to0}\frac{\eta_{\mathrm{sp}}}{C}=\lim_{c\to0}\frac{\ln\eta_{\mathrm{r}}}{C} \qquad (7)$$

According to Eqs. (5) and (6), we can get two straight lines by plotting $\frac{\eta_{\mathrm{sp}}}{C}\sim C$ *and* $\frac{\ln\eta_{\mathrm{r}}}{C}\sim C$, respectively. The two straight lines are extrapolated to the point where the concentration C tends to 0, and the average value of the intercept of the two straight lines is the intrinsic viscosity $[\eta]$.

2.4.2 One-point method

The intrinsic viscosity is calculated according to the one-point equation proposed by Cheng , and can be expressed as follows[14]:

$$[\eta]=\frac{1}{C}\sqrt{\frac{1}{\mathrm{k}+\beta}\left(\eta_{\mathrm{sp}}-\ln\eta_{\mathrm{r}}\right)}=\frac{1}{C}\sqrt{2\left(\eta_{\mathrm{sp}}-\ln\eta_{\mathrm{r}}\right)} \qquad (8)$$

2.5 Polydispersity Correction

The polymer has dispersibility and the measured molecular weight of the polymer is an average value. In many investigations, the average molecular weight was determined and the viscosity average molecular weight satisfies the MHS equation:

$$[\eta]=KM_{v}^{a}=Kq_{\mathrm{MHS}}M_{\mathrm{w}}^{a} \qquad (9)$$

where K and a are the characteristic parameters of the polymer. q_{MHS} is a polydispersity correction factor and can be calculated by the following statistical equation[15,16]:

$$q_{\mathrm{MHS}}=\left(M_{\mathrm{w}}/M_{\mathrm{n}}\right)^{b}\left(M_{\mathrm{z}}/M_{\mathrm{w}}\right)^{c} \qquad (10)$$

b and c can be calculated from the empirical equation associated with the exponent a[17,18]:

$$c=0.113957-0.844587a+0.730956a^{2} \qquad (11)$$

$$b=k_{1}+k_{2}\left[\frac{M_{\mathrm{z}}}{M_{\mathrm{w}}}-1\right]^{k_{3}} \qquad (12)$$

$$k_{1}=0.048663-0.265996a+0.364119a^{2}-0.146682a^{3} \qquad (13)$$

$$k_2 = -0.096601 + 0.18030a - 0.084709a^2 \quad (14)$$

$$k_3 = -0.252499 + 2.31988a - 0.889977a^2 \quad (15)$$

According to the consecutive steps, the estimation of q_{MHS} requires prior knowledge of the viscometric constant a. An iterative procedure proposed by Kasaai [11] can be used to circumvent the difficulty.

3. **Results and discussions**

3.1 The molecular weight of PHA

The average molecular weight (M_{n}, M_v, M_{w}) and *MWD* ($M_{\mathrm{w}}/M_{\mathrm{n}}$) of the samples (S1~S8) were determined by GPC, and the results are shown in Table 1. From Table 1, the $M_{\mathrm{w}}/M_{\mathrm{n}}$ value of the samples is in the range of 1.013~1.216, indicating the *MWD* value of the samples is narrow. On the other hand, the acid value and hydroxyl value of the samples were measured respectively, and the number-average molecular weight obtained by eq. (3) is also listed in Table 1. From Table 1, the number average molecular weight measured by GPC is consistent with that by the end-group analysis method with the average relative deviation (ARD%) of 1.59%. ARD% is defined as follows: .

$$\mathrm{A}RD\% = \frac{1}{8}\sum_{\mathrm{i=1}}^{8} \frac{\left|M_{\mathrm{n,i}}^{\mathrm{E}} - M_{\mathrm{n,i}}^{\mathrm{G}}\right|}{M_{\mathrm{n,i}}^{\mathrm{G}}} \times 100\% \quad (16)$$

where the superscripts G and E represent GPC and end group analysis, respectively.

Table 1. Average molecular weight (M_n, M_ν, M_w) of S1~S8 determined by GPC and end-group analysis

Sample	M_n^G (g/mol)	M_ν^G (g/mol)	M_w^G (g/mol)	$\frac{M_w^G}{M_n^G}$	M_n^E (g/mol)	*ARD* (%)
S1	1028	1180	1184	1.152	1066	3.70
S2	2080	2256	2360	1.135	2037	2.07
S3	3081	3410	3556	1.154	3052	0.94
S4	3951	4484	4710	1.192	3876	1.90
S5	5174	5676	5986	1.157	5234	1.16
S6	6098	6670	6726	1.103	6185	1.43
S7	7135	8404	8676	1.216	7048	1.22
S8	8354	9266	9315	1.115	8377	0.28

^{G} determined by GPG ; ^{E} determined by end-group analysis.

