

1 Relationship of intrinsic viscosity to molecular weight for 2 poly(ethylene adipate)

3 ABSTRACT

4 In this work, an accurate and swift method, one-point method, was used to determine the
5 intrinsic viscosity of poly (ethylene adipate) (PEA). On the basis of Mark-Houwink-Sakurada
6 (MHS) equation, the relationship between the intrinsic viscosity and molecular weight was
7 built for PEA ($M_w \leq 11000$) in tetrahydrofuran at 298K. Thus, two series of PEA samples with
8 broad and narrow molecular weight distribution (MWD) were prepared by the polymerization
9 between adipic acid and ethylene glycol. The average molecular weights (M_n , M_v , M_w and M_z)
10 were measured by using Gel-Permeation chromatography (GPC). The constants, a and K of
11 MHS equation for the PEA samples dissolved in tetrahydrofuran at 298K were determined by a
12 numerical method, and the influence of polydispersity correction factor (q_{MHS}) on the
13 relationships were studied for PEA with narrow MWD (1.107-1.219) and broad MWD
14 (1.754-1.872).

15 **Keywords:** One-point method; Poly(ethylene adipate); Intrinsic viscosity; Molecular weight;
16 Mark-Houwink-Sakurada.

17

18 1. INTRODUCTION

19 As one of the main raw materials used in the polyurethane industry, poly (ethylene adipate)
20 (PEA) with different molecular weight is widely used in the production of flexible or rigid
21 polyurethane foam, polyurethane rubber, polyurethane elastomer and hot melt adhesives [1-4].
22 Especially, when used as a raw material for hot melt adhesives, the higher the molecular weight

of PEA, the faster the setting speed of hot melt adhesives [5], and the setting speed can affect the bonding rate of the hot melt adhesives. Thus, it is significant to determine the molecular weight of PEA by an easy and effective method. Han, G. C et. al [6] studied the properties of poly(1,4-butylene adipate). Harris, R. F et. al [7] investigated polyurethane elastomers based on molecular weight advanced poly(ethylene ether carbonate) diols. However, no research work about the properties of PEA has been reported.

Now in the polyurethane industry, many ways including Gel-Permeation chromatography (GPC) [8-9], end-group analysis [10], lighting-scattering [11], H-NMR [12] and viscometry can be used to determine the molecular weight of PEA. But during the polyurethane production, determination of molecular weight (M_n , M_w and M_z) should be fast and simple, and among these methods above, only viscometry can satisfy the requirements.

According to Mark-Houwink-Sakurada (MHS) equation [13-15], the relationship between viscosity-average molecular weight (M_v) and intrinsic viscosity ($[\eta]$) can be described as follows:

$$[\eta] = KM_v^a \quad (1)$$

where K and a are constants for a certain solvent and temperature. By determining $[\eta]$ of PEA samples with different molecular weight, we may obtain the values of K and a .

In the traditional way, the intrinsic viscosity of polymer is determined by dilution extrapolation method which means we need to determine the specific viscosity of the polymer with four different concentrations for each sample. Cheng, R.Y et. al [16] proposed an accurate and swift method (one-point method) for determining the intrinsic viscosity of polymer samples.

44 Thus, in this work, two series of PEA samples with broad and narrow MWD were
45 prepared by the polymerization of adipic acid and ethylene glycol. GPC was used to determine
46 the molecular weight of the samples. The intrinsic viscosities of the PEA samples dissolved in
47 tetrahydrofuran at 298K were determined by one-point method and verified by the dilution
48 extrapolation method. Lastly, the MHS constants (K and a) for PEA were obtained.

49

50 **2. EXPERIMENTAL**

51 **2.1 Materials**

52 The PEA samples were prepared by the polycondensation between adipic acid and
53 ethylene glycol. Adipic acid (Sinopharm), Ethylene Glycol (Wuxi Jani chemical Co. LTD) are
54 all of chemically pure-grade. Tetrahydrofuran is all of analytical grade. Distilled water was
55 also used.

56 **2.2 Synthesis of PEA**

57 The synthesis of PEA consists of two main stages: esterification and polymerization.

58 In the first stage, the esterification reaction of adipic acid and ethylene glycol (molar
59 ratio=1:1.2~1.4) was carried out at the temperature of 413K-423K in a 250 ml four-neck
60 flask (200rpm) which was equipped with a single-blade, a platinum sensor and a fractionating
61 column allowing the withdrawal of water during the reaction. Nitrogen (50ml/min) was
62 continuously bubbled through the reactor for the furthest remove of water from the mixture.
63 The reactor was heated with the oil jacket, and the reaction temperature was controlled
64 automatically by adjusting the oil temperature which was maintained within $\pm 0.5K$.

