Analysis of Molecular Interactions between Polystyrene and Toluene Utilizing ^{1}H NMR, ^{13}C, IR Spectroscopy and Ultrasonic Techniques

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Abstract: *This study investigated the molecular interaction between polystyrene and toluene through experiments conducted at varying concentrations and two fixed temperatures. 1H NMR, 13C NMR, and IR spectroscopy were used to evaluate changes in the chemical structure of the polymer, revealing the nature of the interaction between polystyrene and toluene as concentration and temperature varied. Our results demonstrated that the abrupt changes in thermo-physical properties of polymeric solutions at characteristic temperatures and concentrations were due to structural interactions, such as polymer chain association, segmental motion, frictional force between the layers of the polymer, and hydrogen bonding. These findings contribute to a better understanding of the physiochemical behavior of polymeric solutions, which has important implications for various industries that utilize such materials.*

Keywords: Acoustical parameters, Molecular interactions, Structuralproperties, Spectral studies, Segmental motion, Chain stiffness of the polymer

1. Introduction

Transport and acoustical properties of polymeric solutions are key to understanding their behavior in polymer processing industries [1,2]. Numerous studies have investigated the molecular interaction of polymers using physical methods such as ^{1}HNMR, ^{13}C, and IR spectra [3]. Recently, ultrasonic studies have gained attention in research on liquid and polymeric solutions [4,5]. Ultrasonic measurements have been used to identify the nature of molecular interaction between polymers and solvents, and are also used in polymer processing. Given the widespread use of polystyrene in the plastics industry and its presence in several elastomeric copolymers [6], it is important to understand the mechanism of its structural interactions. Polystyrene is probably the most widely studied linear chain molecule in polymer science.

Advances in ultrasonic, viscometric, and spectral studies have enabled accurate measurements of geometric and thermodynamic properties. In this study, the focus is on the structural interactions of polystyrene with toluene at different concentrations and temperatures using ultrasonic techniques [7,8,9]. Acoustical parameters such as adiabatic compressibility, acoustic impedance, relaxation time, free energy, intermolecular free length, etc., are related to the molecular structure of polystyrene. The chemical structure of polystyrene can 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.

This paper reports on interesting properties of polystyrene in toluene, such as molecular rearrangement, hydrogen bonding, molecular relaxation, electronic environment, and structural interactions, using ultrasonic velocity, ^{1}HNMR,

[13]C, and IR spectra. The thermo-physical and thermo-acoustical nature of polystyrene solutions at different concentrations and temperatures are discussed within a theoretical framework. The characteristic properties and temperature dependence of polystyrene solutions in each concentration region are also analyzed. The deviations observed are attributed to rotational hindrance of the polymer chain or segmental motions, resulting in chain stiffness. The thermodynamic behavior may also be influenced by the friction of the individual units, which plays a minor role in comparison to thermodynamic interaction among the various units in long chain molecules.

2. Experimental and Theoretical Methods

Polystyrene was sourced from Sigma Aldrich, Mumbai, India, while analytical reagent (AR) grade and spectroscopic regent (SR) grade toluene, with a minimum assay of 99.9%, was obtained from Adarsh Chemicals in Chennai, India. To prepare the polymeric solution, polystyrene was dissolved in toluene by weight/volume to obtain a primary solution of 0.0189 kgL-1, which was further diluted with half the volume of toluene to obtain concentrations of 0.0094, 0.0047, and 0.0024 kgL-1. The solution was mixed thoroughly using a magnetic stirrer (REMI make) at a rate of 1000 rpm to obtain a homogeneous mixture.

