Study of Some Physical Behavior for Polycarbonate in Two Different Solvents at Room Temperature

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ABSTRACT

The goal of this research was to study some Rheological and optical properties of poly carbonate in (chloroform and toluene) with different concentrations to know the physical behavior of this polymer in two solvents at room temperature.It was determined that the value of polymer solution in these two solvents with different concentrations and the optical absorption, average viscosity molecular weight Effective molecular radius. The results have shown that the values of density, (shear, relative, specific, reduced, original) viscosities, Effective molecular radius and average viscosity molecular weight, increase with poly carbonate concentration in two solvents.The results also showed that prepared concentrations density was significantly influenced by the density of solvents used; this influence was not in the same magnitude for the rest of measurements and calculations. This may be due to the dynamic behavior of the polymer in a solvent.

Keywords: Polycarbonate, Mark-Houwink, viscosity, chloroform, toluene, physical behavior, solvents, absorption

دراسة بعض الخصائص للسلوك الفيزيائي للبوليكاربونيت في مذيبين مختلفين في درجة حرارة الغرفة

الخلاصة

يهدف البحث إلى دراسة بعض الخصائص الريولوجية والبصرية للبولي كاربونيت في (الكلوروفورم والتلوين) لمعرفة سلوك البوليمر الفيزيائي في هذين المذيبين المختلفين,وفي درجة حرارة الغرفة .تم تعيين قيم بعض أنواع اللزوجة للبوليمر المذاب في هذين المذيبين وبتراكيز مختلفة وكذلك الامتصاصية الضوئية و تم حساب معدل الوزن الجزيئي اللزوجي و نصف القطر الجزيئي الفعال.لوحظ إن قيم كل من الكثافة، اللزوجة القصية ، اللزوجة النسبية، اللزوجة النوعية، اللزوجة المختزلة،اللزوجة الأصيلة ووزن الجزيئي تزداد بزيادة تركيز البولي كاربونيت في المذيبين.كما أظهرت النتائج تأثر كثافة التركيز المحضرة بشكل واضح بكثافة المذيبات المستخدمة ولم يكن هذا بنفس المقدار في بقية القياسات والحسابات وقد يعود هذا إلى السلوك الديناميكي للبوليمر في المذيبات.

INTRODUCTION

The static and dynamic properties of a polycarbonate chain in dilute solution have long been the subject of investigation [1–4].

It was therefore worth-wile to obtain information about its behavior in different solvents. Solvents are ubiquitous we depend on them when we apply pastes and coatings, remove stains or old adhesives, and consolidate flaking media. The solubility behavior of an unknown substance often gives us a clue to its identification, and the change in solubility of a known material can provide essential information about its ageing characteristics. The effectiveness of a solvent depends on its ability to adequately dissolve one material while leaving other materials unaffected. The selection of solvents or solvent blends to satisfy such criterion is a fine art, based on experience, trial and error, and intuition guided [5, 6].

The physical properties of a polymer solution depend on solvent, temperature, and concentration. At low concentrations, the polymer chains are separated from each other, where each chain occupies a spherical volume of radius Rg. In this solution, the polymer-polymer interactions are small and the polymer coil volume is determined by polymer-solvent thermodynamic interactions. The hydrodynamic volume occupied by a given polymer mass is the intrinsic viscosity, which is a parameter that can be determined by dilute solution viscosity measurements [6].

Toluene C_7H_8, also known as methylbenzene (M.W. 92.14gm./mol.)is a clear, water-insoluble liquid with the typical smell of paint thinners (The boiling point is 110.6 °C and freezing point is -94.99 °C).[4] It is an aromatic hydrocarbon that is widely used as an industrial feedstock and as a solvent. Like other solvents, it's also used as an inhalant drug for its intoxicating properties; however, this can potentially cause severe neurological harm [5, 7].

Toluene reacts as a normal aromatic hydrocarbon towards electrophilic aromatic substitution [8, 9]. In addition, it is used as a solvent to create a solution of carbon nanotubes. It is also used as a cement for fine polystyrene kits, Industrial uses of toluene include dealkylation to benzene, and the disproportionation to a mixture of benzene and xylene in the BTX process. It is also used as a carbon source for making Multi-Wall Carbon Nanotubes, Toluene can be used as an octane booster in gasoline fuels used in internal combustion engines [4].

