

Effect of GAMMA Rays on some types of viscosity and optical properties for polycarbonate in chloroform at room temperature

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ABSTRACT

Some types of viscosity for polycarbonate aqueous solution in Chloroform with concentration of 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5% were determined for two kinds of samples, first non-radiated & the second, irradiated with Co^{60} source for a rate of 508 rad/min for 20 minutes.

The results show that the values of shear, relative, specific & reduced viscosity were increased with increasing the concentration of polycarbonate in chloroform, Also the properties which had been determined in this work, increased after radiation, this could be attributed to penetration of ionizing radiation in the polymer structure & cross linking the chains.

Key words: GAMMA Rays, Polycarbonate, Viscosity.

الخلاصة

تم تعيين قيم بعض أنواع اللزوجة لبولي كاربونيت المذاب في الكلوروفورم وبتراكيز 1، 1.5، 2، 2.5، 3، 3.5، 4، 4.5 و 5% قبل وبعد تشعيعها بمصدر Co^{60} وبمعدل 508 راد لكل دقيقة ولمدة 20 دقيقة. أظهرت النتائج إن قيم كل من اللزوجة القصية، اللزوجة النسبية، اللزوجة النوعية، اللزوجة المختزلة تزداد بزيادة تركيز البولي كاربونيت في الكلوروفورم. كذلك تزداد قيم الخصائص المقاسة والمحسوبة بعد التشعيع وقد يكون ذلك بسبب التشابك في التركيب الجزيئي لهذا البوليمر لاختراق أشعة كما لبنية مولدات حالة التشابك في البنية التركيبية للبوليمر.

INTRODUCTION

Many articles consist of the effect of radiations on polycarbonate radiation especially in chloroform has been published ⁽¹⁻⁴⁾.

The aim of this work is to study some rheological and optical properties of polycarbonate in chloroform solvent at different concentrations before and after radiation by GAMMA source (Co^{60}).

There are a number of methods for determining experimentally the molecular weights of polymers. These include both the measurement of number-average and weight-average molecular weights. It will be seen that solution viscosity offers a very convenient method but it is not an absolute method and does not give one of the simple averages. The resolution of molecular lengths into fractions and therefore measurement of molecular weight distribution is also possible experimentally. Unlike small molecules, however, the molecular weight of a polymer is not one unique value. Rather, a given polymer will have a distribution of molecular weights. The distribution will depend on the way the polymer is produced. For polymers we should not speak of a molecular weight, but rather of the distribution of molecular weight, $P(M)$, or of the average molecular weight, $\bar{P}(M)$. Polymer physical properties will be functions of the molecular weight distribution function ⁽⁵⁾. The molecular weights of polymers are much larger than the small molecules usually encountered in organic chemistry. Most chain-reaction and step-reaction polymerizations produce chains with many different lengths, so polymers also differ from small molecules in that the polymer molecular weights are average values. ⁽⁶⁾

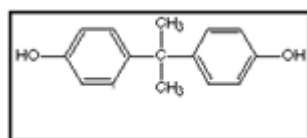
The viscometer used to measure dilute solution viscosity is usually a capillary viscometer. This viscometer uses the Poiseuille equation for laminar pressure flow in a capillary tube. Intrinsic viscosity is theoretically a primary technique, in that for the theta solvation conditions secondary standards are not necessary. In usual practice, at non-theta conditions, intrinsic viscosity relies on knowledge of the Mark-Houwink coefficients for the thermal and solvent conditions of measurement. ⁽⁵⁾

Beer-Lambert Law, more commonly known as Beer's Law, states that the optical absorbance of a chromophore in a transparent solvent varies linearly with both the sample cell path length and the chromophore concentration. Beer's Law is the simple solution to the more general description of Maxwell's far-field equations describing the interaction of light with matter. In practice, Beer's Law is accurate enough for a range of chromophores, solvents and concentrations, and is a widely used relationship in quantitative spectroscopy. Absorbance is measured in a spectrophotometer by passing a collimated beam of light at wavelength λ through a plane parallel slab of material that is normal to the beam. For liquids, the sample is held in an optically flat, transparent container called a cuvette. ⁽⁷⁾