65 After the esterification reaction of 3 to 4 hours, the polymerization reaction was started by

66 raising the reaction temperature to 493K-503K via temperature programmed mode at 2.66kPa.
67 The polymerization reaction lasted for about 8 hours until the designed molecular weight was
68 obtained. Then the products were extracted by multistage precipitation fractionation [17] to
69 obtain the PEA samples with broad and narrow MWD.

70 **2.3 Gel-Permeation chromatography**

71 A GPC equipment (Waters-1515) connected to a refractive index detector was used to
72 determine the average molecular weights (M_n , M_v , M_w and M_z) of the PEA samples. Separation
73 was carried out at 303K using tetrahydrofuran of chromatographic grade as eluent with a flow
74 rate of 1 mL/min. The average molecular weights and areas of fractions of various molecular
75 weights were calculated with Breeze 2 software.

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77 **2.4 Intrinsic viscosity**

78 In this work, the intrinsic viscosities of PEA samples were measured by the Dilution
79 extrapolation method and the one-point method respectively.

80 **2.4.1 Dilution extrapolation method**

81 The intrinsic viscosity of PEA samples dissolved in tetrahydrofuran at 298K was
82 measured in the capillary of the dilution type by extrapolation to zero concentration of specific
83 viscosity measurements obtained at four different concentration levels viscometer (0.4-0.5mm)
84 and the relationship of the PEA solution concentration with the viscosity was analyzed by
85 dilution extrapolation method.

86 **2.4.2 One-point method**

87 According to the empirical formula proposed by Cheng, R.Y et. al [16], the intrinsic

viscosity can be obtained as follows:

$$[\eta] = [2(\eta_{sp} - \ln \eta_r)]^{\frac{1}{2}}/C \quad (2)$$

Where η_r is the relative viscosity (dL/g), $\eta_{sp} = \eta_r - 1$ is the specific viscosity(dL/g), C is the PEA solution concentration (g/dL)

2.5 Polydispersity correction factor (q_{MHS})

Generally, M_v is not experimentally accessible, and in many reports, average molecular weights (M_n , M_w and M_z) are used in the MHS equation instead of M_v . MHS equation can be modified [18,19] as follows:

$$[\eta] = KM_v^a = K(M_v/M_w)^a M_w^a = Kq_{MHS}M_w^a \quad (3)$$

Where q_{MHS} and $(M_v/M_w)^a$ are polydispersity correction factors. The value of q_{MHS} is a statistical function of MWD and it can be calculated [20-22] as follows:

$$[\eta] = (M_w/M_n)^b (M_z/M_w)^c \quad (4)$$

Where b and c can be calculated [22, 23] as follows:

$$c = 0.113957 - 0.844597a - 0.730956a^2 \quad (5)$$

$$b = k_1 + k_2[(M_z/M_w) - 1]^{k_3} \quad (6)$$

$$k_1 = 0.048663 - 0.265996a + 0.364119a^2 - 0.146682 a^3 \quad (7)$$

$$k_2 = -0.096601 + 0.1803a - 0.084709a^2 \quad (8)$$

$$k_3 = -0.252499 + 2.31988a - 0.889977a^2 \quad (9)$$

In the light of 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 DISCUSSION

3.1 Molecular weight

The values of M_n , M_v and M_w for the samples 1-7 (PEA with narrow MWD) and that of M_n , M_v , M_w and M_z for samples 8-14 (PEA with broad MWD) which were determined by GPC were shown in Table 1 and Table 2 respectively.