3.2 The Intrinsic Viscosity

The relative viscosity η_r of the samples (S1~S8) dissolved in THF was determined by dilution extrapolation method. The curves of $\ln\eta_r/C \sim C$ and

$\eta_{sp}/C \sim C$ for S2 at different concentrations are shown in Fig. 1. As can be seen from Fig. 1, the above two curves are linear, and the intrinsic viscosity $[\eta]$ of S2 is obtained by the average of the intercepts of the two straight lines. On the other hand, the intrinsic viscosity can also be obtained by using one-point method and is recorded as $[\eta']$. Table 2 lists the $[\eta]$ and $[\eta']$ values of S1~S8. From Table 2, the intrinsic viscosity obtained by the one-point method is consistent with that by the dilution extrapolation method with the average relative deviation (ARD%) of 3.24%. ARD% is calculated as follows:

$$\mathrm{ARD} = \sum_{i=1}^{8} \frac{\left|[\eta]_i - [\eta']_i\right|}{[\eta]_i} \times 100\% \qquad (21)$$

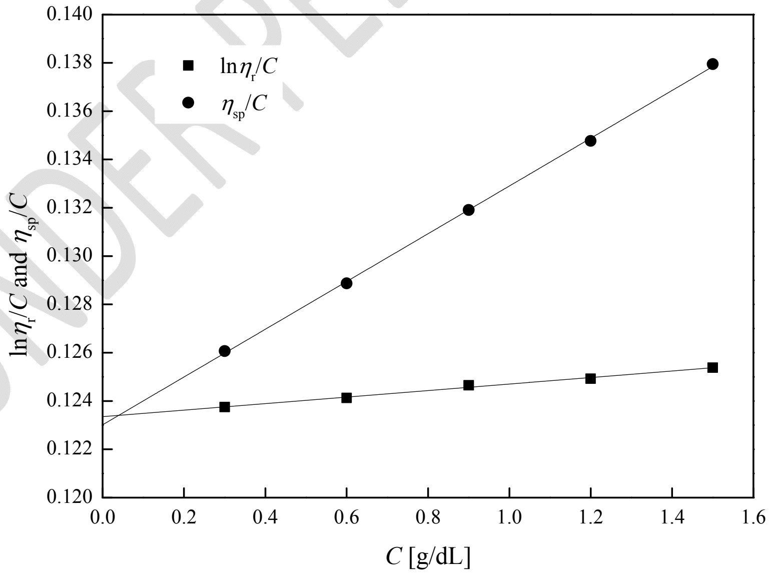

Fig. 1 Intrinsic viscosity for S2

Table 2. Intrinsic viscosity ($[\eta]$ and $[\eta']$) for S1 ~ S8 in THF at 298 K

Sample	M_n (g/mol)	$[\eta]$ (dL/g)	$[\eta']$ (dL/g)	ARD(%)
S1	1028	0.0780	0.0797	2.13
S2	2080	0.1232	0.1270	3.08
S3	3081	0.1614	0.1689	4.65
S4	3951	0.1985	0.2034	2.49
S5	5174	0.2263	0.2337	3.28
S6	6098	0.2471	0.2576	4.24
S7	7135	0.2820	0.2925	3.71
S8	8354	0.3064	0.3135	2.33

3.3 Characteristic parameter determination

According to MHS equation, the relationship between the molecular weight and the intrinsic viscosity of polymers can be expressed as follows：

$$[\eta] = KM^a \tag{22}$$

After determining the characteristic parameters K and a, the average molecular wight of the polymer can be calculated according to the value of the intrinsic viscosity. Take a natural logarithm on either side of eq (22), we can get

$$\ln[\eta] = a\ln M + \ln K \tag{23}$$

3.3.1 Relationship between [*η*] and M$_n$

According to the data shown in Table 2, the plot of $\ln[\eta]$ *vs* $\ln M_n$ is presented in Fig. 2, and the slope and intercept of the obtained line (R^2=0.995) are 0.6564 and -7.098, respectively. The relationship between $[\eta]$ and M_n for the PHA samples (M_n=10^3~10^4) with the narrow *MWD* is:

