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Structure Rheology of Polyethylene Oxide Solution

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Abstract

Intrinsic viscosities have been studied for polyethylene oxide in water which has wide industrial applications. The polyethylene oxide samples had two different structures, the first one was linear and covers a wide range of molecular weight of 1, 3, 10, 20, 35, 99, 370, 1100, 4600, and 8000 kg/mol and the second one was branched and had molecular weights of 0.55 and 40 kg/mol.

Intrinsic viscosities and Huggins constants have been determined for all types and molecular weights mentioned above at 25ºC using a capillary viscometer. The values of Mark-Houwink parameters (K and a) were equal to 0.0068 ml/g and 0.67 respectively, and have not been published for this range of molecular weight in as yet.

Key Words: Polyethylene Oxide, Intrinsic viscosity, Huggins constants, Mark-Houwink parameters.

Introduction

Polyethylene oxide resins are high molecular weight polymers having the common structure:

$$(OCH_2CH_2)_n$$

In which n, is the degree of polymerization, ranges from 2000 to over 100,000 [1]. With a molecular formula of [2]:

$$C_{2n+2}H_{4n+6}O_{n+2}$$

Low molecular weight (M_{wt} <1,000) PEGs are viscous and colorless liquids, while higher molecular weight PEGs are waxy, white solids with melting points proportional to their molecular weights to an upper limit of about 67°C [3], and a flash point of (182-287°C) [2].

Polyethylene oxide, being a polyether, strongly hydrogen, bonds with water. It is non-ionic and undergoes salting-out effects associated with neutral molecules in solution of high dielectric media. Salting-out effects manifest themselves in depressing the upper temperature limit of solubility, and in the reducing the viscosity of both the dilute and concentrated solutions of the polymers. Poly (ethylene oxide) (PEO) is one of the most intensely studied polymers in current materials science and biotechnology because of not only its unique behaviors in solution but also its wide applications [4, 5]. The key properties of PEO are its a soft semi-crystalline thermoplastic that displays a lot of interesting properties and finds many applications due to the wide range of molecular weight in which it is commercially available

(10^2–$8*10^6$ g/mol), chemical stability, solubility both in water and many organic solvents, non-toxicity, rapid clearance from the body, lack of immunogenicity and a Food and Drug Administration (FDA) approval for internal consumption. Films of high molecular weight PEO are tough, ductile, heat-sealable, and because of their high degree of crystallization, resist well to atmospheric moisture [6].

Additionally, architectures based on nonlinear PEO have recently become a focus of scientific interest, due to their branched structures and unique rheological property [7], and their intriguing potential for biomedical and pharmaceutical applications, for instance as multivalent PEGylation reagents Also, it has recently found increasing use as a conducting medium in light-weight, high energy polymer batteries [8], as well as for solid polymer electrolytes [9]. Star-shaped PEOs bear multiple functional end groups adjustable by the number of arms and thus exhibit higher attachment capacity and higher capability for ion-complication in comparison with their linear analogues, combined with reduced degree of crystallization [10]. Star polymers have attracted much attention because of their branched structures and unique rheological property [11, 12], and a very recent review article summarizes the importance of star-shaped PEOs for a variety of purposes [13].

Two fundamentally different approaches for the synthesis of star polymers can be distinguished: the ‘arm-first’ and the ‘core-first’ procedure. The ‘arm-first’ strategy relies on deactivation of living PEO chains by reaction with multifunctional electrophiles. In this manner well-defined star polymers with defined molecular weight of the arms and predetermined functionality can be synthesized. For instance, grafting onto cyclophosphazenes resulted in six- and twelve-arm PEO stars [14]. Multiarm PEO-stars have also been prepared by attachment of PEO chains to different types of dendrimers. The ‘arm-first’ approach, however, requires additional separation of the resulting star-shaped polymer from the linear ‘arms’, which commonly have to be used in excess. Moreover, the arms in such star polymers can only be functionalized via protected functional initiators. In contrast, by the ‘core-first’ approach the growing polymer chains introduce multiple alkoxides that can be functionalized subsequent to the polymerization [15].

Lee et al., and Allen et al., [16, 17] polyethylene oxides biocompatibility and protein adsorption inhibitor capacity make PEO a good candidate for the development of a new drug delivery medicine.