3.2 Intrinsic viscosity

Relative viscosity (η_r) was measured by a capillary viscometer which was maintained at $298 \pm 0.1\text{K}$ using a circulating water bath. Stock solution (1g/dL) was diluted by pure solvent to generate a range of concentrations down to 0.4g/dL. In the usual fashion, relative viscosities were derived as the efflux time of the polymer solution (t_0) divided by that of the pure solvent (t) and the specific viscosity (η_{sp}) was $\eta_r - 1$. Data for $\ln \eta_r / C$ and η_{sp} / C were plotted and regressed (e.g., see Figure 1) to provide the intrinsic viscosity ($[\eta]'$) as the intercept [24]. The values of $[\eta]'$ were listed in Table 1 and 2. According to Eq. (2), relating η_r , η_{sp} with the solution concentration (C), the values of intrinsic viscosities determined by one-point method ($[\eta]$) can be obtained and listed in Table 1 and 2, from which it can be seen that the values of absolute deviation (AD%) are less than 1%, indicating that one-point method can be used to determine the intrinsic viscosity of PEA samples in tetrahydrofuran accurately and fleetly. The AD% is defined as follows:

$$\text{AD\%} = \frac{|[\eta] - [\eta]'}{[\eta]'} \times 100\% \quad (10)$$

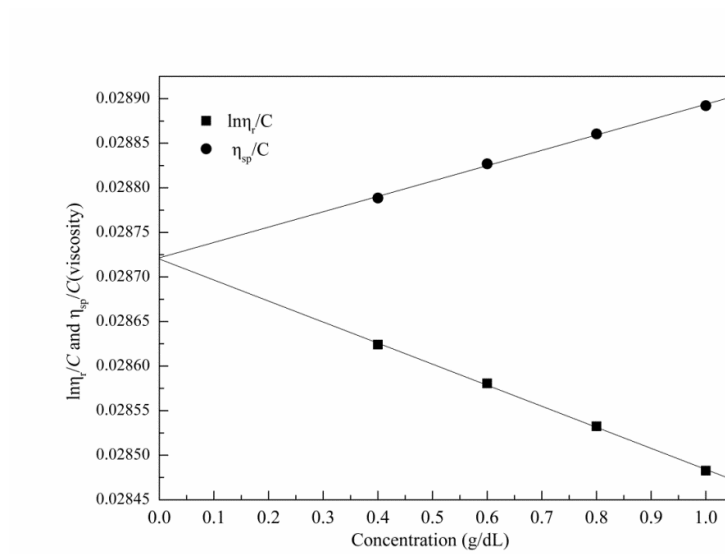


Fig. 1. Intrinsic viscosity for PEA where $M_n = 4454$.

Table 1. Average molecular weights M_n , M_w , M_w/M_n and intrinsic viscosity ($[\eta]'$ and $[\eta]$) of PEA samples with narrow MWD.

Sample	M_n	M_v	M_w	$\frac{M_w}{M_n}$	$[\eta]'$	$[\eta]$	AD
	g/mol	g/mol	g/mol		dL/g	dL/g	
1	1067	1191	1281	1.201	0.00851	0.00849	0.24
2	2109	2440	2335	1.107	0.01563	0.01564	0.06
3	2989	3602	3411	1.141	0.02171	0.02168	0.14
4	3788	4318	4618	1.219	0.02537	0.02539	0.079
5	4454	5135	5176	1.162	0.02872	0.02865	0.24
6	5536	6185	6614	1.195	0.03430	0.03429	0.029
7	6453	7372	7298	1.131	0.03983	0.03980	0.07

127

Table 2. Average molecular weights M_n , M_v , M_w , M_z , M_w/M_n and intrinsic viscosity ($[\eta]'$ and $[\eta]$) of PEA samples with broad MWD.

Sample	M_n	M_v	M_w	M_z	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	$[\eta]'$	$[\eta]$	AD
	g/mol	g/mol	g/mol	g/mol			dL/g	dL/g	%
8	1927	2633	3381	5962	1.755	1.763	0.01481	0.01479	0.14
9	2359	3414	4412	8525	1.870	1.932	0.01792	0.01797	0.28
10	3162	4834	5913	9954	1.872	1.684	0.02316	0.02314	0.09
11	3918	5780	7089	13985	1.809	1.973	0.02631	0.02628	0.15
12	4915	6970	8621	16339	1.754	1.895	0.03010	0.03007	0.1
13	5213	7400	9641	16864	1.849	1.749	0.03131	0.03127	0.13
14	5916	8491	10997	20485	1.859	1.863	0.03520	0.03528	0.23

128

129 3.3 Correction establishment

130 3.3.1 PEA with narrow MWD

131 Figure 2 shows the plot of $\ln \eta$ versus $\log M_n$ for PEA samples with narrow MWD, from
 132 which a straight line can be obtained. The values of a and K were obtained from the slope and
 133 intercept of the line respectively. Then the following equation was obtained:

$$[\eta] = 2.36 \times 10^{-5} M_n^{0.8469} \quad (11)$$

134 The polydispersity correction factor q_{MHS} is used to calculate the viscometric constants a
 135 and K . According to the iterative procedure proposed by Kasaai [11], the value of q_{MHS} was
 136 first calculated for each sample by assuming a as equal to 0.8469 (obtained from Eq. (11)) and
 137 the polydispersity obeys Eq. (11) [24] as follows:

$$M_w/M_n = M_z/M_w \quad (12)$$

138

Table 3. Polydispersity correction factor, q_{MHS} , for each PEA samples.