Ultrasonic velocities (u) were measured for the polymeric solution at temperatures of (313.15 ± 0.1) K and (323.15 ± 0.1) K using a single crystal ultrasonic interferometer with a frequency of 2 MHz (Model-83S) supplied by Mittal enterprises, New Delhi, which has an accuracy of 0.4 m/s at 25°C. The temperature was kept constant using a constant temperature water bath with an accuracy of ± 0.1K. The densities of these solutions were determined at different temperatures using a magnetic float densitometer, following the procedure outlined in reference [10].
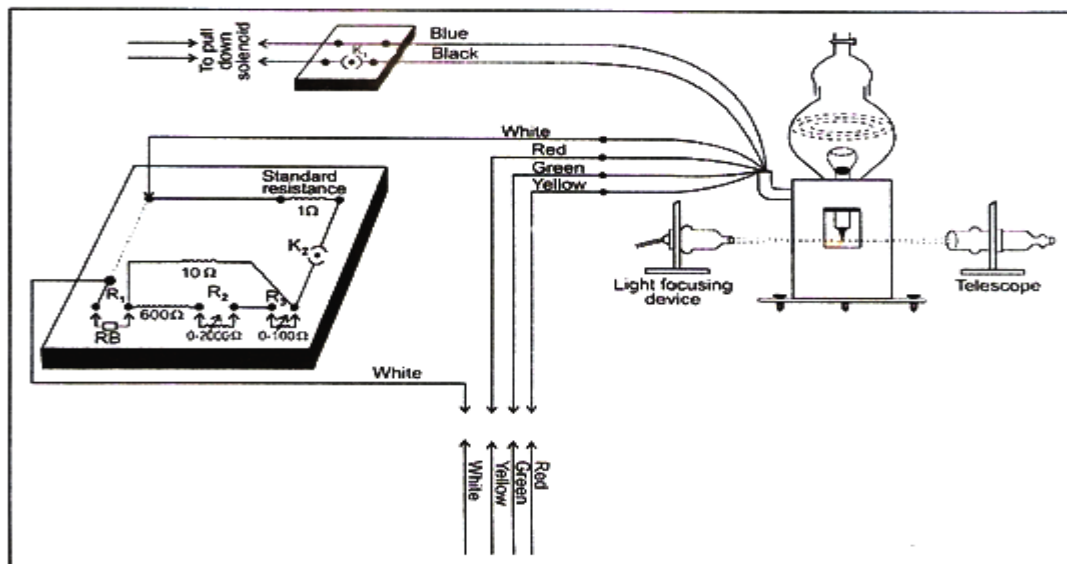
Figure 1: The laboratory set up for the operation of the Magnetic Float Densitometer

The magnetic float densitometer was placed in a Toshniwal constant temperature bath, which was maintained at 25 ± 0.1°C. The solution container used for the experiment was filled with the solvent, toluene, to measure $\rho 0$, or with the polymeric solution (at concentrations of 0.0024, 0.0047, 0.0094, and 0.0189 kgL-1) to measure ρs. The densities of these solutions were determined using Eq. (1).

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

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

The viscosity (η) of unknown polymeric solutions was determined using Ostwald's viscometer, which was filled with a reference liquid (distilled water) and immersed in a water bath. The viscosity measurement involved timing the flow of both the distilled water and the polymeric solution through the viscometer. The time taken for each solution to flow through the viscometer was used in conjunction with Equation (2) to calculate the viscosity (η) of the unknown polymeric solution.

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

Where η_w, ρ_w, and t_w are the viscosity, density, and time of flow of water respectively, and η_s, ρ_s, and t_s are the viscosity, density, and timeof flow ofthe unknown experimental solution respectively. Here, η_w represents the viscosity of the reference liquid (distilled water), t_s represents the time taken for the unknown solution to flow through the viscometer, t_w represents the time taken for the reference liquid to flow through the viscometer, and ρ_s represents the density of the unknown polymeric solution.

The ^{1}H NMR and ^{13}C spectra of the samples were obtained using a Bruker DRX-400 spectrometer, with CDCl$_3$ used as the solvent. The spectrometer was operated at a frequency of 300MHz. In addition, the polymeric solution was subjected to IR absorption spectroscopy, which was carried out using a Baird recording infrared spectrophotometer with a sodium chloride prism. This instrument is a double beam type that operates on the optical null principle, with the atmosphere serving as the reference. The data was recorded using a bolometer, amplifier, and mechanical drive system to measure the IR absorption at each wavelength.

3. Results and Discussion

The study investigates the thermo-physical and acoustical properties of non-aqueous solutions of polystyrene + toluene at different concentrations (0.0024, 0.0047, 0.0094, and 0.0189) and temperatures (313.15 ± 0.1 K and 323.15 ± 0.1 K). Acoustical parameters such as adiabatic compressibility (βad), acoustic impedance (z), relaxation time (τ), and free energy (ΔG) have been calculated and are presented in Table 1. To gain insights into the structural and molecular interactions between polystyrene and toluene, ^{1}H-NMR, ^{13}C-NMR, and IR spectra studies were conducted. The results explain the changes in concentration and their effect on the properties of the solution. Table 1 shows that the viscosity (η) of the solution increases with an increase in molar concentration but decreases with an increase in temperature. This behavior can be attributed to the maximum frictional force generated between the layers of the solution. Furthermore, the density of the polystyrene solution increases as more solute is added due to the increase in the number of polymer chains added to the solution. This increase in density can be understood based on the larger molecular weight of polystyrene compared to toluene. In summary, the study provides valuable insights into the thermo-physical and acoustical properties of non-aqueous solutions of polystyrene + toluene. The results are supported by ^{1}H-NMR, ^{13}C-NMR, and IR spectra studies and highlight the structural and molecular interactions involved in the changes in concentration of the solution.

