

Molecular Characterization of Some Polyethylenes Synthesized by Iranian Petrochemical Industries

Homayoun Hossein Khanli¹, Naser Mohammadi^{2(*)}, Davood Amiri¹ and Mahmood Torabi-Angagi³

(1) Polymer Technology Department, Research Institute of Oil Industries, Rey, Tehran, I.R. Iran

(2) Polymer Engineering Department, Amir Kabir University of Technology, Tehran, I.R. Iran

(3) Chemical Engineering Department, Tehran University, Tehran, I.R. Iran

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ABSTRACT

Molecular characterization of three grades of polyethylene, synthesized by Iranian Petrochemical Industries, was performed by dilute solution viscometry, viscometry at zero shear rate and melt flow index measurements. The results show that for molecular weight measurement with dilute solution viscometry, a threshold elution time of the solvent of 100 s is necessary. Also, the method by which the polymer solution is prepared may affect the value obtained for the average molecular weight. To prevent the molecular weight decrease due to degradation during sample preparation and experimental tests, the residence time of the solution at high temperature should be maintained as short as possible. On the other hand, the molecular weight distribution calculated, based on its relationship with zero shear viscosity and \bar{M}_w , showed comparable agreement with $MF_{1.0} / MF_{2.16}$ for some of the samples.

Key Words: molecular characterization, molecular weight determination, molecular weight distribution, capillarity, hydrodynamic size

INTRODUCTION

Melt rheology of various polyethylenes of various grades depends on at least four factors: molecular weight, molecular weight distribution, branching and its distribution along the polymer chain [1]. On the other hand, the processing of single component and blends of polyethylenes and their final properties are strongly affected by their rheological properties [2].

Therefore, for suitable design of the process

and obtaining the desired final properties, molecular characterization of the polymers is of prime concern.

For determining the molecular weight and its distribution for a polymer, various techniques such as osmometry, light scattering, gel permeation chromatography and dilute solution viscometry can be used [3].

Dilute solution viscometry is one of the most common and cheap techniques. The highest proposed shear rate in dilute viscosity measurement is about 10 s^{-1} , because at higher shear rates the polymer will

(*) To whom correspondence should be addressed. E-mail: mohamadi@cic.aku.ac.ir

be degraded and its rheological properties can be changed [4]. On the other hand, the measurement should be performed at low polymer concentration to forbid polymer chain overlapping which can mislead the measurement to higher molecular weights. The theoretical basis for dilute solution viscometry is plotting the specific viscosity over concentration and the natural logarithm of relative viscosities over concentration against solution concentrations and then extrapolating them to zero concentration based on Huggins of eqn (1) and Kramer's eqns (2) and (3):

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \quad (1)$$

$$\frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2 c \quad (2)$$

The extrapolated quantity of solution viscosity to zero concentration, intrinsic viscosity, based on Mark-Howink-Sakurada relation can be correlated to viscosity average molecular weight:

$$[\eta] = k\bar{M}_v^a \quad (3)$$

In the above equation, $[\eta]$, k and a are intrinsic viscosity, and polymer-solvent constants at certain experimental temperature, respectively. The viscosity average molecular weight, \bar{M}_v , according to definition, depends on molecular weight and its amount for each species:

$$\bar{M}_v = \left[\sum_{i=1}^n w_i \bar{M}_i^a \right]^{1/a} \quad (4)$$

For most polymers, \bar{M}_v is about 10-20% lower than \bar{M}_w [3]. Also, \bar{M}_n can be calculated from the \bar{M}_v of a polymer as shown by eqn (5) [5].

$$\bar{M}_n = \frac{\bar{M}_v}{[\Gamma(2+a)]^{0.5}} \quad (5)$$

The $\Gamma(2+a)$ term is the lambda function of $2+a$.

It should be noted that intrinsic viscosity is

affected by molecular weight and the structure of polymer chain. For example, the presence of short ethyl or butyl branches in low-density polyethylene has a minor effect on viscosity, whereas, the long branches can raise the viscosity of the solution.