Narrow MWD		Broad MWD	
Sample	q_{MHS}	Sample	q_{MHS}
1	0.985	8	0.931
2	0.992	9	0.919
3	0.993	10	0.936
4	0.989	11	0.919
5	0.992	12	0.923
6	0.992	13	0.932
7	0.995	14	0.925

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By plotting $(\log[\eta] - \log q_{MHS})$ versus $\log M_w$ (measured by GPC) for PEA samples

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with narrow MWD, a straight line was obtained and a new value of a was obtained from the

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slope of the line. The procedure was repeated until two successive values of a differed by less

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than 0.001. The values of q_{MHS} for PEA samples with narrow MWD were listed in Table 3

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and the average value of q_{MHS} is 0.991. Then the plot of $(\log[\eta] - \log q_{MHS})$ versus $\log M_w$

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was shown in Figure 3, and the values of constants a and K were obtained from the slope and

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intercept respectively. The MHS equations for PEA samples with narrow MWD in the M_w

146

range of 1000-7500 were obtained as follows:

$$[\eta] = 2.116 \times 10^{-5} M_v^{0.8469} = 2.116 \times 10^{-5} q_{MHS} M_w^{0.8469}$$

147

$$= 2.097 \times 10^{-5} M_w^{0.8469} \quad (13)$$

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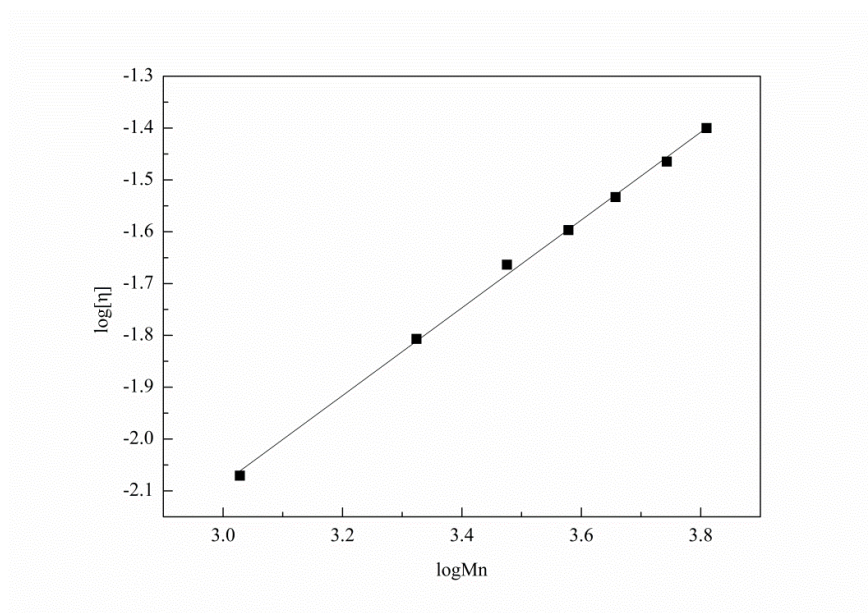


Fig.2. Relation of $\log \eta$ and $\log M_n$ for PEA samples with narrow MWD in tetrahydrofuran at 298K