$$[\eta] = 8.268\times10^{-4} M_n^{\ 0.6564} \tag{24}$$

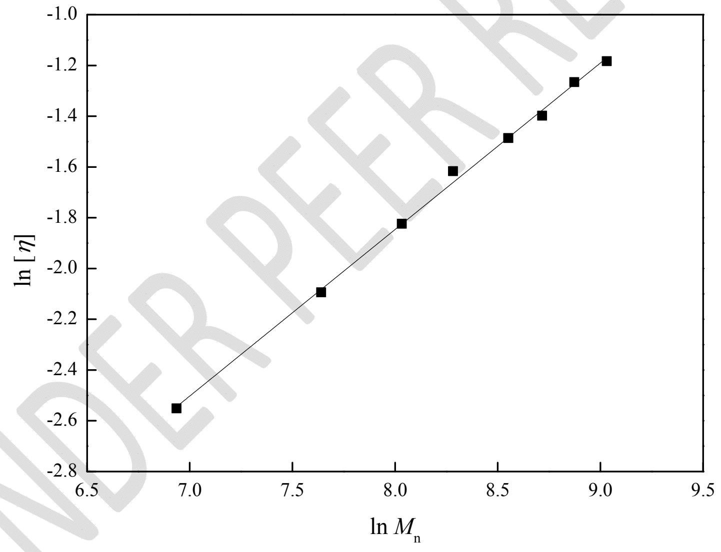

Fig. 2. Relation of $\ln[\eta]$ and $\ln M_n$ for S1~S8 in THF at 298 K

3.3.2 Relationship between [*η*] and M$_v$

According to the data shown in Table 2 and Table 1, the plot of $\ln[\eta]$ *vs* $\ln M_v$ is presented in Fig. 3, and the slope and intercept of the obtained line (R^2=0.990) are

0.6564 and -7.171, respectively. The relationship between $[\eta]$ and M_v for the PHA samples (1000-10000) with the narrow distribution is:

$$[\eta] = 7.686 \times 10^{-4} M_v^{\ 0.6564} \qquad (25)$$

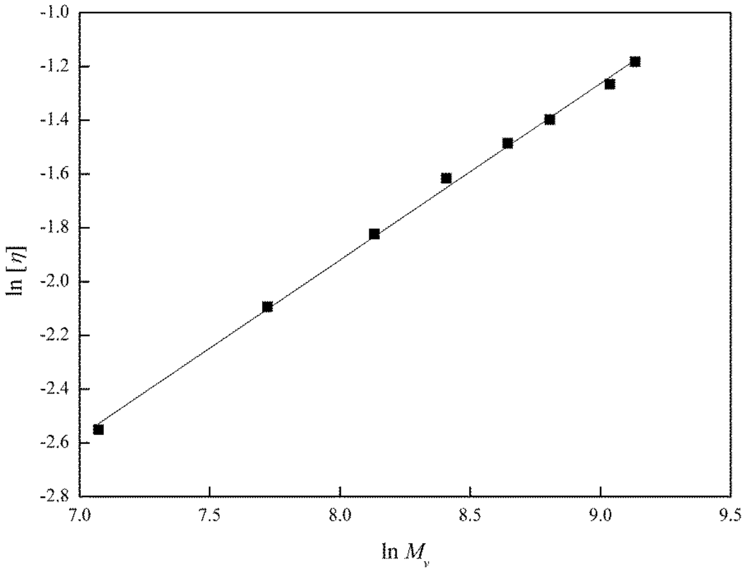

Fig. 3. Relation of $\ln[\eta]$ and $\ln M_\eta$ for S1~S8 in THF at 298 K

3.3.3 Relationship between [*η*] and M_w

The multi-dispersion correction factor q_{MHS} in eq. (13) is used to calculate the relationship between [η] and M_w. For PHA with narrow MWD, it is assumed that[18]:

$$\frac{M_z}{M_w} = \frac{M_w}{M_n} \qquad (26)$$

For computation, Kasaai[19,20] found a simple and practical iterative calculation method. According to the iterative procedure, an initial value of q_{MHS} was first calculated for each sample by assuming *a* is equal to unity or 0.6564 (the exponent in eq (24)) and the poly dispersity obeys eq (26). Then, plotting $\ln q_{\mathrm{MHS}}$ against $\ln M_{\mathrm{w}}$ (measured by GPC), a straight line was obtained and a new value of *a* was obtained from the slope of the line. The procedure was repeated until two successive values of *a* differed by less than 0.001. The final values of q_{MHS} for PHA samples (S1~S8) with narrow MWD were tabulated in Table 3 and the average value of q_{MHS} was 0.980. The plot of ($\ln[\eta]$-$\ln q_{\mathrm{MHS}}$) versus $\log M_{\mathrm{w}}$ was shown in Fig. 4. This plot yields a straight line (R^2=0.997) whose slope and intercept provided the constants *a* and *K*, respectively. Therefore, we can get the MHS equations for the PHA samples (1000-10000) :