Villain et al., [18] polyethylene oxide can be used to substitute some biopolymers as implant for tissue replacement or augmentation.

Dormidontova, [19] the specific chemical structure of PEO, HO−[(CH2)n − O]x − H with n = 2, confers to this polymer very unusual interactions with water. Indeed, while poly (mthylene oxide) with n = 1 and poly (butylenes oxide) with n = 3, are both hydrophobic and insoluble in water, PEO is known as the simplest hydrosoluble hydrocarbon polymer, regarding its chemical structure.

Its solubility in water originates from the competition between PEO–water and water– water hydrogen bonding, delicately balanced by hydrophobic interactions induced by the ethylene components. The rupture of hydrogen bonds with increasing temperature is responsible for the decrease of its solubility upon heating, lower critical solution temperature behaviour.

Daoust and St Cyr, [20] near room temperature, the water solubility of

PEO is found to depend also on the polymer concentration. Indeed, water is a good solvent at low concentration and high temperature while it becomes a bad solvent at intermediate concentration, close to the critical concentration

Gray and Armand, [21]; Wright, [22] PEO is used for applications requiring high cation solvation and good electrochemical stability such as solid electrolytes used in lithium polymer cells, but surprisingly, it appears to be fragile and very sensitive to thermal [23], photochemical [24, 25], and ultrasound [26, 27].

Madras and McCoy, [28] they investigated the degradations in the bulk and in solution for polymer solutions, thermal and photochemical degradations have been observed for temperatures higher than 50ºC and for samples exposed to irradiation corresponding to natural outdoor aging (λ > 300 nm). Both degradation processes induce the formation of format and ester groups. The release of formic acid ions (HCOO−) is responsible for a drastic decrease of the pH, leading to a random chain scission. In the case of ultrasound degradation, chain scission is due to intense shear stresses arising from the collapse of transient cavitations bubbles. Contrary to thermal and photochemical degradations, the resulting rupture of covalent bonds occurs preferentially in the middle of polymer chains, up to molecular weight of about 2 $*10^4$ g/mol below which the polymer will not undergo scission. It has to be noticed that sonication produces heat, leading to some local increases of temperature and consequently associated thermodegradation, even if the temperature of the sample is externally controlled. Consequently, PEO in water requires controlled and precise conditions when handling, which make it a delicate polymer to work with. These difficulties are enhanced concerning high molecular weight PEO due to a more complex structural organization of the macromolecule.

Hammouda et al., [29] low molecular weight PEO obtained from controlled polymerization techniques, high molecular weight PEO are obtained from condensation of low molecular weight PEO through multifunctional agent, leading to form both hydrophobic regions and branched structures. Proposes that PEO solutions below 70◦C are phase-separated systems in which aggregates form a concentrated phase that coexists with a dilute phase of swollen coils. Such phase separation has been ascribed to the upper critical solution temperature behaviour of PEO solutions. However, a recent small angle neutron scattering investigation of PEO aqueous solutions has contradicted this hypothesis, this study pointed out chain ends effects on the clustering in PEO solutions with a molecular weight of $4*10^4$ g/mol. Despite the fact that end groups represent only one unit per 1,000 units, this study has shown that the ability of the PEO to aggregate is enhanced in the presence of non-polar CH3 groups at both ends of the polymer chain while it is strongly reduced in the case of chains end-capped by polar OH groups.

Polik [30] and Duval, [31] they proposed the contribution of hydrophobic interactions, seems to be determinant when PEO chains are end-capped by non-polar groups and would lead to polymer aggregation through –CH2–CH2– groups belonging to the chain and end groups. However, this interpretation cannot explain the ability of PEO chain end-capped with OH groups to form clusters. Several works refer to shear-induced aggregation in PEO aqueous solutions.

Intrinsic Viscosity

The viscosity of a polymer solution (η) is higher than that (η_o) of the pure solvent at a specified temperature and the increase in medium viscosity on dissolving the polymer in the solvent is a function of both molecular weight and concentration of the polymer solute [32].