Chloroform (M.w:119.38 gm. / mol.) is a colorless oily liquid organic compound with formula $CHCl_3$ with a peculiar sickly smell and a burning taste. It is sparingly soluble in water but readily soluble in organic solvents such as ethanol and ether (The boiling point is 61^oC and freezing point is -63.5^oC) [10]. Its a common solvent in the laboratory because it is relatively unreactive, miscible with most organic liquids, and conveniently volatile. It used as a solvent in the pharmaceutical industry and for producing dyes and pesticides. Chloroform is an effective solvent for alkaloids in their base form and thus plant material is commonly extracted with chloroform for pharmaceutical processing, because of containing deuterium (heavy hydrogen, $CDCl_3$), is a common solvent used in NMR spectroscopy. It can be used to bond pieces of acrylic glass (also known under the trade names Perspex and Plexiglas) [11-12].

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Polycarbonate engineering thermoplastics are amorphous, clear polymers that exhibit superior dimensional stability, good electrical properties, good thermal stability, and outstanding impact strength [13].

Polycarbonates are long-chain linear polyesters of carbonic acid and dihydric phenols, it is a versatile, tough plastic used for a variety of applications. The main advantage of polycarbonate over other types of plastic is unbeatable strength combined with light weight. It bends light to a far greater degree than glass or other plastics of equal thickness, because of its high refractive index (1.584 - 1.586). Unlike most thermoplastics, polycarbonate can undergo large plastic deformations without cracking or breaking. As a result, it can be processed and formed at room temperature using sheet metal techniques, such as forming bends on a brake. It is used as dielectric in high stability capacitors [13, 14].

Automated viscometers are commercially available. To measure the viscosity of liquids in the centipoise range, it is, however, more common to use a capillary flow viscometer, unless the measurement is routinely conducted. This classical method is inexpensive, yet can measure the viscosity with a sufficient accuracy [15].

Intrinsic viscosity, which is measured from the flow time of a solution through a simple glass capillary, has considerable historical importance for establishing the very existence of polymer molecules. It also provides considerable physical insight. Intrinsic viscosity determination for polymers can be simplified and considerable time and effort saved via a single measurement of relative viscosity at a known concentration [16].

Absorption Spectroscopic methods of analysis rank among the most widespread and powerful tools for quantitative analysis. Absorption Spectroscopic methods of analysis are based upon the fact that compounds Absorb light radiation of a specific wavelength. In the analysis, the amount of light radiation absorbed by a sample is measured. The light absorption is directly related to the concentration of the colored compound in the sample [15].

EXPERIMENTAL
Material: polycarbonate -Makrolon1 (Bayer) - used in this work has a Typical density (1.20-1.22) g/cm$^{3.}$ Polycarbonates are polymers containing carbonate groups (-O-(C=O)-O-) as shown in the structure below [17].
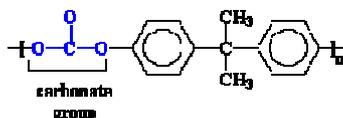
Samples Preparation: Using two solvents (chloroform, toluene) from –GAINLAND CHEMICAL COMPANY- 9 different percentage   concentrations for each solvent from (0.2, 0.4 …. To 1), and from (1, 2, to 5) at room temperatures were prepared by adding a known mass of the polymer to fixed mass of solvents, by using the equation:

$$conc.\% = \frac{m_p}{m_p + m_s} \times 100\% \qquad (1)$$

m_p: mass of polymer.
m_s: mass of solvent.

DENSITY MEASUREMENTS

 The densities of the solutions were determined using the density bottle and electrical sensitive balance with precision of ±0.0001%, as shown in fig. (1)

Flow Time: The values of flow times for all samples were measured by using OSTWLD viscometer at room temperature.

