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Determination of Molecular Weight and Viscosity of Irradiated Polystyrene

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Abstract

The varied applications of polystyrene in various fields of life led to examining the cause of radiation influence on some rheological behavior of commercial Polystyrene (PS) solution in the chloroform (CHCl3) solvent. Polystyrene grains shape samples were irradiated using the radioactive element Cesium- 137 with (9 µci) activity for 10, 20, and 30 minutes. The viscosity of the polymer solution depends on the concentration and size (i.e. molecular weight) of the dissolved polymer. Experimental data showed that the radiation dose affected the value of viscosity (shear, relative, specific, and reduced). The viscosity value significantly reduced at 10 min radiation dose and when increasing the dose, the viscosity value increased up to 30 minutes. Deterioration of the polymer structure was recorded for a 10 minutes radiation dose. With the increase of radiation time, which reached 30 minutes, cross-linking was performed due to the substance gaining additional doses of radiation. The molecular weight of polystyrene increased with the increase of irradiation time, but no value was recorded for a molecular weight higher than 56089, which is for not irradiated polystyrene. The study concluded that the radiation dose is able to control the chemical composition of the polymer, therefore the behavior of the polymer in the solvent is determined by the radiation dose to which it is exposed.

Keywords: Cross-linking, Degradation, Effective molecular radius, Viscosity, Polystyrene.

Introduction

Polymers are used in many engineering and chemical industries, so studying the cause of various weathering conditions on the mechanical and physical properties of these materials has become necessary to know the extent to which such materials can tolerate such conditions: high temperatures, corrosive solutions, and all corrosive bases, such as radiation. The effect of weathering conditions and decomposition processes for polymers can occur during any stage of polymer life, as it can occur during: manufacturing processes, moulding and shaping processes and finally during use. Due to the aforementioned reasons, many scientists and researchers have directed their ideas and efforts to study the effect of radiation on polymeric materials due to its advantages, the most important of which is a high strength to weight ratio. The scientific researchers came to focus as much as possible on the importance of polymers and to study the effect of radiation on their various chemical and physical properties in the wider fields according to the properties of the materials involved in their preparation and the surrounding weathering conditions and other factors [1-3].

Polymer solvents have a key role in studying the structure of the polymeric chain, as the solubility of the polymer chain in the solvent has a significant effect on its rheological behavior, starting with the stretching of the polymer chain. A number of factors control the flowing nature of a polymer solution, which makes it difficult to explain the viscosity measurements. For this reason, viscosity measurements are made by means of dilute solutions for the purpose of reducing interactions between the molecules of polymer. So, just the reactions taking place between the polymer and the solvent are specified [1,3].

Polystyrene (PS) is a cheap, transparent polymer that is one of the most important and widely used plastics and is suitable for a variety of applications. As a result of the good resistance of polystyrene to radiation through which the molecules are supplied with energy, a structural change occurs which leads to a change in the average molar mass [4].

The average molar mass is of great significance in the study of polymers' behavior. It characterizes the length of the polymer molecule chains, and this is of great significance and its importance lies in the processing of the polymer and its overall performance. The physical and chemical properties of the product are described by determining the average chain length, or the so-called (average degree of polymerization). Therefore, the length of the polymer chains is very important. As there are many factors that affect the polymeric structure, including radiation. The effect of radiation or the radioactive dose absorbed by the polymer leads to the emergence of free radicals resulting from the degradation of the secondary groups attached to the main chain of the polymer (the backbone), or it may lead to the breaking of the main chain of the polymer, which leads to a decrease in the molecular weight. The method of dissolving the polymer in a suitable solvent is considered one of the most important scientific methods in calculating the molecular weight of the polymer and for this reason, by measuring the viscosity the molecular weight can be calculated as well as the average molar mass [5]. Several interesting studies have included formation on the impact of Gamma irradiation on the polymer, which leads to ionization of the polymer when exposed to ionizing radiation, in addition to the excitation of the molecules. Raouf R. M. et al[6] studied the radiation influence and some of the rheological properties of polyvinyl acetate (PVAC) in chloroform. The results showed that the radiation causes a breakdown of the PVAC chain in the low dose and the crosslinking occurs with increasing exposure time to the radiation source. Solyman W A. et. al.[7] investigated the effect of gamma rays and temperature on the reduced and intrinsic viscosity and calculated the average molecular weight by Mark-Houwink – Sakurada Eq. They observed that after irradiation with gamma rays the polystyrene undergoes crosslinking and degradation with increasing temperature. In this paper, the effect of ionizing radiation from a Cesium -137 source on rheological properties and molecular weight of polystyrene dissolved in chloroform at room temperature was studied.

