



Synthesis and Intrinsic Viscosity-molecular Weight Relationship of Poly(ethylene adipate)

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Authors' contributions

This work was carried out in collaboration between all authors. Authors LC and WX designed the study. Author LC performed the experiment and wrote the first draft of the manuscript. Author ZZ managed the analyses of the study and revised the first draft. All authors read and approved the final manuscript.

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ABSTRACT

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

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

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NOMENCLATURES

PEA : Poly(ethylene adipate)
 MWD : Molecular weight distribution
 q_{MHS} : Polydispersity correction factor
 a : Viscometric constants
 K : Viscometric constants (dL/g)
 M_n : Average molecular weight (g/mol)
 M_z : Average molecular weight (g/mol)
 M_w : Average molecular weight (g/mol)
 M_v : Viscosity-average molecular weight (g/mol)
 $[\eta]$: Intrinsic viscosity (dL/g)
 $[\eta_r]$: Relative viscosity (dL/g)
 η_{sp} : Specific viscosity (dL/g)
 C : PEA solution concentration (g/dL)
 AD : Absolute deviation (%)

1. INTRODUCTION

As one of the main raw materials used in the polyurethane industry, poly(ethylene adipate) (PEA) with different molecular weight is widely used in the production of flexible or rigid polyurethane foam, polyurethane rubber, polyurethane elastomer and hot melt adhesives [1-4]. 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 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.

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

2. EXPERIMENTAL

2.1 Materials

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

2.2 Synthesis of PEA

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

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

After the esterification reaction of 3 to 4 hours, the polymerization reaction was started by raising the reaction temperature to 493K-503K via temperature programmed mode at 2.66k Pa. The polymerization reaction lasted for about 8 hours until the designed molecular weight was obtained. Then the products were extracted by multistage precipitation fractionation [17] to obtain the PEA samples with broad and narrow MWD.

2.3 Gel-permeation Chromatography

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

2.4 Intrinsic Viscosity

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

2.4.1 Dilution extrapolation method

The intrinsic viscosity of PEA samples dissolved in tetrahydrofuran 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 of the PEA solution concentration with the viscosity was analyzed by dilution extrapolation method.

2.4.2 One-point method

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, $\eta_{sp} = \eta_r - 1$ is the specific viscosity, 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:

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

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

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

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

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

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) were determined and 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 $298 \pm 0.1K$ using a circulating water bath. Stock solution (1 g/dL) was diluted by pure solvent to generate a range of concentrations down to 0.4 g/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 Fig. 1) to provide the intrinsic viscosity ($[\eta]'$) as the intercept [24]. The values of $[\eta]'$ were listed in Tables 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 Tables 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 an accurately and fleetly. The AD % is defined as follows:

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

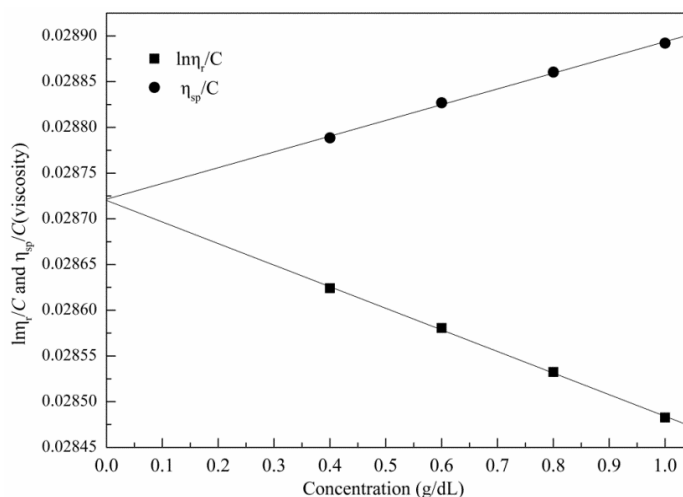


Fig. 1. Intrinsic viscosity for PEA where $M_n = 4454$

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 g/mol	M_v g/mol	M_w g/mol	$\frac{M_w}{M_n}$	$[\eta]'$ dL/g	$[\eta]$ dL/g	AD %
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