If the polymer solution is very dilute, then the viscosities of the solvent and the solution at a given temperature would be proportional to their flow times in a given capillary viscometer such that the relative viscosity η_r expressed by the ratio (η / η_o) would be given by the flow time ratio (t / t_o), where t_o is the flow time of a given volume of the solvent and t is the flow time of the same volume of solution respectively. The parameter called specific viscosity, η_{sp} as defined by $\eta_{sp} = (\eta - \eta_o) / \eta_o = (t - t_o) / t_o$, where specific viscosity per concentration equal to reduced viscosity, and intrinsic viscosity is [32]:

$$[\eta] = \lim_{c \to 0} \eta_{red} \qquad \ldots(1)$$

Intrinsic viscosity [η] may be regarded as a measure of the specific hydrodynamic volume of a dissolved polymer at infinite dilution $C \to 0$ [33]. The intrinsic viscosity measured in a specific solvent is related to the molecular weight M, by the Mark – Houwink equation [34, 35].

$$[\eta] = KM^a \qquad \ldots(2)$$

Where K and a are Mark-Houwink constans that depend upon the type of polymer, solvent, and the temperature of the viscosity determinations [34]. The unit of intrinsic viscosity is an inverse concentration [36].

The concentration dependence of the reduced viscosity can be related to the following equations of Huggins [37, 38].

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \qquad \ldots(3)$$

Where k', is constant for a given polymer–solvent–temperature systems [39].

Experimental Work

Materials

The studied polymer was polyethylene oxide with different molecular weights and types dissolved in water (with conductivity < 0.5 µS/cm). The samples of average molecular weights 1, 3, 10, 20, and 35 kg/mol were obtained from Physical Chemistry Institute, Mainz University, Germany. The samples of average molecular weights 100 , 300 , 1000 , 4000 , and 8000 kg/mol were purchased from Sigma – Aldrich Company , Germany , and the branched polyethylene oxide of molecular weight 0.55 and 40 kg/mol was purchased from Creative PEGWorks, Winston Salem, NC, USA , all samples used as received. The molecular weights given by Sigma – Aldrich checked by viscometric measurements at 30 ºC because the samples specifications were quite imprecise. The various molecular weights of polyethylene oxide were used in the present work to see the difference in their behaviors and how the higher molecular weights are more effective than the lower ones for industrial application, especially for drug reduction [40-44]. The polymer was studied to determine its intrinsic viscosity, critical molecular weight, and viscoelastic properties.

Dissolving Process

For capillary viscometry the dissolving of polymers was normally carried out by taking a certain amount of each molecular weight to obtain a solution with specific viscosity η_{sp} of about 1. From the starting concentration, by further solution dilution with specific viscosities h_{sp} in the range of 0.2 to 1 were obtained which are suitable for the determination of intrinsic viscosities

For the capillary viscometers, a total volume of about 20 ml solution was needed. The polymer was dissolved completely and left at laboratory temperature. Then 15 ml of the homogenous solution was injected inside the capillary and diluted to different concentrations by adding a certain amount of water to the capillary as shown in figure 1.

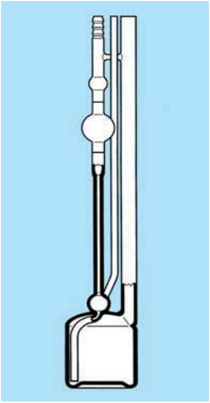

Fig. 1, Schott Ubbelohde Capillary Viscometer

Then the capillary inserted in the water bath type Messgeraetewerk LAUDA, Germany, with double thermostat type (D-60-S) has been set at temperature of (25°C) as shown in figure 2.

Fig. 2, Water bath

Results and Discussion

The measurements of the intrinsic viscosity carried out for the samples (1, 3, 10, 20, 35 kg/mol) that obtained from physical chemistry institute at temperature 25 °C shown in figure 3.

