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MOLECULAR WEIGHT AND ALLIED PROPERTIES OF THE POLYMERS

Dr. A. Raghavendra Rao*, V. Rama Murthy & M. Hari Krishna*****

* Associate Professor, Department of Physics , KKR & KSR Institute of Technology & Science, Guntur, Andhra Pradesh
** Retired Professor, SK University, Anantapuram, Andhra Pradesh
*** Lecturer in Physics, Department of Physics, TJPS College (PG Courses), Guntur, Andhra Pradesh

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Abstract:

There are many experimental methods to determine the molecular weight of the polymers. The viscosity, sedimentation centrifugation, light scattering and XRD are few experimental methods in vogue. New experimental methods based on dispersion [1] , glass transition temperature are a few developed recently. Though the empirical relation between glass transition temperature and molecular weight is suggested [2] no detailed approach to correlate glass transition temperature with molecular weight is there so far in literature . In present investigation an algebraic relationship is developed correlating the molecular weight ,glass transition temperature, refractive index and density ,since it has been observed that the molecular weight is directly proportional to density, refractive index and inversely proportional to glass transition temperature. Summing up all these concepts an algebraic relation is developed and applied to arrive at molecular weight of few polymers. The polymers taken for this investigation are Poly vinyl Acetate, Poly Vinyl Chloride, Poly Styrene, Poly Methyl Meta Croylite, Poly Vinyl Benzene, Poly Acryolite, Polyvinyl Alcohol, Poly tetra floro ethylene. The data on density, refractive index and glass transition temperature for these samples were taken from references 3,4, 5 and are utilized to arrive at molecular weights. From the data on refractive index ,density and molecular weight the fallowing related physical parameters like optical dielectric constant ,reflection loss , molar refractivity ,electron polarizabulity and inter ionic distance have been evaluated .A study of variation of these evaluated parameters with molecular weight is made .From the study it has been inferred that the reflection loss ,optical dielectric constant and electron polarizabulity vary almost similar fashion with molecular weight .Where as inter-ionic distance and molar refraction shows a distinct variation .A plausible explanation for these physical dependence of the parameters on molecular weight is given and the merits and demerits are discussed thoroughly.

Key Words: Molecular Weight, Refractive Index, Density, Glass Transition Temperature, Optical Dielectric Constant, Reflection Lass, Molar Refractivity & Electron Polarizability and Inter Ionic Distance and Polymers Like Polyvinyl Acetate.

Introduction:

The molecular weight is a parameter which is uniquely determined for monomers by addition of atomic weights of the constituents. But the molecular weight of the polymers is not unique since the number of atoms in the polymer cannot be exactly estimated. As such there are many analytical methods, developed to determine the molecular weight of the polymers each depending on the specific property .For example the molecular weight based on viscosity is different from the one which is determined by scattering method. But the majority of the methods in literature on the determination of molecular weight involve too much sophistication. They include either static methods like light scattering using light scattering photometer of Bryce and kratcky camera for small angle X – ray scattering studies and the ,hydrodynamic methods ,on the experimental side or much of the computing techniques . However a few methods based on refractive index and dispersion relation measurements[1] and algebraic methods[1] are developed recently ,which are less cumbersome and involve less computation .One such latest method developed in our laboratory is based on the dependence of Glass Transition temperature of the polymers on the molecular weight. The present paper deals with the development of the algebraic relationship between glass transition temperature, refractive index and density. The temperature limit for almost all amorphous polymers ,above which the substance remains soft, flexible and rubbery and below which it become hard ,brittle and glassy characterises the glass transition . Experimentally glass transition temperature can be determined from Dilatometric method and thermo mechanical method. And the vast valuable literature available glass transition temperature [4] and the easy experimental techniques to determine the glass transition temperature leads the author to think of an algebraic relationship. At glass transition temperature the variations in the refractive index and density are found to be not prominent. Thus the transition temperature along with refractive index and density are supposed to be variant with molecular weight.

It is used to measure flexibility variations and mechanical strength response. Thus the glass transition temperature (T_g) is an important parameter and a data on that is sure to give information on molecular weight. A look at the data on the refractive index, Density and Glass Transition temperature of a few polymers led the author to think of the variation of molecular weight directly with density, directly with refractive index and inversely with Glass transition temperature. On combining these three behaviors, a final algebraic relationship is arrived at.