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

Sample	M_n g/mol	M_v g/mol	M_w g/mol	M_z g/mol	$\frac{M_w}{M_n}$	$\frac{M_z}{M_w}$	$[\eta]'$ dL/g	$[\eta]$ dL/g	AD %
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

3.3 Correction Establishment

3.3.1 PEA with narrow MWD

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

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

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

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

By plotting $(\log[\eta] - \log q_{MHS})$ versus $\log M_w$ for PEA samples with narrow MWD, 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 values of q_{MHS} for PEA samples with narrow MWD were listed in Table 3 and the average value of q_{MHS} is 0.991. Then the plot of $(\log[\eta] - \log q_{MHS})$ versus $\log M_w$ was shown in Fig. 3, and the values of constants a and K were obtained from the slope and intercept respectively. The MHS equations for PEA

samples with narrow MWD in the M_w range of 1000-7500 were obtained as follows:

$$[\eta] = 2.116 \times 10^{-5} M_w^{0.8469} = 2.116 \times 10^{-5} q_{MHS} M_w^{0.8469} = 2.097 \times 10^{-5} M_w^{0.8469} \quad (13)$$

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

Based on Eq. (3), the plot of $\log \eta$ versus $\log M_v$ was shown in Fig. 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.

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

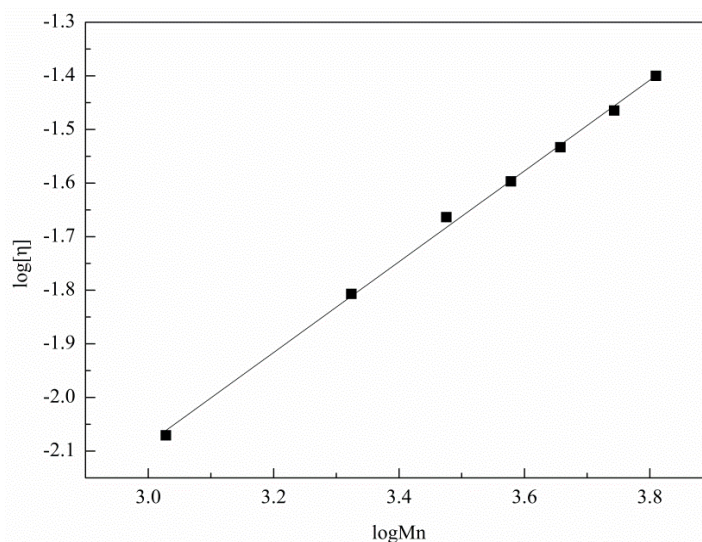


Fig. 2. Relation of $\log \eta$ and $\log M_n$ for PEA samples with narrow MWD in tetrahydrofuran at 298K

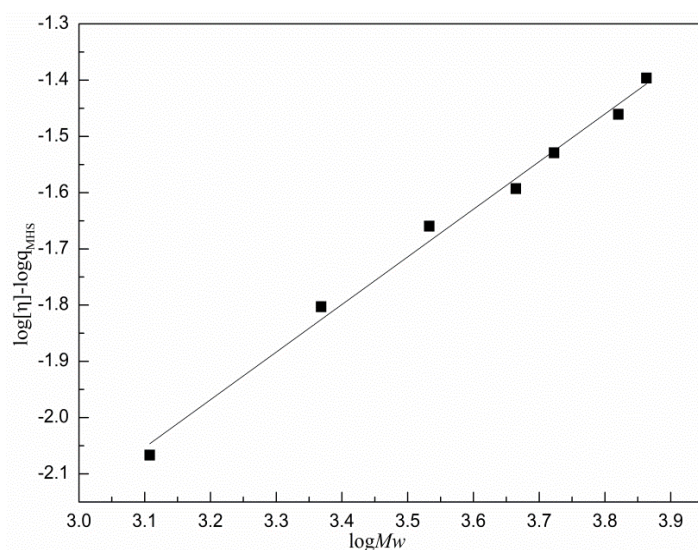


Fig. 3. Relation of $(\log[\eta] - \log q_{MHS})$ and $\log M_w$ for PEA samples with narrow MWD in Tetrahydrofuran at 298K