Another important factor in determination of the rheological properties of polyethylenes is their molecular weight distribution. The best technique for measuring polydispersity index is by gel permeation chromatography. But it needs special columns and should be run at high temperatures. Another alternative for MWD determination is the application of known correlations between zero shear viscosity of the melt and \bar{M}_z/\bar{M}_w and weight or viscosity average molecular weight [6, 7]:

$$\log \eta_0 = -12.296 + 3.36 \log \bar{M}_w + 0.51 \log \frac{\bar{M}_z}{\bar{M}_w} \quad (6)$$

For determination of η_0 , various techniques such as dynamic viscometry can be applied. However, one simple case is the application of falling ball viscometer to polymer melts.

In this technique, a metallic sphere with known diameter and density is fallen in polymer melt and from its speed measurement, zero shear viscosity can be calculated [8].

$$\eta_0 = \frac{1}{18} \frac{d^2(\rho_s - \rho)g}{v} \left(\frac{1-d/D}{1-0.475d/D} \right)^4 \quad (7)$$

In the above equation, ρ , density of polymer melt; ρ_s , density of sphere; g , gravitational acceleration; v , the speed of falling ball; d , the diameter of

Table 1. The materials and their specifications from suppliers.

Material	Code	Melt flow index	Density (g/mL)
		(g/10 min)	
		2.16 kg	
HDPE	IRAPOL 21 GM.44005	0.5*	0.944
LLDPE	IRAPOL 33-020075	0.7-0.8	0.922
LDPE	H 0075	0.7	0.920

* Measured at 5 kg load.

sphere and D , diameter of the container, respectively.

In this research work, the molecular weight and its distribution are measured for three polyolefins via dilute solution viscometry, falling ball viscometry and Mooney viscometry and results are compared with $MFI_{10} / MFI_{2.16}$ ratio which is another well known criterion for molecular weight distribution of polymeric samples.

EXPERIMENTAL

Three polyethylene samples obtained from Iranian Petrochemical Industries were used in this research work (Table 1). For dissolving the polymers and measuring their dilute solution viscosity, two approaches were adopted. In one approach, a certain amount of polyethylene was added to decalin and the mixture was stored at 135 °C for 8 h to obtain a homogeneous solution. In the second approach, the polyethylene powder was left in decalin for seven days at room temperature and then its temperature was raised to 135 °C in 30 min to reach to a homogeneous solution. After solution preparation, the determination of molecular weight of the samples was performed in dilute solution viscometers by different capillary sizes to define the best solution preparation technique.

The criterion for choosing the best approach is to obtain the highest molecular weight of the sample, after satisfying all the requirements

For determination of zero shear viscosity, η_0 , the falling speed of a metallic sphere with diameter of 9.3 mm in polymer melt at 190 °C in a graduated cylinder with 46.68 mm in diameter was measured.

The density of samples was measured by column densitometry in water and alcohol mixture.

The melt density of samples was measured in capillary rheometer. The weight of the melt filling known volume was used for calculation. The η_0 of the sample with highest viscosity (HDPE) was measured by Mooney viscometer. The measured torque was divided by $\dot{\gamma}$ and used as η_0 , because the disc speed is very low (2RPM).

For determination of the melt flow index of the

samples, the regular ASTM D1238 approach with 2.16 and 10 kg weights were used (Ceast Co., Model T. Q., Italy).

RESULTS AND DISCUSSION

Figure 1 shows the molecular weight of two polyethylene samples as a function of the efflux time of the solvent (a measure of capillary size). As one can observe, with increasing the falling time of the solvent in the capillary, the measured molecular weight increases and then levels off. The low molecular weight of the sample in a larger capillary, shorter efflux time can be attributed to the large error in measurement of elution time. Also, the high shear flow rate in capillary and possible polymer degradation can be an important factor [4]. In relation to the peak in molecular weight as a function of falling time at about 104 s it seems that this point is real. This highest molecular weight of the sample can be attributed to the competition of two molecular degradation mechanisms. With using a capillary with