Materials and Methods

Materials:

Polystyrene granules are supplied by Iran Petrochemical Company (PCC) with the following properties, formula (CH_2= CHC_6H_5), and molecular weight in the range (50000-60000). Chloroform (trichloromethane) was manufactured by Sigma-Aldrich Corporation with high purity of 99.5% and used as a solvent.

Samples preparation and Irradiation:

Polystyrene granules were weighed about 20 g in three plastic bags prior to the irradiation process. The irradiation process was conducted by a Cesium-137 source with activity 9 µci, ɣ = 661.66 kev and β = 513.97kev on Polystyrene samples for three periods of irradiation time 10, 20, and 30 minutes at temperature 30 °C. The distance between the source and samples was 15 cm and the radioactive source's energy was 10 g/dose. Samples of non-irradiated and irradiated were prepared by solving a specific weight of polystyrene granules in 100 ml of chloroform at room temperature to get the different concentrations of solutions (0.1, 0.2, 0.4, 0.6, 0.8, 1, 2 and 3 w/w). The samples were stirred for two hours by a magnetic stirrer before doing the measurement to completely dissolve the Polystyrene in chloroform.

Determination of the Viscosity

The shear viscosity of the irradiated and non-irradiated solution was measured using a digital rotary viscometer NDJ-5S at ambient temperature. In order to ensure the accuracy of the results, the experiment was repeated 5 times for each solution.

For each irradiated and non-irradiated solution the relative viscosity (η_{rel}), specific viscosity (η_{sp}), and reduced viscosity (η_{red}) are determined by the following Eqs 1, 2, and 3 respectively [8]:

$$\eta_{rel} = \frac{\eta_s}{\eta_e} \qquad \dots\dots\dots\dots\dots 1$$

$$\eta_{sp} = \eta_{rel} - 1 \qquad \dots\dots\dots\dots\dots 2$$

$$\eta_{red} = \frac{\eta_{sp}}{C} \qquad \dots\dots\dots\dots\dots 3$$

Where η_s is the irradiated and non-irradiated solution viscosity, η_e is the chloroform viscosity, and C is the concentration of the test solution. The intrinsic viscosity, |η| can be determined based on Huggins equation [9] by plotting a graph between reduced viscosity (η_{red}) versus the polystyrene concentration at different irradiation times. The intercept of the graph was considered as the intrinsic viscosity when the curve was extrapolated to zero concentration:

$$\eta_{red} = |\eta| + K_H|\eta|^2C \qquad \dots\dots\dots\dots\dots 4$$

Where K_H (dimensionless) is the Huggin's viscometric constant.

Results and Discussion

Commercial polystyrene was irradiated. The main reason for choosing this material is that it has wide applications in technical practice. All viscosity measurements were performed at room temperature. The objective of these measurements is to describe changes in the polymer structure tested by exposure to the radiation from a cesium -137 source. The viscosity was measured 10 times for all tested samples. Experimentally the value of intrinsic viscosity is determined by plotting a graph for reduced viscosity in accordance with the concentration of samples; the intercept with Y - axis refers to the |η| value. Table 1 the values of intrinsic viscosity |η| for prepared samples.

Table 1. Original viscosity for Polystyrene before and after irradiated

The time of Irradiated (min)	The intrinsic viscosity |η| (ml/gm.)
Not Radiated PS	0.5026
10	0.1119
20	0.1861
30	0.3196

Viscosity average molecular weight (M_α) calculation:

The viscosity average molecular weight (M_α) of irradiated and non-irradiated polystyrene in the chloroform can be determined from the intrinsic viscosity measurements according to Mark Houwink Sakurada equation [10]:

$$|\eta| = KM_v^{\alpha} \qquad \dots\dots\dots\dots\dots 5$$

Where K and α are the Mark-Houwink constants depending on polymer type at a defined temperature and in a specific solvent. For polystyrene the Mark-Houwink parameters K= 15.8 dl/g and α = 0.74 [11]:

The Effective Molecular Radius (r_{eff}):

The effective molecular radius of irradiated and non-irradiated polystyrene in the chloroform solutions can be evaluated using Eq 6 [12,13]:

$$r_{eff} = \sqrt{\frac{\text{slope}}{6.3\times10^{24}}} \qquad \dots\dots\dots\dots\dots 6$$

The shear viscosity value was taken directly from the device. The results illustrated in Fig 1 showed a direct relation between polystyrene concentration (the solute mass in the solvent) and shear viscosity value (the higher the concentration of solute in the solvent the higher the shear viscosity of the polymer). This increase is considered a normal physical condition. In Fig 1 the incremental curve of concentrations can be observed on the radiation dose curve 10, 20, 30 min. Here it should be noted that the effect of radiation from a cesium source caused a structural change in polystyrene, which can be quantified and that agree with those obtained by other authors [14,15]. The first dose rate (10 min.) led to a drop in concentration values as shown in Fig 1. But when the time period for the dose was changed to 20 min., the shear viscosity curve was higher than the first dose rate (10 min) although the upsurge didn't exceed the third dose rate 30 min.