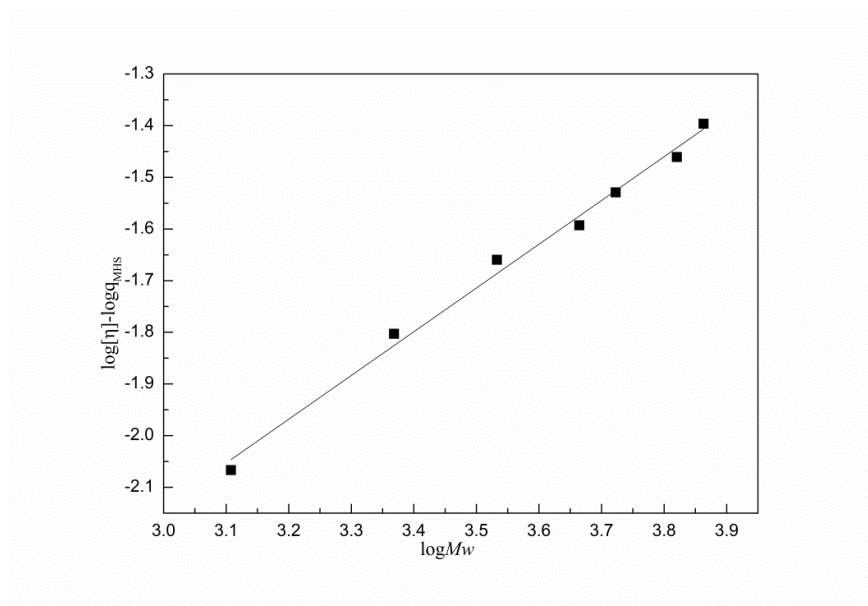
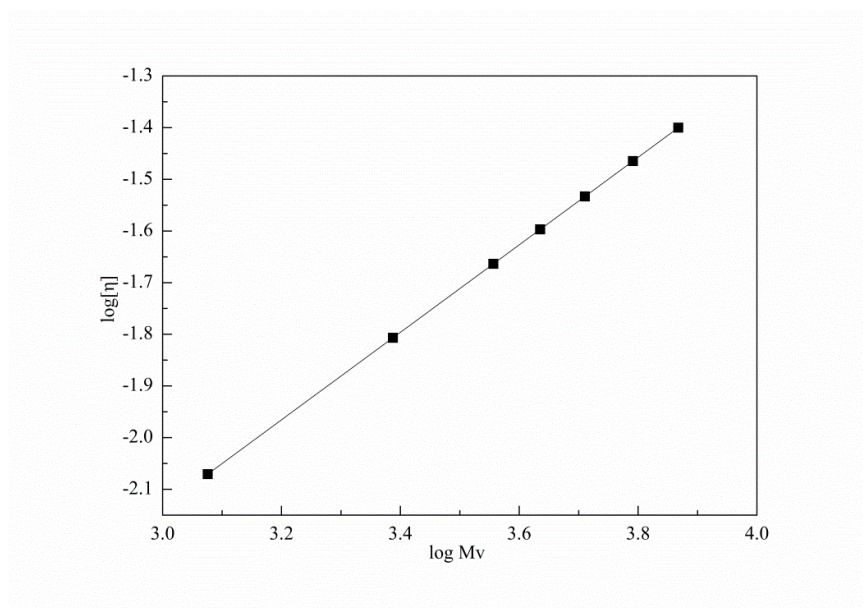


Fig. 3. Relation of $(\log \eta - \log q_{MHS})$ and $\log M_w$ for PEA samples with narrow MWD in Tetrahydrofuran at 298K

Based on Eq. (3), the plot of $\log \eta$ versus $\log M_v$ was shown in Figure 4, a straight line was obtained. The values of a and K were respectively obtained from the slope and intercept of the line to be 0.8469 and 2.116×10^{-5} dL/g, which are in excellent agreement with the results above.

157 From Eqs. (11) and (13), it can be seen that the values of a for M_n , M_w and M_v are
 158 uniform. The high value of a (> 0.5) demonstrates that the secondary force between the
 159 polymer and the solvent molecule is strong. Thus, tetrahydrofuran is a favorable solvent for the
 160 PEAs. Besides, the values of K are the same, indicating that the polydispersity correction factor
 161 (q_{MHS}), has little influence on the relationship of intrinsic viscosity to molecular weight with
 162 narrow MWD.