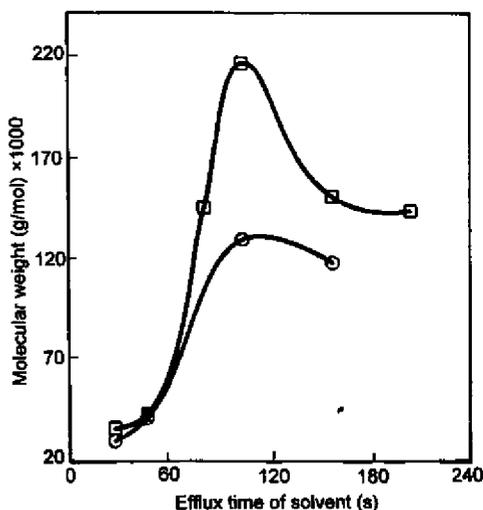


Figure 1. Molecular weight measured via dilute solution viscometry as a function of elution time of the solvent in the capillary for HDPE (\square), and LLDPE (\circ).

smaller diameter, the elution time increases, and consequently the falling speed decreases. Therefore, the degradation via shear rate velocity field diminishes with going to higher elution time. On the other hand, with decreasing the size of the capillary, the ratio of chain size to capillary size decreases and another degradation mechanism, the chain overlap, will be effective. So, the highest molecular weight region is the crossing point of two curves defining the effect of degradation mechanisms.

With comparison of the two curves, one can observe that the safe area for degradation of polymer chain, highest molecular weight region, is more pronounced for HDPE with higher molecular weight. With respect to the curves, a capillary with 100 s for elution time was chosen for molecular weight determination for all samples.

Figure 2 compares the effect of solution preparation approach on molecular weight measured by dilute solution viscometry. As it is observed the shorter time a polymer remains at high temperature, the higher will be its molecular weight. Also, the effect of solution preparation time is weaker for a capillary with bigger diameter. Because the polymer

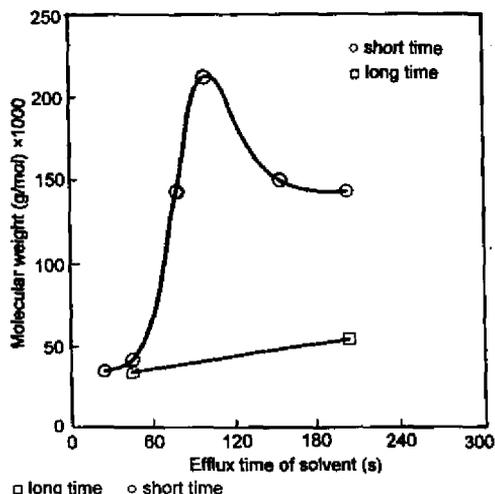


Figure 2. Molecular weight measured by dilute solution viscometry as a function of elution time of the solvent for two preparation approaches.

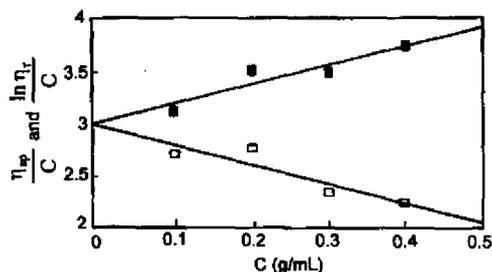


Figure 3. The variation of η_{sp}/c and $\ln \eta_r/c$ as a function of concentration for HDPE in decaline solution at 135 °C.

will be degraded either by high shear field of capillary motion or high temperature residence time for the solution, with going to short residence time for solution preparation and optimum size capillary, the highest molecular weight can be reached. On the other hand, it seems the residence time is the main controlling parameter.

Figure 3 shows the $\ln \eta_r/c$ and η_{sp}/c as function of c for dilute solution viscometry of a PE sample in decalin at 135 °C. It is noticed that, the crossing point of two lines is almost near to the vertical axis and it

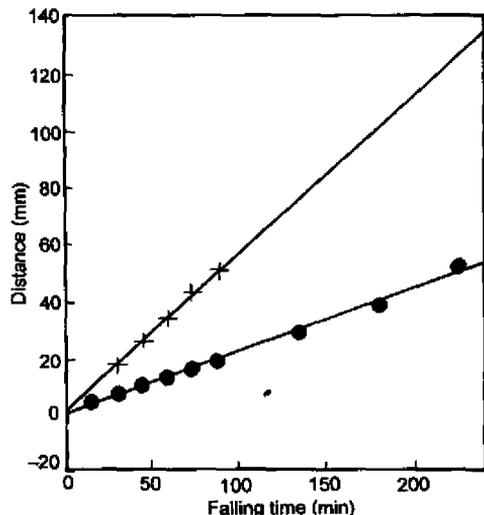


Figure 4. The distance travelled by metallic falling ball in LDPE, •, and LLDPE, +, melt at 190 °C, with time.