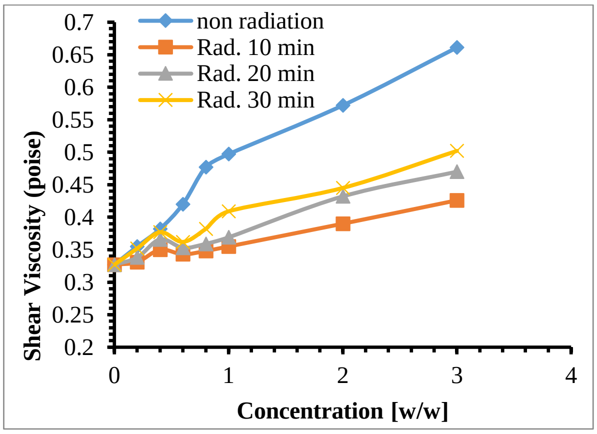

Figure 1. Shear viscosity variation with concentration for Polystyrene in Chloroform

Table 2, shows the average molecular weight for Polystyrene before and after irradiation. Table 3 demonstrates the value of effective molecular radius for all polystyrene/chloroform samples that evaluated using the Eq 6 [12]:

Table 2. The values of the Average molecular weight of polystyrene before and after irradiation

The time of Irradiation (min)	Average molecular weight
Not-Irradiated PS	56089
10	7745
20	15142
30	30884

Table 3. The value of the calculated effective molecular radius before and after irradiation

The time of Irradiation (min)	Effective molecular radius ×10^{-12}	Slope $\frac{\eta_{sp}}{C}$
Not Irradiated PS	0.0876	0.0483
10	0.058	0.0213
20	0.0524	0.0173
30	0.0973	0.0597

The initial effect of radiation is exciting the electrons that form the chemical bond, (it is worth noting that the lifetime of the excited bond is greater than the lifetime of thermal vibration through the material), and as a result, a break in the main chain or side chain occurs resulting in a decrease in the viscosity value, and that behavior was observed during the first dose rate of this experiment. After an increase in the time of the irradiation (20, 30 min.), a case of re-union of the broken bonds occurred, which led to the reunification of the broken bonds between them. The excited state does not persist for a long time as the bond combines with another and leads to a change in structure formation. A broken bond, which is either a free radical or an ion, is very active. After the free radical formation process, different reactions may take place.

Figs 2 and 3 show the relative and specific viscosities, which calculated using Eq 4 and Eq 5 were for irradiated and Non-irradiated polystyrene samples.

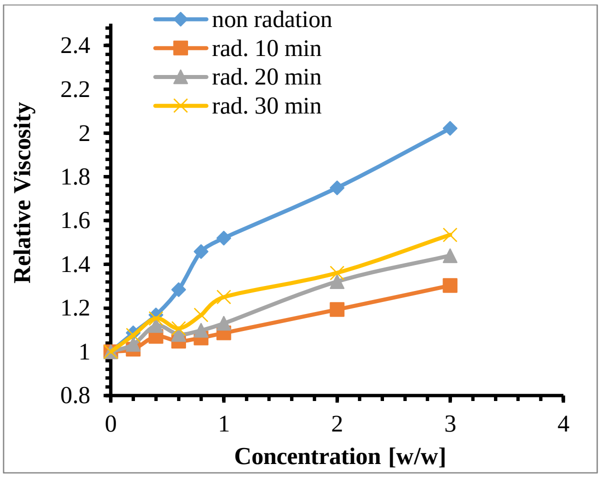

Figure 2. Variation of the relative viscosity with concentration for polystyrene in Chloroform

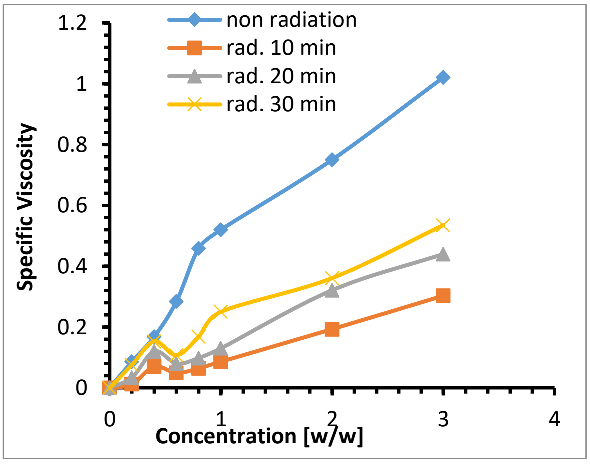

Figure 3. Variation of the specific viscosity with concentration for Polystyrene in Chloroform