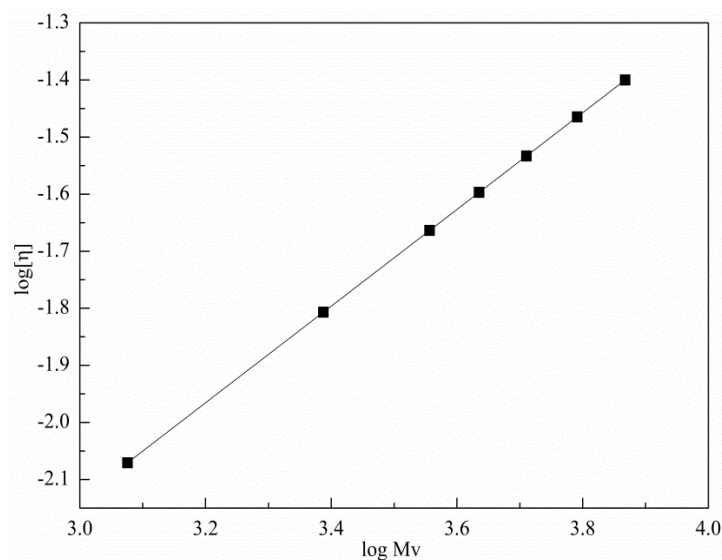


Fig. 4. Relation of $\log[\eta]$ and $\log M_v$ for PEA samples with narrow MWD in Tetrahydrofuran at 298K

3.3.2 PEA with broad MWD

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

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

The values of a and K for PEA with broad MWD were determined by the interactive procedure

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

$$[\eta] = 4.512 \times 10^{-5} M_v^{0.7330} = 4.512 \times 10^{-5} q_{MHS} M_w^{0.7330} \\ = 4.178 \times 10^{-5} M_w^{0.7330} \quad (15)$$

By plotting $\log \eta$ versus $\log M_v$ for PEA samples with broad MWD, a straight line was obtained as shown in Fig. 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 correspond correction factor, q_{MHS} , has a great influence on the relationship of intrinsic viscosity to molecular weight for PEA with broad MWD.

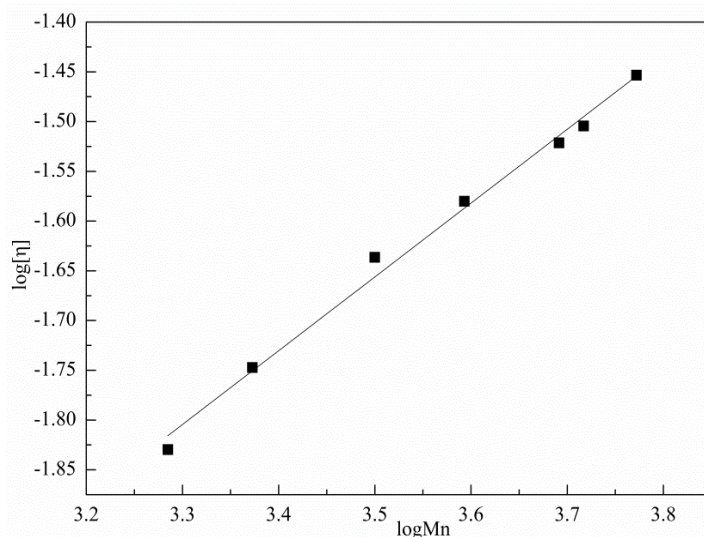


Fig. 5. Relation of $\log \eta$ and $\log M_n$ for PEA samples with broad MWD in tetrahydrofuran at 298K