163
 164 **Fig. 4. Relation of $\log[\eta]$ and $\log M_v$ for PEA samples with narrow MWD in Tetrahydrofuran at 298K**

165
 166 **3.3.2 PEA with broad MWD**

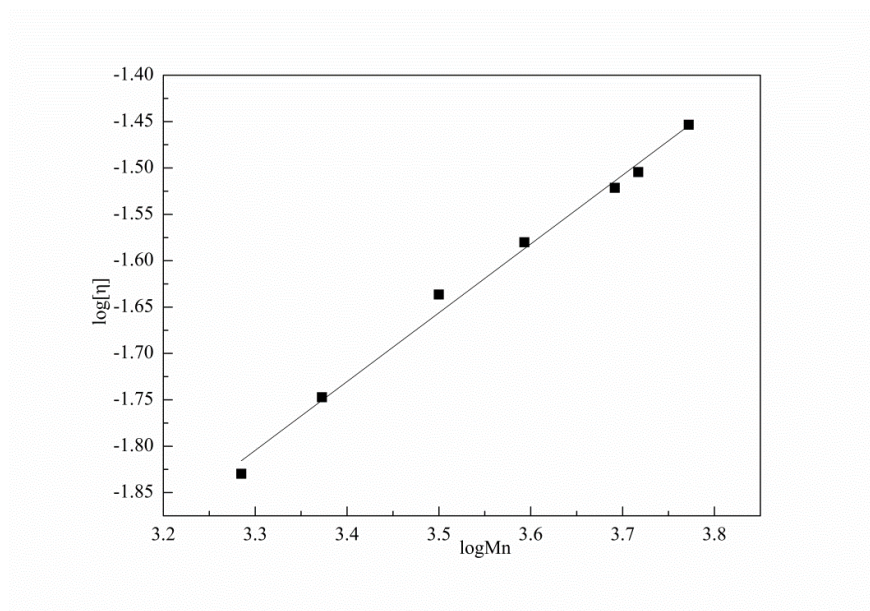
167 Figure 5 shows $\ln \eta$ versus $\log M_n$ for PEA samples with broad MWD, which yielded a
 168 straight line. The corresponding MHS equation can be obtained as follows:

$$[\eta] = 5.589 \times 10^{-5} M_n^{0.7419} \quad (14)$$

169 The values of a and K for PEA with broad MWD were determined by the interactive
 170 procedure described above. The initial value of q_{MHS} of each PEA sample was measured by

171 using the value of a in Eq. (14). The final values of q_{MHS} were obtained and listed in Table 3,
 172 the average value of q_{MHS} was 0.926. Figure 6 shows the plot of $(\log[\eta] - \log q_{MHS})$ versus
 173 $\log M_w$ which yielded a straight line, and the values of a and K were obtained from the slope
 174 and the intercept of this line. The MHS equations for PEA samples with broad MWD in the
 175 M_w range of 1000-10000 were obtained as follows:

$$\begin{aligned}
 [\eta] &= 4.512 \times 10^{-5} M_v^{0.7330} = 4.512 \times 10^{-5} q_{MHS} M_w^{0.7330} \\
 &= 4.178 \times 10^{-5} M_w^{0.7330}
 \end{aligned}
 \tag{15}$$



177

178 **Fig. 5. Relation of $\log \eta$ and $\log M_n$ for PEA samples with broad MWD in tetrahydrofuran at 298K**

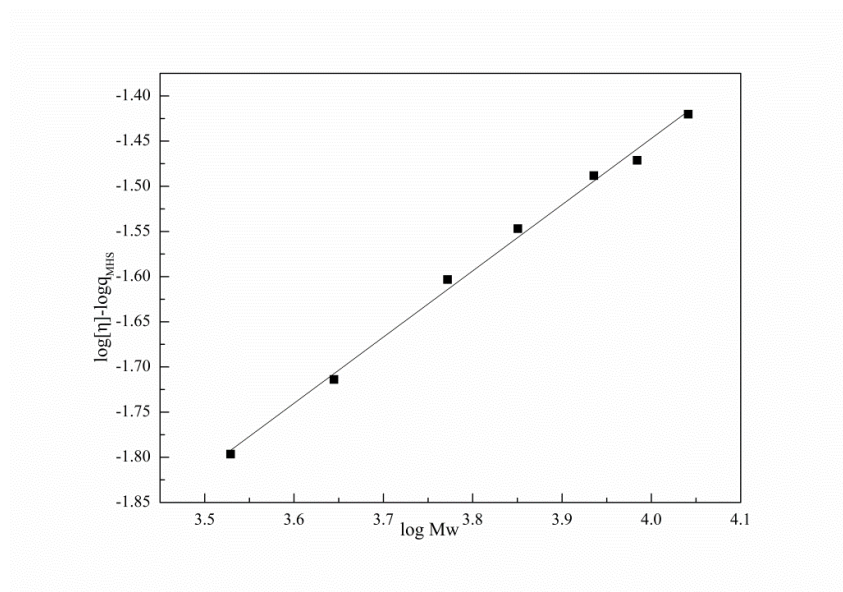


Fig. 6. Relation of $(\log[\eta] - \log q_{MHS})$ and $\log M_w$ for PEA samples with narrow MWD in Tetrahydrofuran at 298K

By plotting $\log \eta$ versus $\log M_v$ for PEA samples with broad MWD, a straight line was obtained as shown in Figure 7, the values of a and K were obtained as 0.733 and 4.603×10^{-5} dL/g, which are in excellent agreement with the results above.