EXPERIMENTAL

Material

Polycarbonates are long-chain linear polyesters of carbonic acid and dihydric phenols,



Used in making canopies for supersonic aircraft, bubble helmets for astronauts, break-resistant windows, and bullet-resistant laminates for banks and armored cars. It is also used for computer housings where mechanical, electrical and re-resistance properties are needed. It is also used in steam-sterilizable food-processing equipment ⁽⁸⁾. The properties of polypropylene are shown in Table 1.

Samples preparation

Using Chloroform (from GAINLAND CHEMICAL COMPANY), 9 different concentrations of each sample at room temperatures were prepared (1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5%); the solutions were prepared by adding a known weight of the polymer to fixed volume of Chloroform. The properties of Chloroform are shown in Table 2.

Viscosity measurements

For determining the viscosities of the solutions we used (HAAKE / Rotovisco Rv-20) viscometer at room temperature to find the shear viscosity digitally.

Irradiation method

The main source of (GAMMA) rays used in this work was Co^{60} with low dose rate irradiation, about 508 rad / min for 20 minutes on a disk shape samples with a thickness about 0.5 cm, where used in order to obtain dose uniformly during the irradiation. The distance between the source and the sample was 10 cm. ⁽¹¹⁾

THEORETICAL CALCULATION

Relative, specific & reduced viscosity:

The above viscosities were calculated by using the following relations ⁽⁹⁾:

$$\eta_{rel} = \eta_s / \eta_w = t_s / t_w \quad (1)$$

$$\eta_{sp} = \eta_{rel} - 1 \quad (2)$$

$$\eta_{red} = \eta_{sp} / C \quad (3)$$

Where:

η_{rel} is the relative viscosity

η_s is the viscosity of solution

η_w is the viscosity of solvent

t_s & t_w are the flow time of the solution and solvent respectively

η_{sp} is the specific viscosity

C is the sample's concentration.

Intrinsic viscosity $[\eta]$:

Plotting a graph for η_{re} against concentration of all samples had been drawn; the intercept with Y - axis of this graph is $[\eta]$.

Molecular weight (Mv):

An empirical equation is used to describe the intrinsic viscosity / molecular weight relationship, the Mark-Houwink equation,

$$[\eta] = KM_v^a \quad (4)$$

Where (a) and (K) are constants for specific polymer / solvent / temperature.

The values of $|\eta|$ had been taken from table (3), and the constants (K, a) are depended on polymer type at a temperature range of 15 – 25°C⁽¹⁰⁾. The value of the M_v of this polymer was calculated from following relation⁽¹¹⁾:

$|\eta| = 4.83 \times 10^{-4} M_v^{0.82}$, the calculated values are shown in table (4).

Molar absorption coefficient (α):

To calculate the optical absorption coefficient (α) of the samples, Lambert-Beer law equation was used:

$$\log \frac{I_0}{I} = A = \alpha \cdot C \cdot L \quad (5)$$

Where

I_0 the intensity of incident beams of light for special wavelength.

I the absorbed intensity of the same beam.

α the optical absorption coefficient

A the absorbance of the same beam.

L the length of solution the light pass through, cm

If we plot A against C , and if we substitute $L=1$ cm. in equation 5 which represents the thickness of the test tube, therefore^[12]

$$\alpha = A / C \quad (6)$$

RESULTS & DISCUSSION

The result of most measured and calculated physical properties for polycarbonate as shown in most figures and tables are increased with concentration due to phenyl groups and methyl groups in its structure. These results are concurring with the results found by Robertson⁽¹³⁾ who used another solvent. The value of intrinsic viscosity and average viscosity molecular weight determined in this work (tables 3 & 5) increase after irradiation by Co^{60} source could be attributed to formation of very reactive intermediates products (excited states, ions and free radicals), which result in rearrangements and/or formation of new bonds and this agreed with the conclusion of J.H. Donnell⁽¹⁴⁾

The optical absorption coefficient (α) is calculated using equation 5 as shown in table 5. The results show that it decreased after radiating the polymer.