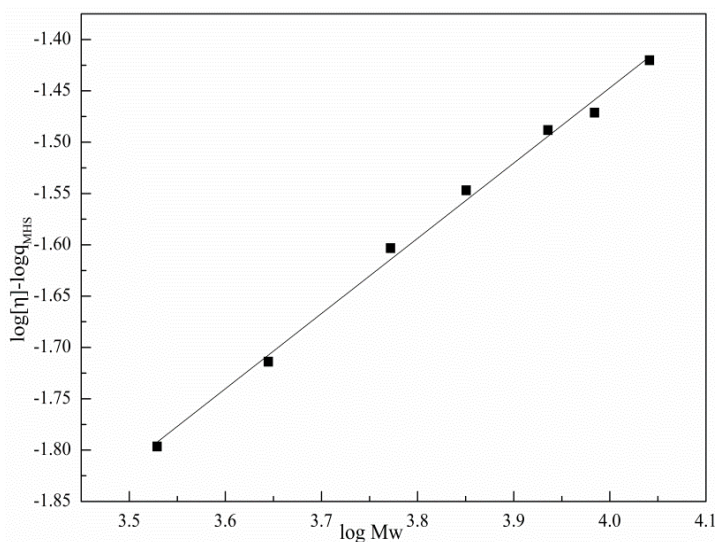


Fig. 6. Relation of $(\log [\eta] - \log q_{MHS})$ and $\log M_w$ for PEA samples with narrow MWD in Tetrahydrofuran at 298K

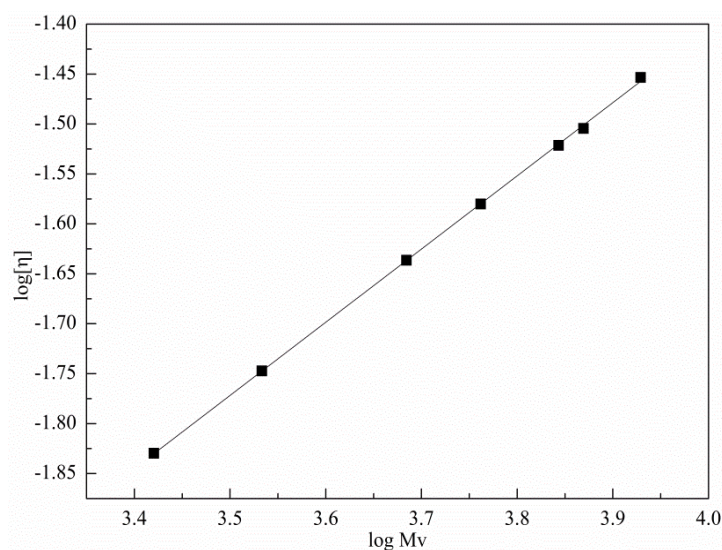


Fig. 7. Relation of $\log[\eta]$ and $\log M_v$ for PEA samples with broad MWD in Tetrahydrofuran at 298K

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:

$$[\eta] = 2.116 \times 10^{-5} M_v^{0.8469} = 2.116 \times 10^{-5} q_{MHS} M_w^{0.8469} \\ = 2.097 \times 10^{-5} M_w^{0.8469} \quad (\text{Narrow MWD})$$

$$[\eta] = 4.512 \times 10^{-5} M_v^{0.7330} = 4.512 \times 10^{-5} q_{MHS} M_w^{0.7330} \\ = 4.178 \times 10^{-5} M_w^{0.7330} \quad (\text{Broad MWD})$$