Formula:

The relationship developed connecting T_g with molecular weight, density and refractive index reads as

$$\mathbf{Log\ M = Log\rho + \frac{1}{\sqrt{T_g}}\left[\frac{n - 1.128}{0.0048}\right] - - - - (1)}$$

Where M – is molecular weight of the polymer. n – is refractive index of the polymer, ρ – is the density of the polymer and T_g – is the glass transition temperature of the polymer.

From the available data on density and refractive index and calculated molecular weight, a few physical parameters like optical dielectric constant, reflection loss, etc…, are determined using the equations (2) to (5). The dielectric constant (ε) can be calculated using the refractive index of the glass[8].

Di electric constant (ε) = $(n_d)^2$ ------(2)

The reflection loss from the glass surface can be computed from refractive index using Fresnel's formula [9].

$$R = \left[\frac{n_d - 1}{n_d + 1}\right]^2 - - - - (3)$$

The molar refractivity (Rm) for each glass can be evaluated using[10]

$$R_M = \left(\frac{n_d^2 - 1}{n_d^2 + 2}\right)\frac{M}{\rho} - - - - - (4)$$

The electronic polarizability can be expressed as [11]

$$\alpha_M = \frac{3}{4\pi N}\left(\frac{n_d^2 - 1}{n_d^2 + 2}\right) - - - - - - (5)$$

The inter-ionic separation can be determined as [12]

$$r_i = \left(\frac{1}{N}\right)^{(1/3)} - - - - (6)$$

The work is presented on the following polymers and a brief account of the same is also furnished

The data used for calculation of molecular weight are given in table I. The molecular weights of the polymers calculated by making the use of expression is given in table II, where in the values of molecular weights obtained from other standard methods are also cited. Taking the data of refractive index ,density and molecular weight of these polymers the related properties, viz, optical dielectric constant ,reflection lass , molar refractivity ,electron polarizabulity and inter ionic distance are calculated and are presented in table III. The data on dielectric constant and other allied properties and their variation with molecular weight of the polymers is depicted in graphs 1, 2 and 3.

Poly Vinyl Acetate[13]:

The monomer of vinyl acetate is conveniently prepared by the reaction of acetylene with acetic acid. Acetaldehyde is produced by the oxidation of olefins or hydrocarbons .vinyl acetate is largely polymerized by emulsion polymerization .poly vinyl acetate is leathery, colorless thermoplastic material ,which softens at relatively low temperatures and which is relatively stable to light and oxygen. The polymers are clear and non crystalline .The chief applications of polyvinyl acetates are as binders for water based or emulsion paints.

Poly Vinyl Chloride[14]:

The vinyl chloride monomer (VCM) is prepared from chlorine, acetylene and ethylene. The polymerization of vinyl chloride gives poly vinyl chloride4.PVC is tough, strong thermoplastic material, which has an excellent combination of physical and electrical properties. The products are usually characterized as plasticized or rigid types.PVC is one of the most versatile plastics. The plasticized polymer is an elastic material and is used to shower curtains, flower coverings, raincoats, dish pans, dolls, wire insulations and film etc...

Poly Styrene:

Styrene is produced by the dehydrogenation of ethyl benzene which, in turn, is obtained by the alkylation of benzene with ethylene polystyrene is hard transparent, glass like thermoplastic resin. It is characterized by excellent electrical insulation properties, relatively high resistance to water; high refractive index and low softing temperature .Polystyrene may also be fabricated in the form, which is used in packing food-service articles and insulating panels.

Poly Vinyl Alcohol:

The poly vinyl alcohol can be produced commercially from poly vinyl acetate. It is used in the grease resistant coating and paper adhesives, for treating paper and textiles and as emulsifiers and thickeners. It is water soluble solvent.

Poly (Methyl Methacrylate):

PMMA is a transparent thermoplastic, often used as a lightweight or shatter resistance alternative to safety glass .It is sometimes called acrylic glass chemically, it is the synthetic polymer of methyl methacrylate.