Reduced viscosity was plotted against concentrations as shown in Fig 4. which represents the relation between reduced viscosity and concentration of polymer at different exposure times to radiation. The intersection of the reduced viscosity line with the y-axis results in the intrinsic viscosity value. Thus, by putting the value of intrinsic viscosity in the Mark-Houwink equation (Eq 5), the molecular weight of polystyrene is calculated as the radiation dose varies. Moreover, the slope of the line can be substituted in Eq 6 to calculate the effective molecular radius

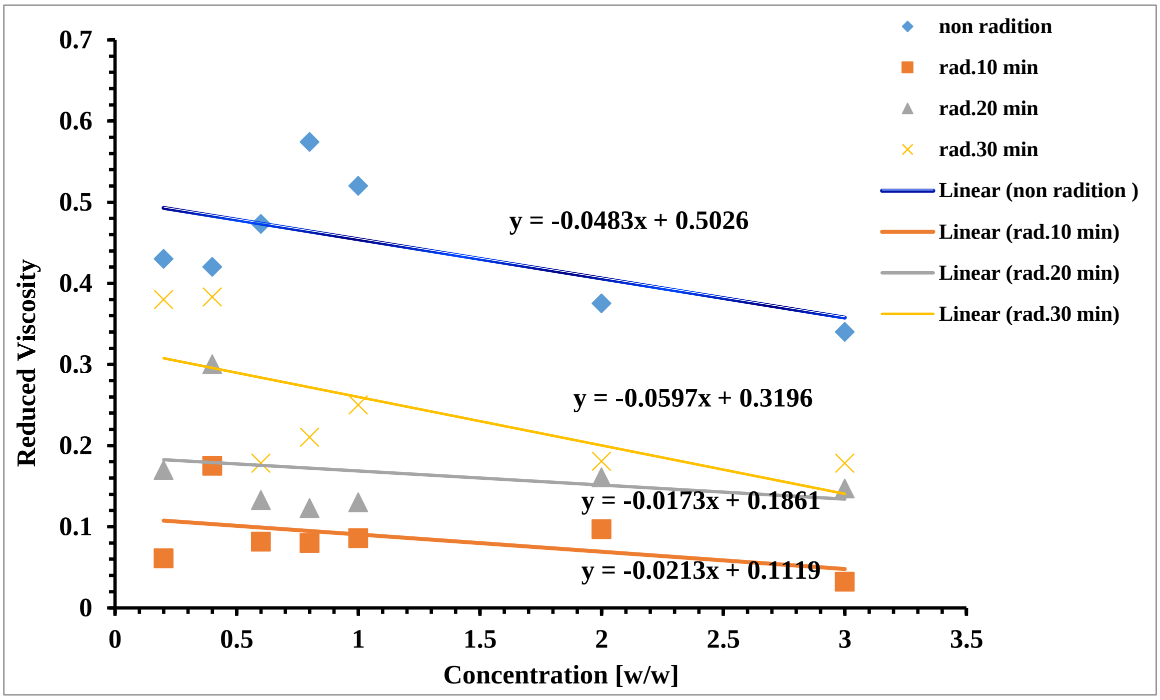

Figure 4. Variation of the reduced viscosity with concentration for Polystyrene in Chloroform

Over time, as a natural polymer behavior, polymers deteriorate due to environmental factors such as exposure to sunlight (aging behavior), and this effect is similar to the deterioration in the polymer structure after exposure to radiation [16].