The experimental procedure to measure the viscosity of solutions and solvent by using U-tube viscometer which must be clean in order to obtain accurate results were used the following steps:

- Prepare a water bath at 20°C.
- Put the solvent and place it in the U-tube viscometer.
- The solvent in the viscometer has reached an equilibrium temperature with the water bath.
- Measure the viscosity of the solvent by timing the flow of the liquid through the capillary. Follow the instructions that came with your specific viscometer.
- Put the solution in the U-tube viscometer and check that the temperature has reached equilibrium with the water bath.
- After the solution temperature will be constant, measure the time that it takes for the solution to pass through the bulb on the viscometer.

Absorbance: Using (Genesys 10 UV thermo) spectrophotometer after scanning the values of wavelengths of each concentration of these samples which their absorbance were maximum, fixing this wavelength and the absorbance of these samples were measured for different concentrations at 20°C as shown in fig.(6)

THEORETICAL CALCULATION

Shear Viscosity (H_S):

These values were calculated for all samples, using the following relation

$$\frac{h_s}{r_s \cdot t_s} = \frac{h_w}{r_w \cdot t_w} \qquad ..(2)$$

Where;

η_s & t_s are shear viscosity & flow time for the samples &
η_w & t_w are the same parameters for distilled water.
ρ_s & ρ_w are the densities of each sample & water.[18], as shown in fig.(2).

RELATIVE, SPECIFIC & REDUCED VISCOSITY (H_{REL}, H_{SP}, H_{RED}):

The above viscosities were calculated by using the following relations:

$$\eta_{erl} = \eta_s / \eta_w = t_s / t_w \qquad …(3)$$

$$\eta_{sp} = \eta_{rel} - 1 \qquad ..(4)$$

$$\eta_{red} = \eta_{sp} / C \qquad ..(5)$$

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Where: *C* is the sample's concentration [18].
The values of these viscosities for all samples are shown in figs. (2, 3, 4) for different concentrations.

Intrinsic Viscosity |H|:

Plotting a graph for η_{re} against concentration of all samples had been drawn; the intercept with Y - axis of this graph is |η|.The calculated values of |η| were tabulated in table (1).

Average Viscosity Number Molecular Weight ($\overline{M_v}$):

An empirical equation is used to molecular-weight determination is based upon the determination of the intrinsic viscosity of a polymer in solution through measurements of solution viscosity. Molecular weight is related to intrinsic viscosity by the Mark-Houwink equation given as

$$|\eta| = K\overline{M_v^a} \qquad \qquad \dots(6)$$

Where M_v is the viscosity average molecular weight, and both α and K are empirical (Mark-Houwink) constants that are specific for polymer, solvent, and temperature.

The values of |η| had been taken from table (1), and the constants (K, α) are depended on polymer type. The value of the M_v of this polymer was calculated from following relation [19].
For toluene |η| =0.00285 $M_v^{0.68}$, and for chloroform |η| =0.00483 $M_v^{0.82}$ the calculated values are shown in table (3).

Molar Absorption Coefficient (A_E)
To calculate (a_e) of the samples, the following equation was used:

$$\log\frac{I_o}{I} = A = a_e/C \qquad \qquad \dots(7)$$

Where
(Io) the intensity of incident beam of light for special wavelength.
(I) the absorbed intensity of the same beam
(A) the absorbance of the same beam.

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 [20].

$$a_e = A / C \qquad \qquad \dots(8)$$

Effective Molecular Radius (R_{EFF}.)
Using the equation from ref. [21], the effective molecular radius for samples were calculated.

$$r_{eff.} = \sqrt{\frac{slope}{6.3\times10^{24}}}$$

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Where the slope is for graph plotted between $|\eta|$ and the molar concentration for all samples as shown in table (2).

RESULTS & DISCUSSION

All measured and calculated Physical properties for samples in different concentrations are shown in figures (1-6) and tables (1-4).

The results of most measured and calculated values for all samples show an increase in polymer concentration in two solvents was accompanied by an increase in most of physical properties linearly, except some of them as in graphs and tables.

The concentration of the polymer in the good solvent can be as high as 100%, yet the solution as shown remains clear and uniform. The solvents dissolve the polymer well are "good solvents" (as in chloroform), they lower the free energy substantially [15].