It is produced by emulsion polymerization, solution polymerization and bulk polymerization. Generally radical initiation is used but anionic polymerization of PMMA can also be performed. PMMA produced by radical polymerization is static and completely amorphous.

Poly Tetrafluro Ethylene:

The monomer of tetra fluro ethylene can be polymerized readily and conveniently by emulsion polymerization under pressure, using free radical catalysts such as peroxides or persulphates. The polymer is insoluble and resistant to heat (up to 250 0 c) and chemical attack, PTFE bearings, valve seats, and package gaskets. The containers and tubing can with stand relatively severe conditions. Because of its excellent insulating properties, it is useful when a dielectric material is required for service at high temperature. The non adhesive quality is often turned to advantage in the use of PTFE to coat articles such as non sticking frying pans and other kitchen ware.

Table 1: Molecular parameters like refractive index, density and glass transition temperature

S.No	Name of the polymer	Refractive Index	Density Gms/cc	Glass transition temperature[1,15]
1	Poly vinyl Acetate	1.466	1.186	305
2	Poly Vinyl Chloride	1.541	1.392	254
3	Poly Styrene	5.590	1.111	378
4	Poly Methyl Meta Croylite	1.492	1.188	378
5	Poly Vinyl Benzene	1.526	0.950	528
6	Poly Acryolite	1.518	1.175	370
7	Polyvinyl Alcohol	1.625	1.025	358
8	Poly tetra floro ethylene	1.380	2.200	355

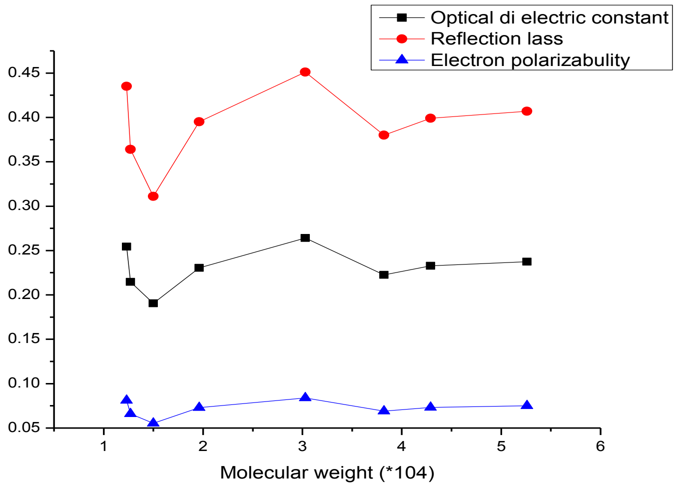
Table 2: Molecular weights of the polymers

S.No	Name of the Polymer	Molecular weight of the Polymer* 10^4			
		From Glass Transition Temp (Present Work)	From Refractive Index	From Densities	Standard [15]
1	Poly vinyl Acetate	1.27	13.39	4.390	0.3 – 150
2	Poly Vinyl Chloride	5.26	22.22	7.05	1.0- 40
3	Poly Styrene	1.23	6.19	7.52	1.0- 400
4	Poly Methyl Meta Croylite	3.83	15.71	14.45	1.0- 700
5	Poly Vinyl Benzene	4.29	--	--	1.0- 200
6	Poly Acryolite	1.97	18.06	30.20	1.0- 400
7	Polyvinyl Alcohol	30.41	6.39	12.819	1.0- 400
8	Poly tetra floro ethylene	1.51	3.69	53.165	1.0- 400

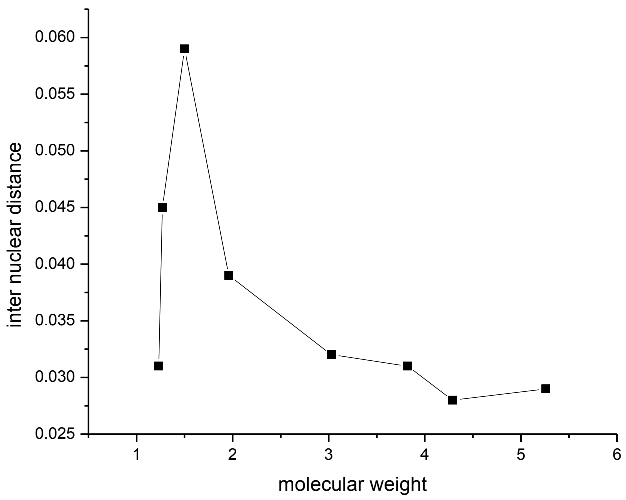
Table 3: Variation of physical parameters with molecular weight

