



Studies of Molecular Interaction of Polystyrene with Toluene in the presence of Et₄NI salt using Ultrasonic Technique

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Abstract : The study of polymeric solution has always been a new subject among all the researchers whether about its physiochemical behavior or thermo-physical properties. We have investigated the influence of tetraethyl ammonium iodide (Et₄NI) salt on the molecular interaction between polystyrene and toluene at 313.15 and 323.15K.

In this study, an attempt was made to compute the viscosity and ultrasonic velocity of polymeric solution (polystyrene + toluene + Et₄NI) of different concentrations (0.0024, 0.0047, 0.0094 and 0.0189kgL⁻¹). Magnetic Float Densitometer, estimated density from these experimental data, we have calculated some acoustical parameters like β_{ad} , L_f , τ , z using standard empirical relationship. The effect of Et₄NI salt on molecular interactions were analysed and interpreted in terms of solute – solvent interactions. The abrupt change in thermo-physical properties of polymeric solution at characteristic temperature and concentration is due to structural interaction like association, H-bonding between polystyrene and toluene molecules.

Keywords - Polymeric solution, Et₄NI salt, ultrasonic studies, structural interactions and acoustical parameters.

I. INTRODUCTION

The study of polymer solutions has attracted attention to many researchers in current years [1-4] because the ultrasonic velocity provides valuable information about the nature of liquid systems. Based on molecular association, complex formation and other structural changes that affect the thermal behavior of the system, which in succession gives almost exact change in ultrasonic velocity and the state of any solution (N. Karunanidhi et.al 1999). The thermo-physical properties of solution may be investigated with the help of propagation of ultrasonic waves in the medium (S.C Bhatt et.al 1999) [5].

Our previous work was assigned with the observation of inter and intra molecular interactions in polystyrene and toluene solution at different temperature and concentration in the absence of salt. Further, study was continued by adding R₄NI salt and observed the influence of tetraalkylammonium cation (Et₄N⁺) on thermo-physical behaviour and the nature of structural interactions with polymeric solution of polystyrene and toluene at 313.15 and 323.15K. In the present work, some thermo acoustical parameters were explained with the help of ultrasonic and transport studies to investigate the internal structural of molecular interactions at different temperatures.

Polystyrene is a synthetic aromatic polymer made from the monomer unit styrene. Polystyrene can be solid or foamed is an expensive resin per unit weight rather poor barrier to oxygen and water vapor and has a relatively low melting point. Polystyrene is naturally transparent, but can be coloured with colorants, used in protective packaging (such as packing peanuts, CD and DVD cases), containers (such as “clamshells”), lids, bottles, trays, tremblers, disposable cutlery and in the making of models. Toluene is a colourless, flammable, non-corrosive solvent with benzene like odour, used in aviation gasoline and high octane blending stock, and as a solvent for paints, coatings, gums and resins.

Since many years, ultrasonic studies in liquid and polymeric solutions have been the major subject of research to solve many industrial problems. The information about the thermo physical and acoustical properties of polymeric solution is very essential for polymer industries. Such properties of polymeric solution are triggered to improve the quality of manufacturing things. By review literature [6], it was clear that some acoustical measurements were used to identify the nature of molecular interactions between polymer and solvent. Furthermore, ultrasonic techniques had been significantly used in polymer processing and chemical reaction. It appears necessary to know something about the mechanism of structural interaction of polystyrene to assist in explaining molecular interactions in some plastic and synthetic rubber like materials containing styrene. In polymer science, polystyrene is probably the most extensively investigated linear chain molecule with no actual result expected, although some recent measurements in different laboratories have shown quite good experimental agreement [7]. A new situation occurred, with

the facilities of ultrasonic and viscometrical studies, which allow very accurate measurement of the geometric and thermodynamic interaction properties.

The monomer unit characterizes a polymer of a particular group. The study of structural interactions of polystyrene with toluene has been suggested as one such study treated with polymer of different concentration as an association at various temperature using ultrasonic techniques [8, 9]. The molecular structure of polymer has been related to acoustical parameters such as adiabatic compressibility, acoustic impedance, relaxation time, free energy, inter molecular free length. This gives polystyrene relatively simple structure in regard to molecular interaction. The chemical structure of polystyrene may be divided into three parts: the benzene ring, the tertiary carbon atom bearing a single hydrogen atom and the methylene connecting bridge in which the secondary carbon atom holds two hydrogen atoms.

