Intrinsic Viscosity-molecular Weight Relationship of Poly (Hexanediol Adipate)

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Authors’ contributions

This work was carried out in collaboration among all authors. Authors JL, ZZ and WX designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors DH and BT managed the analyses of the study. Author ZZ managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

In this work, a series of poly(Hexanediol adipate)(PHA) samples (10³ < Mn < 10⁴) with narrow molecular weight distribution were prepared by the polymerization between adilic acid and 1,6-hexandiol. End-group analysis was applied to determine the number average molecular weight (Mn) of PHA. Gel permeation chromatography (GPC) was employed to obtain the average molecular weights (Mn, Mv, Mw). 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. 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.

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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 crystalization rate of PUR has a significant effect on the bonding cure rate. There are many traditional methods to determine the molecular weight of polyester polyol, but only viscosity method to determine $M_n$ can satisfy the requirements. Ajaya Bhattarai determined the molecular weight of sodium polystyrene-sulphonate from viscosity measurement [3].

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 in the present research work. The intrinsic viscosity ($[\eta]$) of the samples dissolved in tetrahydrofuran (THF) were determined by the dilution extrapolation method and the one-point method. According to Mark-Houwink-Sakurada (MHS) [4,5,6] equation, the relationship between $[\eta]$ and the average molecular weights ($M_n$, $M_w$, $M_v$) 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 measured by Gel-permeation Chromatography (GPC) ($M_n$: number average molecular weight; $M_w$: viscosity average molecular weight; $M_v$: weight-average molecular weight) and end-group analysis ($M_n$).

2.3.1 Gel-permeation chromatography [7,8]

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 ($M_n$, $M_w$, $M_v$) 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 [9]

End group analysis is suitable for determining the molecular weight of a polymer having a $M_w$ 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 [10,11] and described briefly as follows: the PHA 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:

$$A_v (\text{mgKOH/g}) = \frac{M_{\text{KOH}} \times c_{\text{KOH}} \times (V_e - V_s)}{m_s}$$  \hspace{1cm} (1)
Where $M_{\text{KOH}}$ (56.1 g/mol) is the molar mass of KOH, $C_{\text{KOH}}$ 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 Intrinsic Viscosity

The intrinsic viscosity of the PHA sample can be described as follows:

$$\eta_0 = [\eta] + k[\eta]^2 C$$

(5)

$$\ln \eta_t = [\eta] \cdot \beta [\eta]^2 C$$

(6)

Where $k$ and $\beta$ are constants related to temperature and solvent, $C$(g/dL) is the concentration of the polymer solution, the relationship between $[\eta]$ and $\eta_0$ (or $\eta_t$) is defined as follows:

$$[\eta] = \lim_{c \to 0} \frac{\eta_0}{C} = \lim_{c \to 0} \frac{\ln \eta_t}{C}$$

(7)

According to Eqs. (5) and (6), we can get two straight lines by plotting $\eta_0/C \sim C$ and $\ln \eta_t/C \sim C$, 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 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 ($\eta_0$) and the relative viscosity ($\eta_t$) are defined as follows:

$$\eta_0 = \eta - \eta_0 = \frac{t-t_0}{t_0} = \eta_t - 1$$

(4)

Where $\eta$ and $\eta_0$ 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 [13] (or the Kraemer equation [14]) can be used to describe the relationship between $\eta_0$ (or $\eta_t$) and the concentration of the polymer solution as follows:

$$\eta_0/C = [\eta] + k[\eta]^2 C$$

(5)

$$\ln \eta_t/C = [\eta] \cdot \beta [\eta]^2 C$$

(6)

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[15]:

$$[\eta] = \frac{1}{C} \sqrt{\frac{1}{k + \beta} (\eta_0 \ln \eta_0) - \frac{1}{C} \sqrt{2(\eta_0 \ln \eta_0)}}$$

(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:

$$[\eta] = KM_v^a = Kq_{MHS}M_w^a$$

(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 [16,17]:

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RESULTS AND DISCUSSIONS

3.1 The Molecular Weight of Pha

The average molecular weight \(M_n, M_v, M_w\) and MWD \(M_v/M_n\) of the samples (S1~S8) were determined by GPC, and the results are shown in Table 1. From Table 1, the \(M_w/M_v\) 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: 

\[
ARD\% = \frac{1}{8} \sum_{i=1}^{8} \left| \frac{M_{ni}^E - M_{ni}^G}{M_{ni}^G} \right| \times 100\% 
\]  

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

3.2 The Intrinsic Viscosity

The relative viscosity \(\eta_r\) of the samples (S1~S8) dissolved in THF was determined by dilution extrapolation method. The curves of \(\ln \eta_r/C \sim C\) and \(\eta_r/C \sim C\) 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 \(\eta_i\) 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 \(\eta_i'.\) Table 2 lists the \(\eta_i\) and \(\eta_i'\) 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:

\[
ARD = \frac{1}{8} \sum_{i=1}^{8} \left| \frac{\eta_i}{\eta_i'} \right| \times 100\% 
\]  