The influence of solvent density (chloroform- 1.483 g/cm^3 & toluene- 0.8669 g/cm^3) on the solution is obvious fig(1) therefore, an approach of the values to solvent density is evident, in return to the viscosity figs.(2-5) and absorption fig(6) increase with concentration we see that the polymer percentage concentration influence on it, and this could be due to overlap concentration of polymer coils [15].

The increase in chloroform slope could attributed to the swelling difference for polymer molecular wrapping in solvents, this leads to volume variance. The real volume of this spherical swollen wrap will be bigger than the calculated as shown in figs. (2-5) [22].

We find that chain compression increases monotonically with increasing solvent density in accord with previous studies of the hard-sphere and hard-disk chain-in-solvent systems [23].

The investigation of UV and invisible spectrum of polymer in solution states have established, this polymer appears to be a good transparent at low wavelengths, this could attributed to The inflexibility and the lack of mobility of crystalline structure (the amorphous nature of the polymer) allows for light transparency. This result suggests that weak absorption exist in the region (280-700) nm [24].

CONCLUSIONS

- In looking over figures, it is readily apparent that according to solubility parameter a solvent "spectrum" is obtained, with solvents occupying positions in proximity to other solvents of comparable "strength". Therefore toluene and chloroform are homologous solvents to polycarbonate since these solvents have similar internal energies.
- As interaction causing association between two types of molecules forming the complex could come close to each other, leaving sufficient space around them. Therefore, these surrounding molecules could be compressed in this polymer, the motion of polymer macro-molecules could be affect by inter-chain for macro-molecules may indirectly have an influence on each other's by way of mutual interactions with other molecules when these are solvent molecules.
- Measurements of viscosity provide a good method for evaluation of polymer as its molecular weights, and for estimation of chain configuration in solution measurements.

- It was found that with an increment of solvent/polymer interaction parameters, the miscibility gaps decreased.

REFERENCES

[1] Perez ,J.M., J.L. Vilas, J.M. Laza, S. Arnaiz, F. Mijangos, E. Bilbao, M. Rodriguez and L.M. Leon, "Effect of reprocessing and accelerated ageing on thermal and mechanical polycarbonate properties", Journal of Materials Processing Technology, Volume 210, Issue 5, 2010.

[2]Ricardo P. W., Keneth S. V.; Joao C. M., "Dynamic behavior of gamma-irradiated polycarbonate", Material (Rio J.) Vol.15, No.2, Mexico, 2010.

[3] Iqbal, M., and Z., Man and H., Mukhtar and B.K., Dutta," Solvent effect on morphology and CO2/CH4 separation performance of asymmetric polycarbonate membranes", Journal of Membrane Science, 2008.

[4]Camarena, J.P.; Espinoza-Gómez, H.; Somanathan, R.; Tiznado, H.; Vélez-López, E.; Romero-Rivera,   R.; Martínez-López,   M.A.; Avalos-Borjaa,   M.; Bek, A.; Alonso-Nuñez, G.; Rogel-Hernández, E.," Molecular Assembly of Multi-Wall Carbon Nanotubes with Amino Crown Ether: Synthesis and Characterization", Journal of Nanoscience and Nanotechnology, Vol. 11, No. 6, 2011.

[5]Wypych, G.," Handbook of Solvents", Chemical Technique Publishing, George, 2001.

[6] Burke, John "Solubility Parameters: Theory and Application", The American Institute for Conservation, Vol.3, 1984.

[7]V.D.M. Verlag Dr. Mueller" Toluene" AG & Co. Kg, 2010.

[8]B. S. Furnell et. al., "Vogel's Textbook of Practical Organic Chemistry", 5th edition, Longman/Wiley, New York, 1989.

[9]J. March, "Advanced Organic Chemistry", 4th ed., Wiley, New York, 1992.

[10] Kirk-Othmer," Encyclopedia of Chemical Technology", John Wiley & Sons, Inc., 2001.

[11] P. watts,"Chloroform", Concise International Chemical Assessment Document 58, Geneva, 2004.