In the present paper, some of the interesting properties of polystyrene in toluene like molecular rearrangement, hydrogen bonding, molecular relaxation and structural interactions using ultrasonic velocity have been reported. Polystyrene completely dissolved in toluene solvent often ranges from lower to higher concentration. In each concentration, thermo-physical and thermo acoustical nature of polystyrene solution shows characteristic properties dependent upon temperature. The deviations are caused by the rotational hindrance of the polymer chain with alkyl chain or segmental motion giving stiffness to chain [10]. The thermodynamic behaviour may in addition be influence by the friction force of the individual units.

Material :

Polystyrene was obtained of Sigma Aldrich, from Mumbai, India. Toluene used was of analytical reagent (AR) grade of minimum assay of 99.9% obtained, from Chennai, India. The polymeric solution was prepared by dissolving polystyrene in toluene w/v to get 0.014 and 0.016M by adding the calculated amount of tetra ethyl ammonium salt (R_4NI) in polymeric solution (polystyrene + toluene). To make homogeneous liquid mixture of polymeric solution used magnetic stirrer [REMI make] at a rate of 1000 rpm.

Ultrasonic velocities (u) of polymeric solutions were measured at 313.15 and 323.15K using Single Crystal Ultrasonic Interferometer at a fixed 2 MHz frequency (Model-83S) supplied by Mittal enterprises, New Delhi, has an accuracy of 0.4 m/sec at 25°C. The temperature was kept constant, by constant temperature water bath with an accuracy of $\pm 0.1K$.

Equations :

The densities (d) of these solutions were determined at different temperatures by Magnetic Float Densitometer [11], using Eq1.

$$\text{Density (d)} = (W + w + f \times I) / (V + w/d_{pt}) \quad (1)$$

The terms involved in this equation have their usual meaning. The data of solution, *i.e.*, weight, w used, current, I , passing in the circuit, ρ_{pt} , density of Pt and V , volume of float.

The viscosity (η) measurements were done through Ostwald's viscometer. The viscometer is filled with reference liquid (distilled water) and then immersed in water bath. Using the time taken for the distilled water and mixture, the viscosity (η) of unknown polymeric solutions were determined by using Eq.2.

$$\eta_s / \eta_w = \rho_s / \rho_w \times t_s / t_w \quad (2)$$

Where η_w , ρ_w and t_w are the viscosity, density and time-flow of water respectively and η_s , ρ_s and t_s are the viscosity, density and time-flow of unknown experimental solution respectively.

In addition to these, some important acoustical parameters were calculated using standard empirical relationship like -

$$\text{Adiabatic Compressibility, } \beta_{ad} = 1/U^2 \rho \quad (3)$$

Where, ρ = density & U = ultrasonic velocity.

$$\text{Intermolecular free length, } L_f = K_T \beta_{ad}^{1/2} \quad (4)$$

Where, K_T is a temperature dependent constant called Jacobson constant equal to $93.875 + 0.345T$.

$$\text{Acoustic impedance, } Z = U\rho \quad (5)$$

Where, U = ultrasonic velocity & ρ = density

$$\text{Free energy, } \Delta G = RT \ln(kT\tau/h) \quad (6)$$

Where, k = Boltzmann constant, T = Absolute temperature and h = Plank's constant.

$$\text{Relaxation time, } \tau = 4\eta/3\beta_{ad} \quad (7)$$

Where, η = Viscosity & β_{ad} = Adiabatic compressibility

Method:

The process was started with the measuring of weight of the polymer (Polystyrene).

The next process was to discover the molecular weight of the polystyrene. For this step there were so many methods but we chose the viscosity method over all of them. Two temperatures were chosen as 40 & 50 degree centigrade to precede the work. At the above temperature and with the calculating concentrations (0.0024, 0.0047, 0.0094 & 0.0189 kgL⁻¹) further the work moved up and in the presence of tetra ethyl cation the molecular interactions were performed.