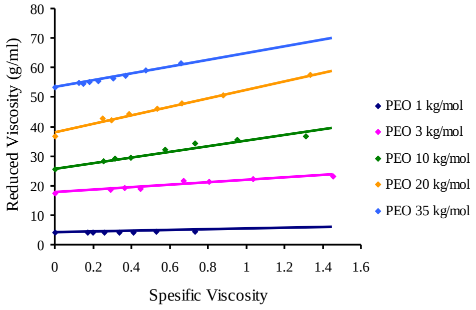

Fig. 3, Reduced Viscosity versus Specific Viscosity for PEO in Water at 25°C

Fig. 3 shows that the polyethylene oxide (PEO) behaves as neutral polymer in water. Neutral polymers have the property that the reduced viscosity increases with increasing of the specific viscosity and polymer concentration, because the structure of PEO may not contain ionic groups [45]. Otherwise if the polymer contains e.g. a carboxyl groups the reduced viscosity would decrease with increasing the specific viscosity and concentration of the polymer: in dilute solution the effective electrostatic repulsion extends the polymer coil, while in more concentrated solution the electric charge of the chain are shielded by counter ions [46].

The measurements were done at 30 ºC in water to check the value of high molecular weights samples of polyethylene oxide obtained from Sigma Aldirch company because only a very broad molecular weight range was given in the specification. At 30 ºC reliable values of k and a can be taken from the literature [47].

The values of intrinsic viscosities obtained by capillary measurements using Schott Ubbelohde capillary viscometer size as shown in figure 4.

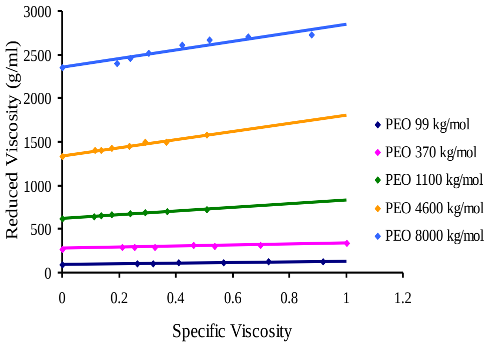

Fig. 4, Reduced Viscosity versus Specific Viscosity for PEO in Water at 30 °C

The results of the measurement of the capillary viscometer at 30 ˚C give values of molecular weights which are approximately the same that were obtained from Sigma Aldirch, company as shown in table below:

Table 1, The values of the Calculated Molecular Weight and Intrinsic Viscosity of PEO Samples were Obtained from Sigma Aldrich at 30 ºC

Obtained Molecular Weight (kg/mol)	Intrinsic Viscosity [η] (ml/g)	Calculated Molecular Weight (kg/mol)
Linear PEO 100	98.6	99
Linear PEO 300	274.1	370
Linear PEO 1000	622.8	1100
Linear PEO 4000	1273.2	4600
Linear PEO 8000	2353.3	8000*

* All the measurements at 30 ºC show results close to what obtained from Sigma Aldirch Company expect these for 8000 kg/mol sample which had a wide range of error, so it used with this error because the other results were reasonable.

The measurements of the intrinsic viscosity carried out for the measured values of the samples that obtained from Sigma Aldirch, company at 25 °C as shown in figure 5.

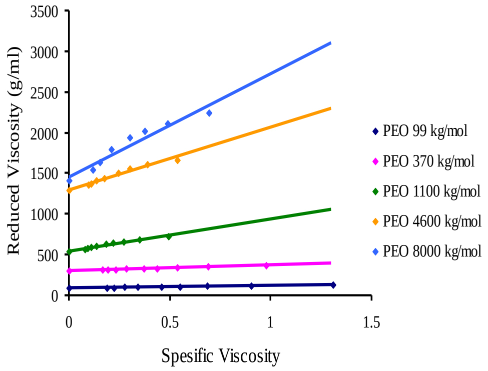

Fig. 5, Reduced Viscosity versus Specific Viscosity for PEO in Water at 25 °C

Figure 5 shows that polyethylene oxide (PEO) with high molecular weight also behaves as a neutral polymer in water. The reduced viscosity is a linear function of specific viscosity as for the concentration where it increases with increasing the specific viscosity of the polymer, while for 8000 kg/mol molecular weight the reduced viscosity shows a non-linear increasing with the specific viscosity. This special behavior for the highest molecular weight sample is due to aggregation effects or shear thinning which was observed in measurements with the rotational viscometer.

For the branched polyethylene oxide the measured values are shown in figure 6.