S.No	Name of the Polymer	Molecular Weight *10^4	Optical Dielectric Constant*10	Reflection Loss	Molar Refractivity *10^5	Electron Polarizability	Inter Ionic Distance
1	Poly Styrene	1.230	0.2544	0.435	0.2886	0.0811	0.031
2	Polyvinyl Acetate	1.270	0.2146	0.364	0.2713	0.0660	0.045
3	Polytetra Floro Ethylene	1.5	0.1904	0.311	0.1687	0.0553	0.059
4	Poly Acryolite	1.960	0.2304	0.395	0.4280	0.073	0.039
5	Polyvinyl Alcohol	3.030	0.2641	0.451	0.7775	0.084	0.032
6	Poly Methyl Meta Croylite	3.820	0.2226	0.380	0.8201	0.069	0.031
7	Poly Vinyl Benzene	4.290	0.2328	0.399	1.1608	0.0733	0.028
8	Poly Vinyl Chloride	5.260	0.2374	0.407	0.9741	0.075	0.029

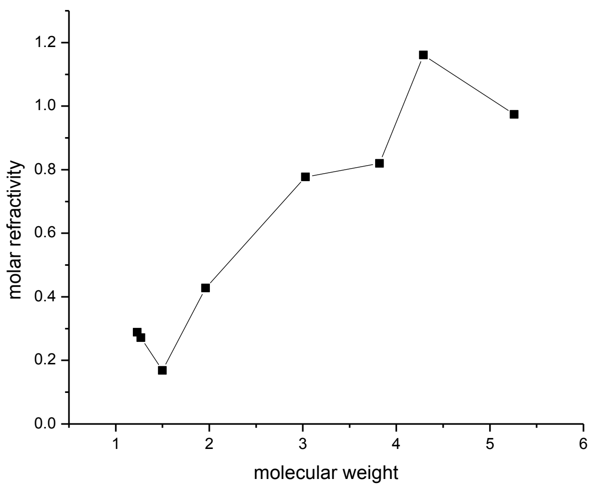
Graph 1: Variation of Physical Properties with Molecular weight



Graph 2: Variation of inter nuclear distance with molecular weight



Graph 3: Variation of molar refraction with molecular weight



Results and Discussion:

The values of molecular weight from this method is found to be well within the range of the values reported .This suggests that any small variation in the state of the polymer due to stress or thermal or electrical impulse will automatically bring changes in respective values of density, refractive index and glass transition temperature so as not to affect the molecular weight. This is easy method for determining the molecular weight and easy for comparison of molecular weight obtained and comparability of this method related to others is also proved. A close look at the properties of optical dielectric constant ,reflection loss , molar refractivity ,electron polarizability and inter ionic distance shows similar variation .The dielectric constant ,reflection lass and electron polarizability show a gradual gradation in values as they proceed from highly unsaturated styrene to least unsaturated flouroethylene . Similarly the presence of poly vinyl alcohol contributes to maximum properties of dielectric constant, electron polarizability and reflection loss and gradually falls to a minimum at vinyl chloride .With the exception of poly vinyl alcohol the general properties of dielectric constant, reflection loss and electron polarizability of poly vinyl acetate, poly vinyl benzene, poly vinyl chloride shows almost the same behavior. From the data on poly styrene and poly vinyl alcohol it shows that a replacement of an OH group by benzene ring, there is no change in physical properties like optical dielectric constant, reflection loss and electron polarizability. The presence of unsaturated bonds like C=O and C-O decreases the optical dielectric constant, reflection loss and electron polarizabulity due to the hindrance to electrons polarizing forces. Highly electro negative character of florins gives positive hindrance to polarizability, dielectric constant and reflection lass so these values are minimum. The maximum inter ionic distance in poly tetra tetrafloro ethylene is attributed to high electro negative character of C-F bonds.

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