II. RESULTS AND DISCUSSION

Thermo-physical and acoustical parameters were determined for polymeric solutions of polystyrene and toluene with tetra ethyl ammonium iodide salt at 313.15 and 323.1K. The calculated acoustical parameters like β_{ad} , z , τ , L_f have been reported in Table 1. The structural and molecular interactions involved between polystyrene and toluene with respect to change in molar concentration of tetraethyl ammonium salt were explained using above parameters. In the present work, the viscosity (η) increases with increase in molar concentration but decreases with rise of temperature given in Table 1. In all cases, such change may be due to maximum frictional force produced between polymer chains. It was found that the density of the polymeric solution increases with polystyrene content because the number of polymer chain increases and the solution becomes denser. Increase in the density of the solution can be understood on the basis of larger molecular weight of polystyrene compared to toluene.

Polyethylene consists of non-polar, saturated, high molecular weight hydrocarbons with chemical formula $(C_2H_4)_n$. It is of low strength, shows hardness and rigidity, but has high ductility and impact strength as well as low friction. Toluene, also known as methylbenzene has a chemical formula C_7H_8 . Et₄NI is a quaternary ammonium compound with the formula $C_8H_{20}N^+I^-$ used as a source of tetraethyl ammonium ions in pharmacological studies as well as organic chemical synthesis. Here, observed the role of smallest tetra alkyl ammonium chain length cation (R_4N^+) on the thermo-physical properties as well as nature of molecular interactions of polymeric solution of polystyrene and toluene.

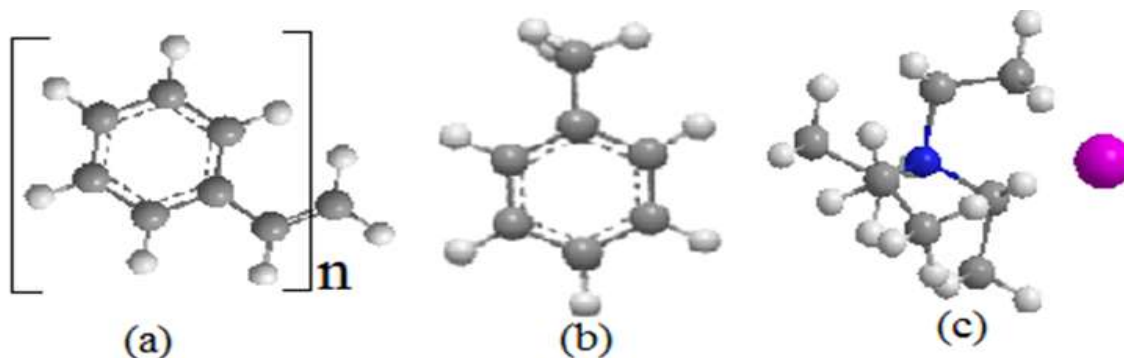


Fig. 1 – 3-Model: (a) Polystyrene, (b) - Toluene & (c) - Tetra Ethyl Ammonium Iodide (Et₄NI)

Tables 1: Experimental calculated values of thermo-physical and acoustical parameters for polymeric solution of Polystyrene + Toluene without and with R₄NI salt.