$$
\begin{aligned}
[\eta] &= 7.686\times10^{-4} M_{v}^{\ 0.6564} = 7.686\times10^{-4} q_{\mathrm{MHS}} M_{\mathrm{w}}^{\ 0.6564} \\
&= 7.531\times10^{-4} M_{\mathrm{w}}^{\ 0.6564}
\end{aligned}
\qquad (27)
$$

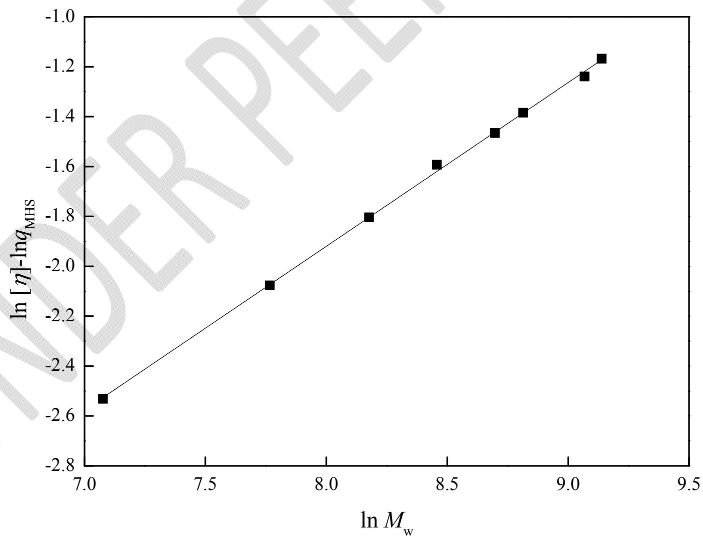

Fig.4. Relation of $\ln[\eta]$ - $\ln q_{\mathrm{MHS}}$ and $\ln M_{\mathrm{w}}$ for S1~S8 in THF at 25□

Table 3. Polydispersity correction factor q_{MHS} for S1~S8

Sample	M_w (g/mol)	M_ν (g/mol)	q_{MHS}
S1	1184	1180	0.981
S2	2360	2256	0.983
S3	3556	3401	0.980
S4	4721	4484	0.976
S5	6090	5676	0.980
S6	6726	6670	0.987
S7	8676	8404	0.973
S8	9423	9266	0.985

From eq. (27), it can be seen that the values of characteristic parameters a of M_n, M_ν and M_w are equal for the PHA samples with narrow MWD, and the values of K are slightly different. The value of a (0.6564) is between 0.5 and 1, indicating that there is a strong two-stage inertial force between PHA and THF. Therefore, THF is a benign solvent for the PHA samples. The characteristic parameters K of M_w and M_ν are nearly equal, which indicates that the multi-dispersion correction factor q_{MHS} of PHA (MWD=1.103-1.216) has slightly effect on the MHS equation when the molecular weight range is less than 10000.

4. Summary

In this work, the poly(Hexanediol adipate) (PHA) samples (S1~S8) with the narrow MWD (1.103-1.216) were prepared. The molecular weight of S1~S8 were determined by GPC (M_{n}, M_{ν} and M_{w}) and the end-group analysis method(M_{n}). The intrinsic viscosity $[\eta]$ of the samples in THF solvents under 25 □ was determined by dilution extrapolation method and one-point method, respectively. . This study resulted in the following MHS equations for PHA having narrow MWD in the M_{n} range of 1000~10000:

$$\begin{aligned}[\eta] &= 8.268\times10^{-4} M_{\mathrm{n}}^{\ 0.6564} \\ &= 7.686\times10^{-4} M_{\nu}^{\ 0.6564} = 7.686\times10^{-4} q_{\mathrm{MHS}} M_{\mathrm{w}}^{\ 0.6564} \\ &= 7.531\times10^{-4} M_{\mathrm{w}}^{\ 0.6564}\end{aligned}$$

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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