Table 2. The characterization results for three polyethylene grades.

Material	MFI (2.16 kg, 190 °C)	Density (g/mL)	\bar{M}_v (g/mol)	$\frac{\bar{M}_z}{\bar{M}_w}$	MFI ₁₀ /MFI _{2.16}
LDPE	0.17*	0.920	137000	29.5	13.06
LLDPE	0.8*	0.922	129000***	7.4	6.87
HDPE	0.13*-0.51**	0.935	215000	2.35	9.2

(*) measured at 190 °C with 2.16 kg load; (**) measured at 190 °C with 5 kg load; (***) measured by k and a of HDPE.

seems that the error for this assumption is less than 10%. Another check for the correctness of the result is that the slope of the η_{sp}/c versus c is positive and for $\ln\eta_r/c$ versus c is negative and total amount of their slopes is about 0.5.

Figure 4 shows the distance that falling sphere travels as a function of time in the melt at 190 °C. The error in the measurement can be ignored and the average speed can be determined from the slope of the best line passing through the results. On the other hand, the MFI of HDPE is so high that the sphere could not fall in its melt. So, for η_0 measurement, the Mooney rheometer was used. In this experiment, the melt viscosity was measured based on Mooney number and then its torque was calculated based on the catalogue of the instrument (Shimadzu Co., SMV-

201, Japan):

$$2000 T = 169.2 M \quad (8)$$

In the above equation, T and M are torque (kgf.cm) and Mooney number, respectively. From the torque, shear stress and from the rotational speed of the disc, the shear rate can be calculated via the known equations for parallel plate rheometer. Since the shear rates are very small, η_0 can be calculated from dividing the shear stress by shear rate.

Table 2 presents the results of dilute solution viscometry, \bar{M}_z/\bar{M}_w , melt flow index ratios and the density of the samples. Unfortunately, the NMR measurements for determination of chain branching density could not be registered, even though the authors tried very hard to perform this experiment. As can be expected, the density of the samples increases by moving to more linear PE chains from LDPE to HDPE. The \bar{M}_z/\bar{M}_w , a measure of polydispersities of samples in LLDPE is almost the same of what has been calculated based on MFI₁₀/MFI_{2.16} criterion. But in two other cases, the differences are large (Figure 5). The differences in polydispersities measured via two approaches can be attributed to the application of the equation of HDPE for all samples and the experience one needs to reach to accurate data. For reaching more accurate data, the known scaling concepts can be applied as well [9].

CONCLUSION

The results of this research work show that with performing some fundamental and inexpensive experiments, valuable data about molecular character-

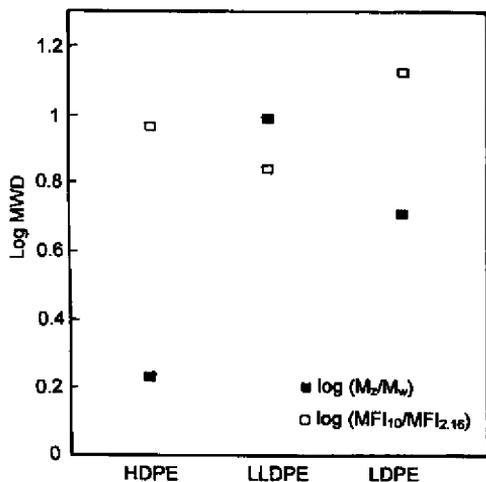


Figure 5. The comparison of two polydispersity indices for three grades of polyethylene.

istics of polymers can be deduced. For example, the $\overline{M}_z/\overline{M}_w$ ratio is almost the same as what one can obtain from $MFI_{1.0}/MFI_{2.16}$ experiment for LLDPE sample. In LDPE and HDPE, the values are too afar, but with conducting more experiments to mastef the experimental approach, it is possible to find solution for the problem.

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