Salt	(At 313.15±1) K								
Et ₄ NI (g)	C (kgL ⁻¹)	ρ (Kgm ⁻³)	$\eta \times 10^{-3}$ (NSm ⁻²)	u (ms ⁻¹)	$\beta_{ad} \times 10^{-10}$ (kg ⁻¹ ms ²)	$z \times 10^3$ (kgm ⁻² s ⁻¹)	$\tau \times 10^{-10}$ (s)	$\Delta G \times 10^{-21}$ (gJmol ⁻¹)	$L_f \times 10^{-11}$ (m)
Without Salt	0.0024	960.4	0.5756	1224	6.9502	1175.5296	5.049	28.1787	5.5757
	0.0047	961.6	0.5860	1232	6.8516	1184.6912	5.245	28.2500	5.5362
	0.0094	962.5	0.5979	1244	6.7136	1197.3500	5.462	28.3265	5.4802
	0.0189	963.5	0.6083	1256	6.5794	1210.1560	5.637	28.3854	5.4249
With Salt	0.0024	1014.0	0.6155	1212	6.7142	1228.9680	5.151	28.2163	5.4802
	0.0047	1017.2	0.6254	1224	6.5621	1245.0528	5.350	28.2874	5.4178
	0.0094	1020.2	0.6383	1236	6.4160	1260.9672	5.585	28.3679	5.3570
	0.0189	1022.9	0.6479	1248	6.2773	1276.5792	5.800	28.4389	5.2995
Without Salt	(At 323.15±1) K								
	0.0024	953.3	0.5086	1200	7.2849	1143.9600	4.733	29.0136	5.8163
	0.0047	954.4	0.5193	1208	7.1803	1152.9152	4.901	29.0816	5.7743
	0.0094	955.4	0.5287	1216	7.0786	1161.7664	5.061	29.1441	5.7331
	0.0189	956.4	0.5393	1224	6.9793	1170.6336	5.238	29.2107	5.6928
With Salt	0.0024	1012.8	0.5303	1188	6.9961	1203.2064	4.708	29.0040	5.6997
	0.0047	1015.6	0.5352	1196	6.8840	1214.6576	4.831	29.0542	5.6541
	0.0094	1018.9	0.5415	1204	6.7714	1226.7556	4.970	29.1089	5.6075
	0.0189	1022.2	0.5492	1212	6.6593	1238.9064	5.123	29.1675	5.5609

Generally, the values of ultrasonic velocity increases with concentration, which suggests that the solution involves strong solute-solvent interaction. On other hand with rise of temperature, there is a decrease in ultrasonic velocity suggesting that the thermal energy is responsible for the excess of repulsive forces between the polymeric layers.

Figures :