[12] F.P. Miller, A. F. Vandome, J. Mc Brewster," Chloroform", VDM Publishing House Ltd., 2010.

[13] Volker Serini "Polycarbonates" Ullmann's Encyclopedia of Industrial Chemistry, Wiley, Weinheim, 2000.

[14] Naylor S. de Melo, Ricardo P. Weber and Joao C., "Toughness behavior of gamma-irradiated polycarbonate", Polymer Testing, Vol. 26, Is. 3, 2007.

[15] Iwao Teraoka," Polymer solutions", John Wiley & Sons, Inc. 2002.

[16] John R. Nero, Subhas K. Sikdar "One-point determination of intrinsic viscosity for polycarbonate, poly (phenylene oxide), and polyetherimide"Vol.27,1s.12,2003.

[17] James E. Mark "Polymer data handbook" Oxford University Press, Inc. 1999.

[18] Subhi .K. Hasson, Raouf M. Raouf,"The effect of GAMMA radiation on some physical properties and molecular structure of aqueous solutions of (PVA), Journal of basic and applied sciences, Is.No.8, Tripoli, 2000.

[19] H.A. Barnes," Handbook of Elementary Rheology" ,University of Wales, Cambrean Printers ,England , 2000.

[20] J. D. J. Ingle and S. R. Crouch, Spectrochemical Analysis, Prentice Hall, New Jersey, 1988.

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[21] S.K.Hassun, Jr. Iraq. Sc. of physics and math., Iraq, 1994.
[22] A.A.Tagger, Trs, A.A.muhamed, "chemical physics of polymers", Mussel University, 1984.
[23] Mark P. Taylora" Conformation of a polymer chain in solution: An exact density expansion approach", Journal of chemical physics, Vol. 121, No. 21, 2004.
[24] Zerbi, G. "Modern Polymer Spectroscopy", Wiley, 1999.

Table (1) The Values of original viscosity for polycarbonate in Chloroform and Toluene

Original viscosity (di/gm)	Solvents
0.3202	Chloroform
0.2568	Toluene

Table (2) The Values of Effective molecular radius for polycarbonate in Chloroform and Toluene

Effective molecular radius $r_{eff.}$(m)	Slope η_{sp} / C	Solvent
3.783×10^{-13}	0.9016	Chloroform
3.737×10^{-13}	0.088	Toluene

Table (3) The Values of average viscosity molecular weight for polycarbonate in Chloroform and Toluene

Average viscosity molecular weight	Solvent
701.5416059	Chloroform
749.2600679	Toluene

Table (4) Molar absorption Coefficient for polycarbonate in Chloroform and Toluene

Molar absorption Coefficient	Solvent
0.0513	Chloroform
0.0822	Toluene

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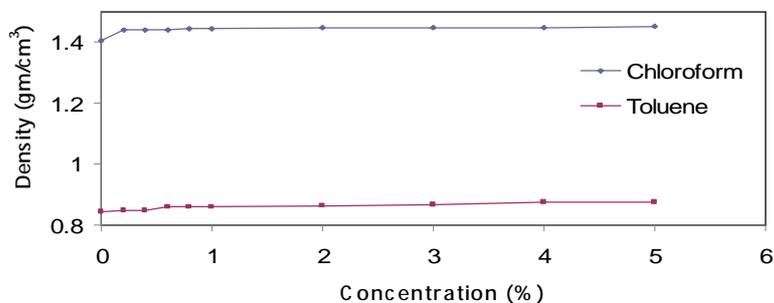
**Figure(1)Dencity of polycarbonate in chloroform
and toluene with concentration**
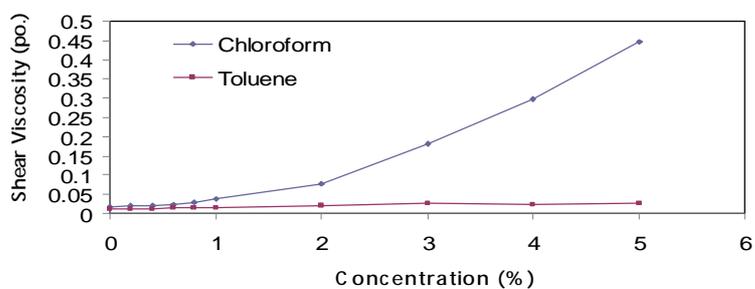
**Figure(2)Shear Viscosity of polycarbonate in chloroform
and toluene with concentration**
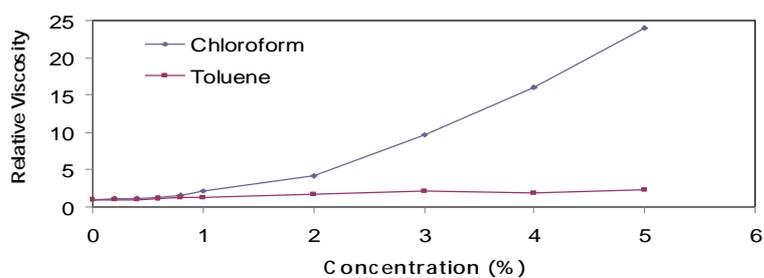
**Figure(3)Relative Viscosity of polycarbonate
in chloroform and toluene with concentration**