The molecular weight after the first dose 10 rad decreased significantly and showed an increase after the second and third doses 20, 30 rad due to the crosslinking occurring in the polymer chain which was generated from the rearrangement of the polymeric structure. But the increment in molecular weight value after irradiation couldn't get close to the original value of non-irradiated polystyrene (56089) (note that the radiation doses that are higher than 30 rad showed results very similar to the results of the radiation dose of 30 rad that the change in the value of molecular weight can be ignored). The increase in molecular weight after radiation occurs due to the presence of hydrogen acetate [13]. Which can be found in the molecular structure of polystyrene (H- type cross-linking)[16]. In this paper, irradiated samples that were exposed to open air are fundamentally different from those that are irradiated in a vacuum, and this difference results in an increase in peroxide cleavage formed due to the presence of oxygen. The interaction between radiation and matter results in the formation of two complexes that are close to each other while leaving sufficient space between them. Therefore, the nearby molecules may agglomerate into this polymer to form macro-molecules; as a result, the viscosity curve has a bowl-shape. The gamma radiation leads to the emission of C=O and C-O from the surface of the polymer (oxidation of the polystyrene surface). This is followed by oxidation in the internal structure, which is directly proportional to the increase in the radiation dose, and the carbonyl group is released. It's worth mentioning that the effective molecular radius value increases at the dose (30 rad)[6]. The variation in the values of molecular weight led to the differing value of the effective molecular radius. Finally, the dissolved polystyrene has the ability to augment the value of effective molecular radius as mentioned due to macro-molecule formation.

The effect of irradiation on the molecular weight of polystyrene, which is evidence for a variation in the molecular weight in irradiation time, indicates that radiation has a noticeable result on the decomposition of polystyrene molecular weight.

Conclusion

After conducting research and studying the effect of irradiation on polystyrene in different radiation doses, in addition to studying its effect on the rheological properties and molecular weight in addition to the effective molecular radius, the most important conclusions of this study were touched:

1. Cesium-137 has been used because it is a source of gamma rays such as Cobalt-60.
2. Radiation caused the disintegration of the polystyrene chain in the lowest dose, and this is due to the disintegration of the sub-chains of the structural structure. Similarly, cross-linking occurred because of prolonged exposure to the radiation source. So, the dose rate is a significant issue in controlling the molecular weight of the polymer, and the properties of the polymer will depend directly on the radiation dose.
3. Cesium- 137 source has sufficient energy to degrade and rebuild the polymeric chain of polystyrene so; the molecular weight of irradiated polystyrene depends on the absorbed dose of the radioactive element.
4. The viscosity value of polymeric solutions increases with the polymer concentration and molecular weight of the polymer in addition to the size of the polymer chains.

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Author's Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images that are not ours have been included with the necessary permission for re-publication, which is attached to the manuscript. Ethical Clearance: The project was approved by the local ethical committee in Mustansiriyah University.

Author's Contribution Statement

This work was carried out in collaboration between all authors. B. J. N. organized and verified the data. R. M. R. wrote the manuscript. M. A. A. analyzed the data. L. G. read and approved the final manuscript.

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تحديد الوزن الجزيئي واللزوجة للبوليستيرين المشع

بيداء جابر نبهان، رؤوف محمود رؤوف، ميس عبد الرحمن عبد الكريم و لبنى غالب

قسم هندسة المواد, كلية الهندسة , جامعة المستنصرية, بغداد , العراق

الخلاصة

أدت التطبيقات المتنوعة للبوليسترين في مختلف مجالات الحياة إلى فحص سبب تأثير الإشعاع على بعض السلوك الريولوجي لمحلول البوليسترين التجاري (PS) في مذيب الكلوروفورم ($CHCl_3$) . تم تشعيع عينات حبيبات البوليسترين باستخدام العنصر المشع سيزيوم - 137 بنشاط 9 µci لمدة 10 ، 20 ، 30 دقيقة. تعتمد لزوجة محلول البوليمر على تركيز والحجم (أي الوزن الجزيئي) للبوليمر المذاب. أظهرت البيانات التجريبية أن جرعة الإشعاع اثرت على قيمة اللزوجة (القص ، النسبي ، النوعي والمتضائلة). انخفضت قيمة اللزوجة بشكل كبير عند جرعة 10 دقائق الاشعاع وعند زيادة جرعة الاشعاع, زادت قيمة اللزوجة حتى 30 دقيقة . تم تسجيل تدهور في بنية البوليمر لجرعة اشعاع مدتها 10 دقائق. مع زيادة وقت الاشعاع, الذي وصل الى 30 دقيقة, تم اجراء التشابك بسبب اكتساب المادة جرعات إضافية من الإشعاع. زاد الوزن الجزيئي للبوليسترين مع زيادة وقت التشعيع ، ولكن لم تسجيل أي قيمة لوزن جزيئي أعلى من 56089 وهو البوليسترين غير المشعع. وخلصت الدراسة إلى أن جرعة الإشعاع قادرة على التحكم في التركيب الكيميائي للبوليمر, لذلك يتحدد سلوك البوليمر في المذيب بجرعة الإشعاع التي يتعرض لها.

الكلمات المفتاحية: التشابك، التحلل، نصف القطر الجزيئي الفعال، اللزوجة، البوليسترين.