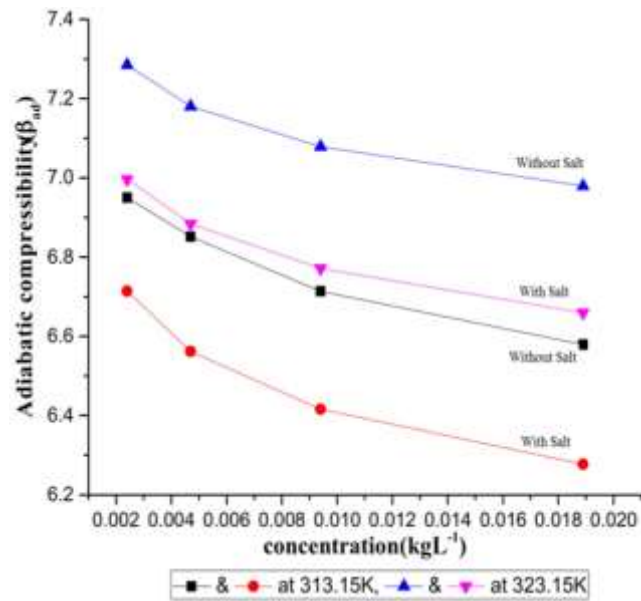


Fig. 2: graph plotted between β_{ad} vs. C

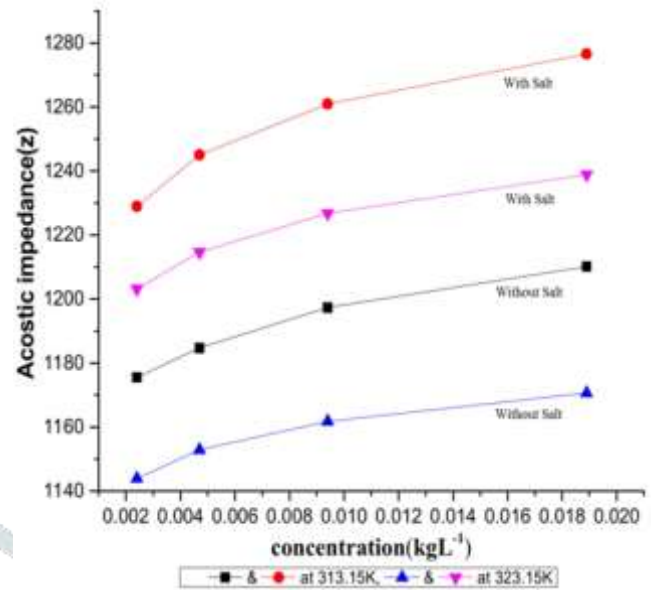


Fig. 3: graph plotted between z vs. C

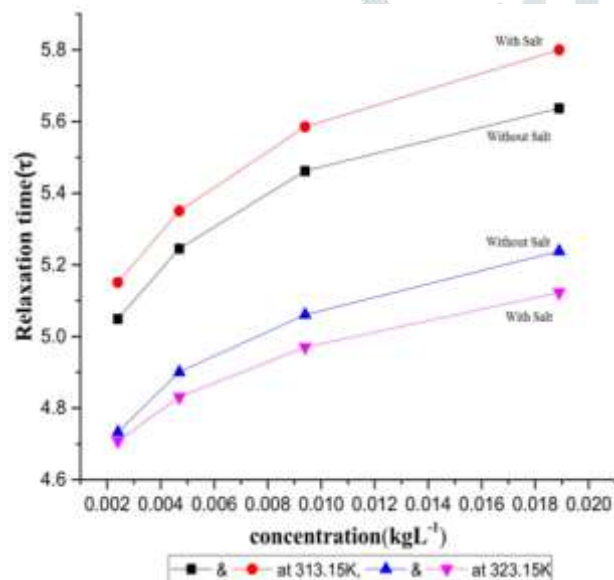


Fig. 4: graph plotted between τ vs. C

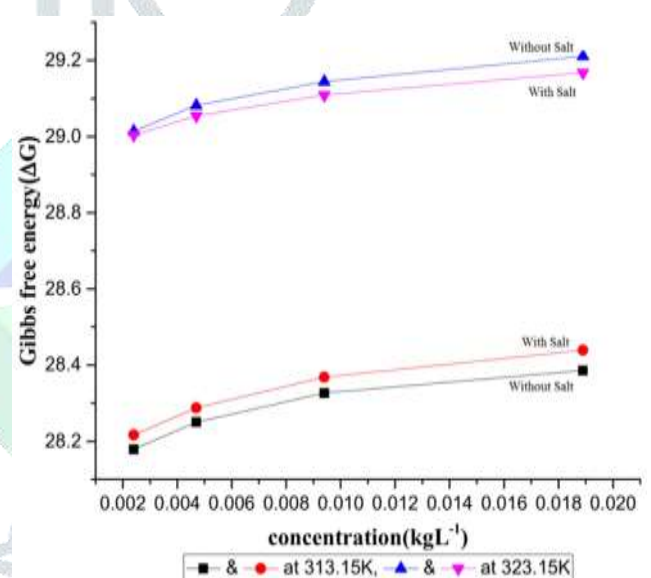


Fig. 5: graph plotted between ΔG vs. C

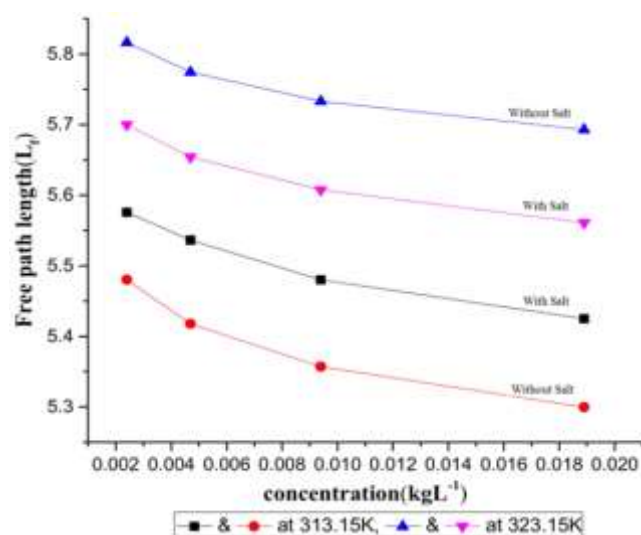


Fig. 6: graph plotted between L_f vs. C

From Fig. 2, found that, β_{ad} decreases with the increase of polystyrene concentration. This gives an indication of closed packing of molecules or attractive molecular interaction with $\text{Et}_4\text{N}^+\text{I}^-$ ions, provide more favourable condition for polystyrene and toluene molecules in association process. $\text{Et}_4\text{N}^+\text{I}^-$ ionic salt absorbed little amount of energy from the system for their ionization or ionic dissociation. Due to this, molecular energy of the system decreases hence polystyrene and toluene molecules comes closer to each other and get associated. Such strong association process may be due to strong H-bonding between polystyrene and toluene molecules. β_{ad} shows a reciprocal nature of ultrasonic velocity, according to Eyring and Kincaid [12], if sound velocity increases, molecular association take place between solute and solvent. At high concentration, the rotational hindrance of monomer unit is maximum due to greater association of solute and solvent molecules resulting into stiffness of polymer chain, hence $\text{Et}_4\text{N}^+\text{I}^-$ salt play an important role in the stiffness of the polymer bone. However, β_{ad} increases with increase in temperature, which is a characteristic of the polymeric solution [13]. This trend shows for all the systems indicating the strengthening of intermolecular forces among polymeric molecules for the selected polymeric system.

The graphical representations of all acoustical parameters at 313.15K and 323.15K with and without addition of 0.0184 g of salt in polymeric solutions.

The values of z depend on the structural changes of the polymeric solution, tells about the elastic properties of the medium. The gradual increase in the value of z with concentration causes strong intermolecular association occurred between polymer and toluene molecules, given in Fig. 3, but enhanced calculated z values are found due to the interaction of ionic salt. On raising the temperature, z values decreases represent the thermal nature of polymeric solution and lesser elasticity with temperature.

For all the systems, increase of polymeric concentration is accompanied by an increase in relaxation time (τ) shown in Fig. 4, which indicates that viscous forces play a dominant role in the relaxation process. The molecular interaction causing association between polymeric and toluene molecules are responsible for increase in the values of τ . Such interaction hardly give reason for the increase in the values of u and indicate that degree of cooperation for relaxation process of the molecule increases the bulk of modulus when polymeric solute is added to solvent with $\text{Et}_4\text{N}^+\text{I}^-$ ionic salt.