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>(M_n^G) (g/mol)</th>
<th>(M_v^G) (g/mol)</th>
<th>(M_w^G) (g/mol)</th>
<th>(\frac{M_w^G}{M_n^G})</th>
<th>(M_v^E) (g/mol)</th>
<th>ARD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1028</td>
<td>1180</td>
<td>1184</td>
<td>1.152</td>
<td>1066</td>
<td>3.70</td>
</tr>
<tr>
<td>S2</td>
<td>2080</td>
<td>2256</td>
<td>2360</td>
<td>1.135</td>
<td>2037</td>
<td>2.07</td>
</tr>
<tr>
<td>S3</td>
<td>3081</td>
<td>3410</td>
<td>3556</td>
<td>1.154</td>
<td>3052</td>
<td>0.94</td>
</tr>
<tr>
<td>S4</td>
<td>3951</td>
<td>4484</td>
<td>4710</td>
<td>1.192</td>
<td>3876</td>
<td>1.90</td>
</tr>
<tr>
<td>S5</td>
<td>5174</td>
<td>5676</td>
<td>5986</td>
<td>1.157</td>
<td>5234</td>
<td>1.16</td>
</tr>
<tr>
<td>S6</td>
<td>6098</td>
<td>6670</td>
<td>6726</td>
<td>1.103</td>
<td>6185</td>
<td>1.43</td>
</tr>
<tr>
<td>S7</td>
<td>7135</td>
<td>8404</td>
<td>8767</td>
<td>1.216</td>
<td>7048</td>
<td>1.22</td>
</tr>
<tr>
<td>S8</td>
<td>8354</td>
<td>9266</td>
<td>9315</td>
<td>1.115</td>
<td>8377</td>
<td>0.28</td>
</tr>
</tbody>
</table>

\(G\) determined by GPC; \(^E\) determined by end-group analysis
Fig. 1. Intrinsic viscosity for s2

Table 2. Intrinsic viscosity ([η] and [η’]) for S1 ~ S8 in THF at 298 K

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

Fig. 2. Relation of ln[η] and ln$M_n$ for S1~S8 in THF at 298 K
Fig. 3. Relation of $\ln[\eta]$ and $\ln M_q$ for S1~S8 in THF at 298 K

Fig. 4. Relation of $\ln[\eta]$, $\ln q_{MHS}$ and $\ln M_w$ for S1~S8 in THF at 25°C

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$ (g/mol)</th>
<th>$M_q$ (g/mol)</th>
<th>$q_{MHS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1184</td>
<td>1180</td>
<td>0.981</td>
</tr>
<tr>
<td>S2</td>
<td>2360</td>
<td>2256</td>
<td>0.983</td>
</tr>
<tr>
<td>S3</td>
<td>3556</td>
<td>3401</td>
<td>0.980</td>
</tr>
<tr>
<td>S4</td>
<td>4721</td>
<td>4484</td>
<td>0.976</td>
</tr>
<tr>
<td>S5</td>
<td>6090</td>
<td>5676</td>
<td>0.980</td>
</tr>
<tr>
<td>S6</td>
<td>6726</td>
<td>6670</td>
<td>0.987</td>
</tr>
<tr>
<td>S7</td>
<td>8676</td>
<td>8404</td>
<td>0.973</td>
</tr>
<tr>
<td>S8</td>
<td>9423</td>
<td>9266</td>
<td>0.985</td>
</tr>
</tbody>
</table>
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:

\[
\eta = KM^a
\]  
(22)

After determining the characteristic parameters \( K \) and \( a \), the average molecular weight 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

\[
\ln[\eta] = a \ln M + \ln K
\]  
(23)

3.3.1 Relationship between \([\eta]\) 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 \((M_n=10^5\sim10^6)\) with the narrow MWD is:

\[
[\eta] = 8.268 \times 10^{-4} M_n^{0.6564}
\]  
(24)

3.3.2 Relationship between \([\eta]\) 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 \((1000\sim10000)\) with the narrow distribution is:

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

3.3.3 Relationship between \([\eta]\) and \(M_w\)

The multi-dispersion correction factor \(q_{\text{MHS}}\) in eq. (13) is used to calculate the relationship between \([\eta]\) and \(M_w\). For PHA with narrow MWD, it is assumed that\([19]\):

\[
\frac{M_v}{M_w} = \frac{M_v}{M_n}
\]  
(26)

For computation, Kasaai [20,21] found a simple and practical iterative calculation method. An initial value of \(q_{\text{MHS}}\) was 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 \(\ln q_{\text{MHS}}\) against \(\ln M_w\) (measured by GPC), a straight line was obtained and a new \(a\) was obtained from the slope of the line. The final values of \(q_{\text{MHS}}\) for PHA samples (S1~S8) with narrow MWD were tabulated in Table 3 and the average value of \(q_{\text{MHS}}\) was 0.980. The plot of \(\ln[\eta] - \ln q_{\text{MHS}}\) versus \(\log M_w\) 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):

\[
[\eta] = 7.686 \times 10^{-4} M_w^{0.6564} = 7.686 \times 10^{-4} q_{\text{MHS}}^{0.6564} = 7.531 \times 10^{-4} M_v^{0.6564}
\]  
(27)

From eq. (27), it can be seen that the values of characteristic parameters \(a\) of \(M_n\), \(M_v\) 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 \(M_v\) and \(M_v\) are nearly equal, which indicates that the multi-dispersion correction factor \(q_{\text{MHS}}\) 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 (\(M_n\), \(M_v\) and \(M_w\)) and the end-group analysis method (\(M_q\)). The intrinsic viscosity \([\eta]\) of the samples in THF solvents under 25°C was determined by dilution extrapolation method and one-point method, respectively. This study resulted in the following MHS equations for PHA with narrow MWD in the \(M_w\) range of 1000~10000:

\[
[\eta] = 8.268 \times 10^{-4} M_n^{0.6564} = 7.686 \times 10^{-4} M_v^{0.6564} = 7.531 \times 10^{-4} M_w^{0.6564}
\]
competencies exist.

Authors have declared that no competing interests exist.

References


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