Low dose radiation very clear in viscosity figures (figures 1 to 4), we see the approach in radiated and non-radiated curves leads to slight increase in average viscosity molecular weight that is because the degree of cross-linking depends upon the polymer and radiation dose. One of the benefits of using irradiation for cross-linking is that the degree of cross-linking can be easily controlled by the amount of dose.

Also the results of UV and visible spectrum of polymer in solution show the existence of both inter and intra-molecular hydrogen bonds, this polymer appears to be a good transparent at 220nm., therefore result suggests that weak absorption exist in the region (240-700) nm., such week absorption may be due the presence of impurity.⁽¹⁶⁾

The ionized gamma irradiation affected the refractive index of polymer (figure 5) and therefore it changes the polarization of the incident light. The difference in the polarization phase shift of the polymer depended on the dose it had been irradiated with.⁽¹⁸⁾

Irradiation in polymers destroys the initial structure by way of cross linking, free radical formation, irreversible bond cleavages etc. that results in the fragmentation of molecules and formation of saturated and unsaturated groups. All these processes introduce the so called defects inside the material that are responsible for change in the optical, electrical, mechanical and chemical properties of the material.⁽¹⁷⁾

Table 1: Properties of polycarbonate

Property	Value
Tensile Strength	0.90 - 1.32 N/mm ²
Notched Impact Strength	3.0 - 32.0 Kj/m ²
Thermal Coefficient of Expansion	100 - 140 x 10 ⁻⁶
Max. Continued Use Temperature	80 °C
Melting Point	160 °C
Glass Transition Temp. (atactic)	-20 °C
Glass Transition Temp. (isotactic)	100 °C
Density	0.906 g/cm ³

Table 2: Properties of Chloroform

Property	Value
Molecular weight	119.38
Boiling point	61.15°C
Vapor pressure	158.4 Torr at 20°C
Freezing point	-63.55°C
Refractive index	1.4458 at 20°C
Density	1.4798 g/mL at 25°C
Dielectric constant	4.81 at 20°C
Viscosity	0.57 cP at 20°C
Surface tension	27.16 dyn/cm at 20°C
Solubility in water	0.815% at 20°C

Table 3: Values of intrinsic viscosity before and after irradiation

Intrinsic viscosity(di/gm)	albumin
0.1772	before irradiation
0.2073	after irradiation

Table 4: Values of average viscosity molecular weight before and after Irradiation for polycarbonate in Chloroform

Mv Average viscosity molecular weight	polycarbonate
278.3281718	before irradiation
355.646892	after irradiation

Table 5: Molar absorption Coefficient for polycarbonate in Chloroform

Molar absorption Coefficient	Solvent
0.0271	before irradiation
0.017	after irradiation

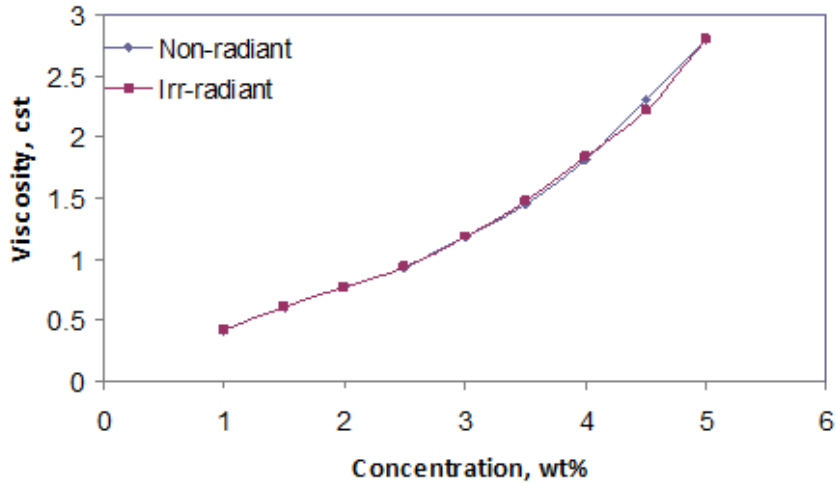


Figure 1: Shear Viscosity of polycarbonate changed with concentration.