The decreasing values of β_{ad} and L_f were observed with the concentration of polystyrene; indicate the formation of strong hydrogen bonding between polystyrene and toluene. The increase in viscous forces plays a dominant role in the relaxation process, shows that the solution is highly ordered due to outstanding H bonding and such solution generally absorbs more ultrasonic energy.

Free energy (ΔG), increases slowly with increasing concentration of polymeric solution, shown in Fig. 5. This trend of curve predicts that several types of molecular interactions, such as molecular reorganization, H-bonding, affect the thermo-physical properties of polymeric solution. The change in free energy hindrance the segmental motion of polymeric chain causes increase in free energy of the solution system. The same trend obtained with temperature variation.

Intermolecular free length (L_f) also follows the same trend as that of β_{ad} , shown in Fig. 6, the decreasing value of L_f with concentration as well as temperature indicates the presence of strong molecular interaction at higher temperature and concentration. At lower concentration range, the polymeric molecules exhibit weak interaction due to dominant repulsive forces over attractive forces. The decreasing trends of L_f indicate that there occurred a significant interaction between the molecules of polystyrene and toluene forming hydrogen bonding [14-17].

Therefore, it can be suggested on the basis of observed experimental data and literature information that the addition of polystyrene to toluene would disrupt their self-associative structure with $\text{Et}_4\text{N}^+\text{I}^-$ ionic salt and stabilizes molecular structure. The present investigation reflects that lower as well higher concentration is more effective than mid-range concentration towards strong molecular interaction.

CONCLUSION

Viscosity studies were performed for polystyrene in toluene with tetraethyl ammonium iodide salt in the concentration range from 0.0024 to 0.0189Kg/L-1 at 313.15 and 323.15K. It may be concluded that on the addition of Et_4NI salt to polystyrene and toluene solution, we have found more favourable condition for strong hydrogen bonding phenomena at higher concentration of polystyrene. The $\text{Et}_4\text{N}^+\text{I}^-$ ionic salt was more effective towards molecular interaction and provides greater stiffness to polymeric chain. Such cooperative phenomena occurred by the absorption of energy of polymeric molecular system by $\text{Et}_4\text{N}^+\text{I}^-$ salt increases the molecular thermal stability of polymeric system. A specific nature of molecular interactions was observed due to less segmental motion and greater chain stiffness of polymer. This effect occurs due to the presence of tetraethyl ammonium iodide salt.