According to Eqs. (14) and (15), it can be found that the polydispersity corresponding correction factor, q_{MHS} , has a great influence on the relationship of intrinsic viscosity to molecular weight for PEA with broad MWD.

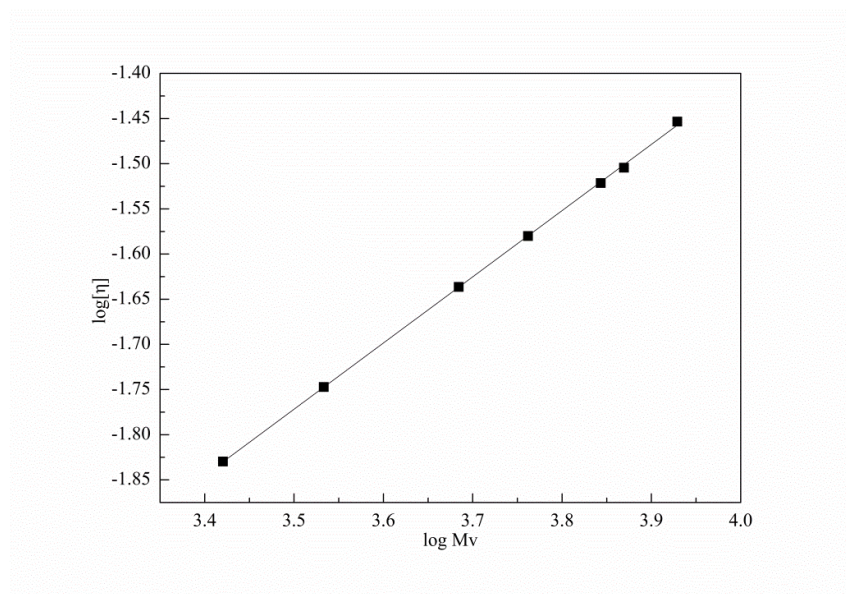


Fig. 7. Relation of $\log[\eta]$ and $\log M_v$ for PEA samples with broad MWD in Tetrahydrofuran at 298K

4. CONCLUSION

In this work, two series of PEA samples with narrow MWD (1.107-1.219) and broad MWD (1.754-1.872) were prepared. Average molecular weights (M_n , M_v , M_w and M_z) were determined by Gel-Permeation chromatography (GPC). The intrinsic viscosity of the PEA samples dissolved in tetrahydrofuran at 298K were determined by one-point method and the dilution extrapolation method respectively, the results demonstrate that one-point method can be used for determining the intrinsic viscosity of PEA samples. The MHS equations for PEA samples in this study were obtained as follows:

$$[\eta] = 2.116 \times 10^{-5} M_v^{0.8469} = 2.116 \times 10^{-5} q_{MHS} M_w^{0.8469}$$

$$= 2.097 \times 10^{-5} M_w^{0.8469} \quad (\text{Narrow MWD})$$

$$[\eta] = 4.512 \times 10^{-5} M_v^{0.7330} = 4.512 \times 10^{-5} q_{MHS} M_w^{0.7330}$$

$$= 4.178 \times 10^{-5} M_w^{0.7330} \quad (\text{Broad MWD})$$

199 **Nomenclature**

200	PEA	poly(ethylene adipate)
201	MWD	molecular weight distribution
202	q_{MHS}	polydispersity correction factor
203	a	viscometric constants
204	K	viscometric constants (dL/g)
205	M_n	average molecular weight (g/mol)
206	M_z	average molecular weight (g/mol)
207	M_w	average molecular weight (g/mol)
208	M_v	viscosity-average molecular weight (g/mol)
209	$[\eta]$	intrinsic viscosity (dL/g)
210	$[\eta_r]$	relative viscosity (dL/g)
211	η_{sp}	specific viscosity(dL/g)
212	C	PEA solution concentration (g/dL)
213	AD	absolute deviation (%)

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