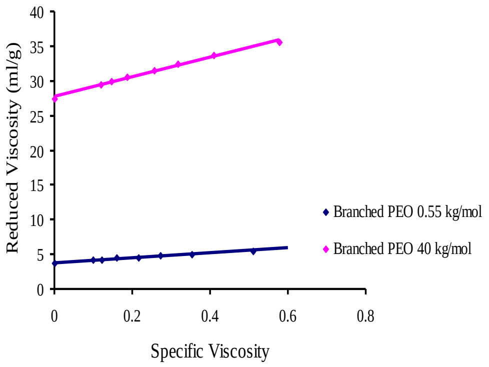

Fig. 6, Reduced Viscosity versus Specific Viscosity for Branched PEO in Water at 25 °C

Figure 6 for the branched polyethylene oxide shows the same influence for reduced viscosity with the specific viscosity where it increases with increasing the concentration as the linear polyethylene oxide.

By using eq. 3, and reduced viscosity equal to $\frac{\eta sp}{c}$, from figures 3 to 6 the relation of reduced viscosity against specific viscosity, usually gives a straight line, the slop of this line is equal to $k'[\eta]^2$ and the intercept is equal to [η], so that Huggin's constant K' can be determined from the slope, the values of intrinsic viscosity shown in table 2.

Table 2, Intrinsic Viscosity of PEO Solution at 25°C

Molecular Weight (kg/mol)	Intrinsic Viscosity (ml/g)
Linear PEO 1	4.1
Linear PEO 3	17.4
Linear PEO 10	25.8
Linear PEO 20	36.8
Linear PEO 35	53.3
Linear PEO 99	88.9
Linear PEO 370	303.5
Linear PEO $11*10^2$	539.1
Linear PEO $46*10^2$	1290.4
Linear PEO $8*10^3$	1410.4
Branch PEO 0.55	3.8
Branch PEO 40	27.5

Figures from 3 to 6 show that the hydrodynamic volume which proportional to $[\eta]$ of PEO in water increase with increasing the molecular weight for both linear and branched polyethylene oxide.

The branched samples show a mach smaller intrinsic viscosity than the linear samples which close to them molecular weight. This effect is explained by the decrease of hydrodynamic volume with increase of branching.

By using equation, $[\eta] = KM^a$ a plot of the log$[\eta]$ versus log M_{wt} for PEO in water at 25°C usually gives a straight line, the intercept of this tine is equal to k and the slope is equal to "a" as shown in figure 7.

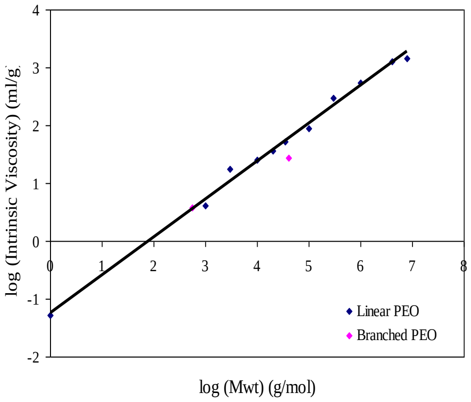

Fig. 7, log (Molecular Weight) versus log (Intrinsic Viscosity) for Different PEO in Water at 25 °C

Table 3, Huggin's constant and Mark Houwink Parameter of PEO in Water at 25 °C

Molecular Weight (kg/mol)	Huggin's Constant (K')	K (ml/g)	a
Linear PEO 1	0.179	0.0068	0.667
Linear PEO 3	0.335		
Linear PEO 10	0.513		
Linear PEO 20	0.683		
Linear PEO 35	0.289		
Linear PEO 99	0.577		
Linear PEO 370	0.284		
Linear PEO 1100	1.016		
Linear PEO 4600	0.757		
Linear PEO 8000	1.477		
Branch PEO 0.55	1.174		
Branch PEO 40	0.67		

Conclusion

For dilute solution of polyethylene oxide in water the reduced viscosity increases with increasing concentration. The PEO behaves as neutral polymer, and intrinsic viscosity of polyethylene oxide in water increases with increasing the molecular weight.

k and a (Mark-Houwink constants) were determined for polyethylene oxide in water at temperature 25 °C also for high molecular weight up to 8000 kg/mol, which has not been mentioned in the literature so far.

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