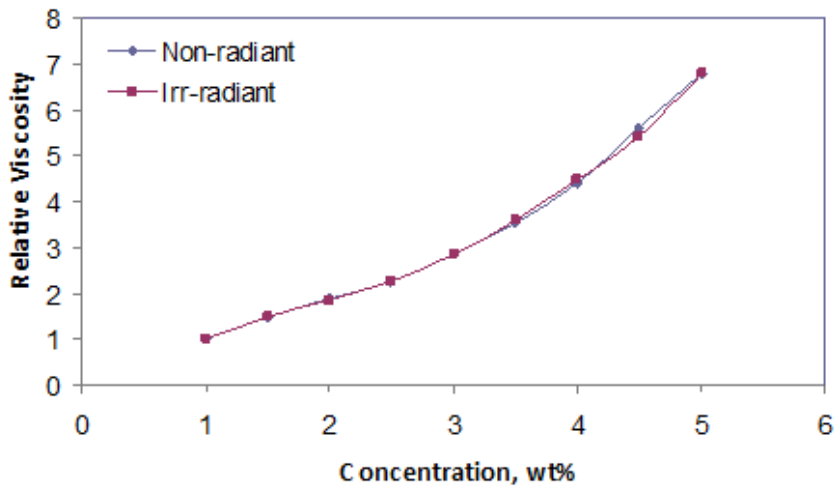


Figure 2: Relative viscosity of polycarbonate changed with concentration.

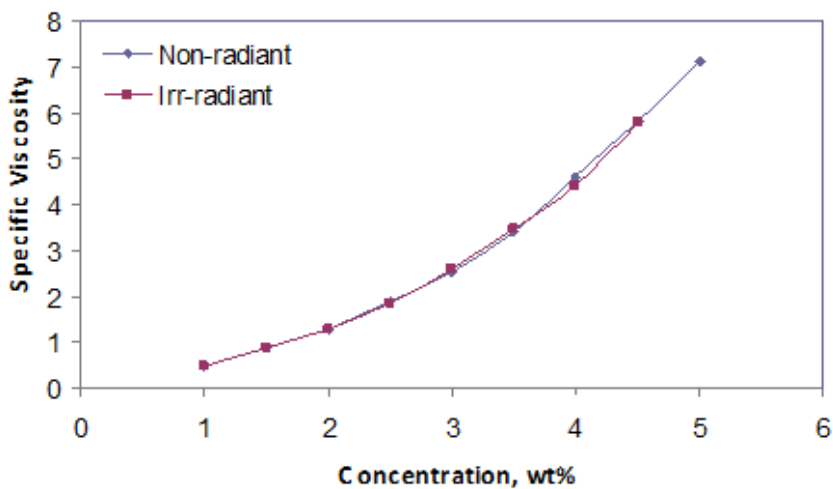


Figure 3: Specific viscosity of polycarbonate changed with concentration.