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REFERENCES

- [1] Sun, Z.; Wang, W.; Fung, Z. (1992). Criteria of polymer miscibility determination by viscometry. *European Polymer Journal*. 28, 1259.
- [2] Yu, A.; Ramesh, P.; Sun, X.; Bekyarova, E.M.; Itkis, E. ; Haddon, R.C. (2008). Enhanced thermal conductivity in hybrid graphite nanoplatelet-carbon nanotube filler for epoxy composites. *Adv. Mater.* 20, 4740 – 4744.
- [3] Ma, A.J.; Chen, W.X.; Hou, Y.G.; Zhang, G. (2010). Dispersion, mechanical and thermal properties of epoxy resin composites filled with the nanometer carbon black . *Ploym. Plastics. Technol. Eng.* 49, 916 – 920.
- [4] Stothers, B. (1972). *C-13 NMR Spectroscopy*. Academic Press. New York. 24, 574.
- [5] Bhatt, S.C.; Singh, Pankaj K. (2010). Investigation of Acoustical Parameters of Polyvinyl Acetate. *Applied Physics Research*. 2.
- [6] Suryanarayana, C.; Pugazendhi, V. (1986). *Indian J. Pure Appl. Phys.* 24, 406.

- [7] Rajkotia, K.M.; Buluja, S.; Parsanaph. (1997). Eur. Polym. J. 33, 1005.
- [8] Maul, J.; Frushour, B.G.; Kontoff, J.R.; Eichenauer, H.; Ott, K.-H. and Schade, C. (2007). Polystyrene and Styrene Copolymers. Ullman's Encyclopedia of Industrial Chemistry Wiley-VCH, Weinheim. 21, 615.
- [9] Vasoya, P.J.; Mehta, N.M.; Patel, V.A.; Parsania, P.H. (2007). Effect of temperature on ultrasonic velocity and thermodynamic parameters of cardo aromatic polysulfonate solutions. Journal of Scientific and Industrial Research. 66, 841–884.
- [10] Kannappan, V.; Santhi, B.S.; Jonathan, D.R. (2014). Ultrasonic investigation on segmental motion of some polymers in solution. Indian Journal of Chemistry A. 53, 688–694.
- [11] Pathak, R.N.; Saxena, I. (1998). Ind. J. Eng. Mat. Sci. 5, 278-784.
- [12] Eyring, J.F.; Kincaid. (1938). Free volumes and free angle ratio of molecules in liquids. J. Chem. Phys. 6, 620-629.
- [13] Arancibia, J.A.; Escandar, G. M. (1999). Complexation study of diclofenac with β -cyclodextrin and spectrofluorimetric determination. Analyst. 124, 1833.
- [14] Lerbret, A.; Affouard, F.; Bordat, P.; Hedoux, A.; Guinet, Y.; Descamps, M. (2011). Slowing down of water dynamics in disaccharide aqueous solutions. J. Non-Cryst. Solids. 357, 695–699.
- [15] Bekiroglu, S.; Sandstrom, A.; Kenneand L.; Sandstrom, C. (2004). Ab initio and NMR studies on the effect of hydration on the chemical shift of hydroxyprotons in carbohydrates using disaccharides and water/methanol/ethers as model systems. Org. Biomol. Chem. 2, 200-205.
- [16] Sandstrom, C.; Baumann, H.; Kenne, L. (1998) The use of chemical shifts of hydroxy protons of oligosaccharides as conformational probes for NMR studies in aqueous solution. Evidence for persistent hydrogen bond interaction in branched trisaccharides. J. Chem. Soc. Perkin. Trans. 2, 2385-2394.
- [17] Wang, S.R.; Tambraparni, M.; Qiu, J.J.; Tipton, J.; Dean, D. (2009). Thermal expansion of graphene composites. Macromolecules. 42, 5251 – 5255.