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Lee SY, Lee JS, Kim BK. Preparation and Properties of Water-borne Polyurethanes. *Polym. Int.* 1997;42:67-76.
2. Chen XD, Zhou NQ, Zhang H. Preparation and properties of cast polyurethane elastomers with molecularly uniform hard segments based on 2,4-toluene diisocyanate and 3,5-dimethylthioltoluenediamine. *J. Biomed. Sci. Eng.* 2009;2:245-253.
3. Michael E. Polyester polyols for polyurethane adhesives. *US. Pat.* 2006;205909A1.
4. Li QA, Sun DC. Synthesis and characterization of high solid content aqueous polyurethane dispersion. *J. Appl. Polym. Sci.* 2007;105:2516-2524.
5. James W, Robert S. Fast setting polyurethane hot melt adhesive composition comprising low hydroxyl number/high molecular weight polyester diol. *US. Pat.* 1999;5939488A1.
6. Han GC, Byoung CK, Seung SI. Effect of molecular weight and branch structure on the crystallization and rheological properties of poly (buty 1 ene adipate). *Polym. Eng. Sci.* 2001;41:1133-1139.
7. Harris RF, Joseph MD, Davidson C, Deporter CD, Dais VA. Polyurethane elastomers based on molecular weight advanced poly (ethylene ether carbonate) diols. *J. Appl. Polym. Sci.* 1990;41:487-507.
8. Shah PV, Method for forming a hot melt adhesive. *EP. Pat.* 2002;119106A1.
9. Singley EJ, Danie A, Person D, Beckman EJ. Determination of Mark-Houwink parameters for poly (N-vinylformamide). *J. Polym. Sci. A: Polym. Chem.* 1997;35:2533-2534.

10. Bormanp WHF. Poly (1, 4-butylene terephthlate). J. Appl. Polym. Sci. 1978;22: 2119-2126.
11. Kasaai MR, Arul J, Charlet G. Intrinsic viscosity–molecular weight relationship for chitosan. J. Polym. Sci. B: Polym. Phys. 2000;38:2591-2598.
12. Beuermann S. Homogeneous phase polymerization of vinylidene fluoride in supercritical carbon dioxide.J. Polym. Sci. Part A: Polym. Chem. 2007;45:5626-5635.
13. Flory PJ. Principles of polymer chemistry. Cornell University Press, Ithaca, NY; 1953.
14. Tanford C. Physical chemistry of macromolecules. Wiley, New York; 1961.
15. Sperling LH. Introduction to Physical Polymer Chemistry. Wiley, New York; 1986.
16. Cheng RS. The extrapolation of viscosity data and the viscosity calculated from one solution concentration .Polymer. Commun. (in Chinese). 1960;4:159-163.
17. Penning JP, John MRS. Miscible blends of two crystalline polymers. 1. Phase behavior and miscibility in blends of poly (vinylidene fluoride) and Poly (1, 4-butylene adipate). Macromol. 1996;29:77-83.
18. Bareiss RE. Polymer Handbook, second ed. Wiley Interscience, New York. 1975.
19. Kurata Y, Tsunashima Y, Iwama M, Kamada K. Polymer Handbook, second ed. Wiley Interscience, New York; 1975.
20. Bareiss RE. Polymer Handbook, fourth ed. Wiley-Interscience, New York; 1999.
21. Kurata M, Tsunashima Y. Polymer Handbook, fourth ed. Wiley-Interscience, New York; 1999.
22. Guaita M, Chiantore O, Munari A, Manaresi P, Pilati F, Toselli M. A general intrinsic viscosity-molecular weight relationship for linear polydisperse polymers-3. Applicability to the evaluation of the mark-houwink-sakurada k and a constants. Eur. Polym. J. 1991;27:385-388.
23. ManaresiP, Munari A,Pilati F, Marianucci E.A general intrinsic viscosity-molecular weights relationship for polydisperse polymers. Eur. Polym. J. 1998;24:575-578.
24. Kasaai MR. Intrinsic viscosity–molecular weight relationship and hydrodynamic volume for pullulan. J. Appl. Polym. Sci. 2006;100:4325-4332.

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