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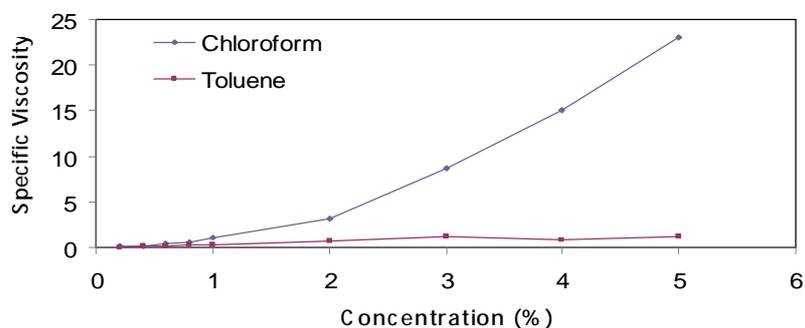
**Figure(4)Specific Viscosity of polycarbonate
in chloroform and toluene with concentration**
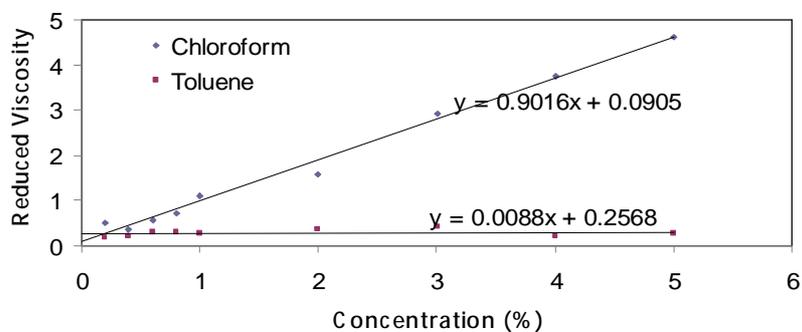
**Figure(5)Reduced Viscosity of polycarbonate in
chloroform and toluene with concentration**
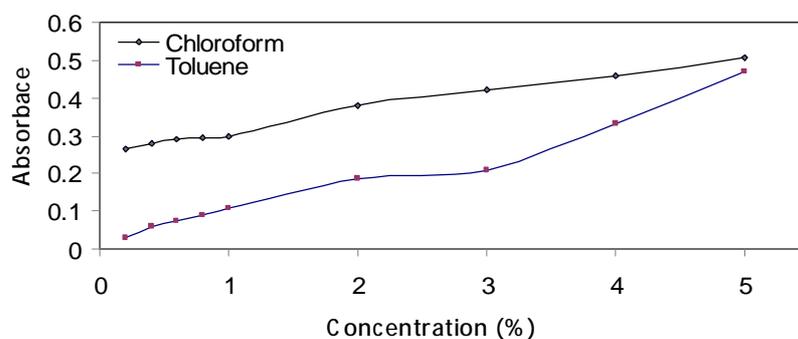
**Figure(6)Absorbance of polycarbonate in chloroform and
toluene with concentration**

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