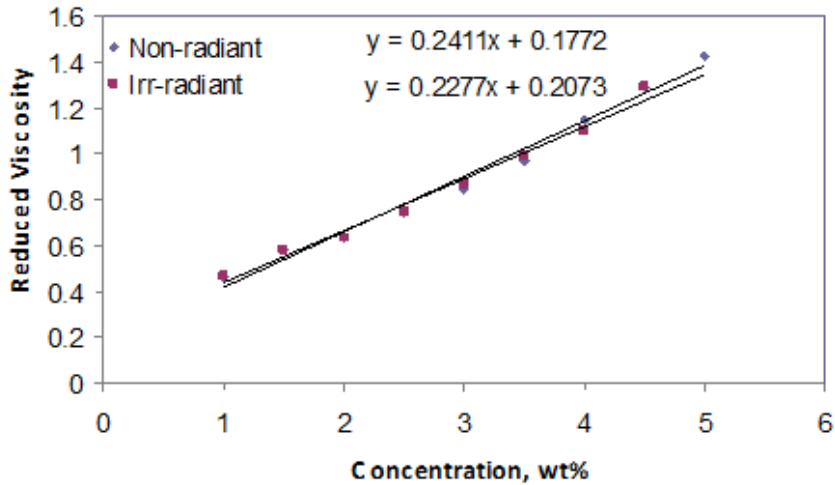


Figure 4: Reduced viscosity of polycarbonate changed with concentration.

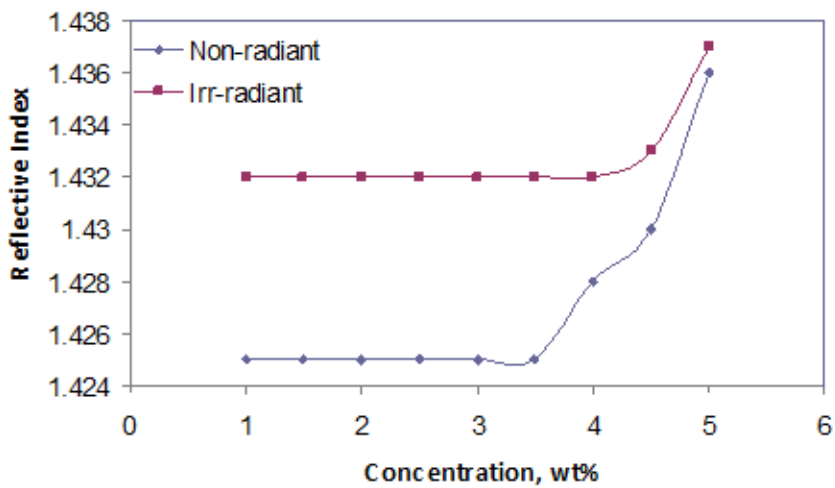


Figure 5: refractive index of polycarbonate changed with concentration

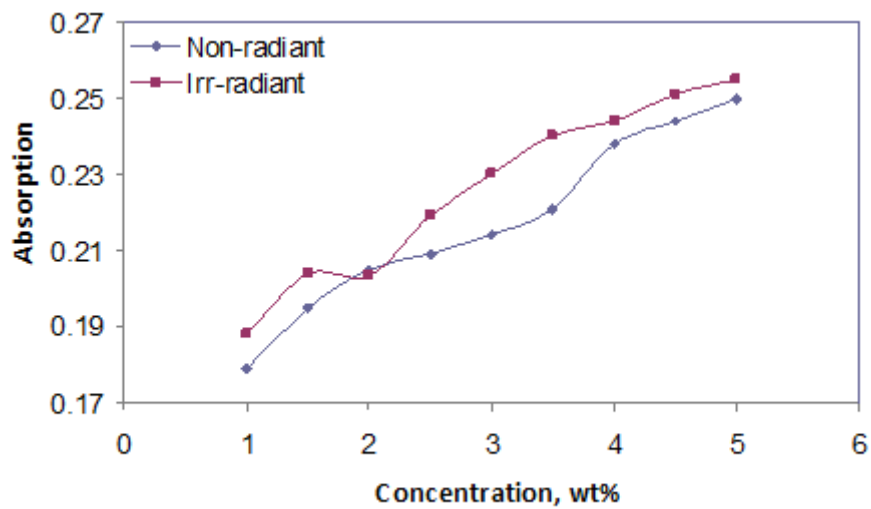


Figure 6: absorption of polycarbonate changed with concentration

CONCLUSION

1. The effect of Co^{60} source on polycarbonate yield increasing in its molecular weight as reported.
2. The free roots & ions in radiated polycarbonate help to cross linking process that happened after radiation.
3. The increasing in molecular weight of this polymer after radiation may be useful to using this polymer in some high molecular weight polymers technology.

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