Table 1: Experimental measured values of thermo-physical and acoustical parameters for polymeric solution (Polystyrene + Toluene) at different temperatures

At 313.15K									
C (kgL^{-1})	P (kgL^{-1})	$\eta \times 10^{-3}$ (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)	$\kappa \times 10^{-8}$(Sm^{-1})
0.0024	760.4	0.4323	1215.2	8.9056	924.0381	5.133	28.1953	6.3116	0.584
0.0047	764.5	0.4468	1225.6	8.7081	936.9712	5.187	28.2151	6.2411	0.697
0.0094	768.5	0.4591	1234.0	8.5453	948.4524	5.230	28.2306	6.1826	0.795
0.0189	772.7	0.4716	1244.0	8.3627	961.2388	5.258	28.2405	6.1162	0.865
At 323.15K									
C (kgL^{-1})	P (kgL^{-1})	$\eta \times 10^{-3}$ (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)	$\kappa \times 10^{-8}$(Sm^{-1})
0.0024	752.6	0.3640	1207.6	9.1115	908.8397	4.422	28.8682	6.5049	0.138
0.0047	752.8	0.3748	1218.4	8.9480	917.2115	4.471	28.8896	6.4462	0.156
0.0094	753.0	0.3876	1227.2	8.8181	924.0816	4.557	28.9261	6.3993	0.175
0.0189	753.2	0.3976	1236.0	8.6906	930.9552	4.607	28.9471	6.3527	0.204

It is found that the ultrasonic velocity (u) of a polymer solution generally increases with concentration which suggests a strong solute-solvent interaction. However, on increasing temperature, there is a decrease in ultrasonic velocity suggesting that exceeds the repulsive forces between polymer chains by thermal energy. From Fig. 2, it is found that adiabatic compressibility decreases with the increase in polymer concentration. This gives an indication of closed packing of molecules or attractive molecular interaction occurring and shows lesser ionic repulsion. Adiabatic compressibility shows a reciprocal nature of ultrasonic velocity. According to Eyring and Kincaid [11], if sound velocity increases then molecular association takes place between solute and solvent, which is reflected in the present investigation. It may be due to the concentration and chain stiffness of polystyrene.

At high concentrations, the rotational hindrance of the monomer unit is at a maximum which results in the stiffness of the polymer chain. Due to this, molecular interaction may be influenced by the friction of the monomer unit. However, the adiabatic compressibility increases with rising temperature, which is characteristic of polymers. This trend shows for all the systems indicating the strengthening of intermolecular forces among polymeric molecules and suggests that segmental motion in onset.

The study reveals that ultrasonic velocity (u) of a polymer solution generally increases with concentration, indicating strong solute-solvent interaction. However, with an increase in temperature, ultrasonic velocity decreases, suggesting that the thermal energy exceeds the repulsive forces between polymer chains. The decrease in ultrasonic velocity is supported by Fig. 2, which shows that adiabatic compressibility decreases with an increase in polymer concentration, indicating the occurrence of attractive molecular interaction and lesser ionic repulsion. Adiabatic compressibility also shows a reciprocal relationship with ultrasonic velocity, as stated by Eyring and Kincaid [11]. The concentration and chain stiffness of polystyrene influence molecular interaction at high concentrations. The rotational hindrance of the monomer unit is at a maximum, resulting in stiffness of the polymer chain. Therefore, the molecular interaction may be influenced by the friction of the monomer unit. Additionally, the adiabatic compressibility increases with rising temperature, indicating the strengthening of intermolecular forces among polymeric

molecules and the onset of segmental motion. This trend is observed for all systems. Overall, the study highlights the complex interplay of various factors that affect the ultrasonic velocity and adiabatic compressibility of polymer solutions. The findings provide valuable insights into the underlying molecular interactions and can contribute to the development of improved polymer-based materials.
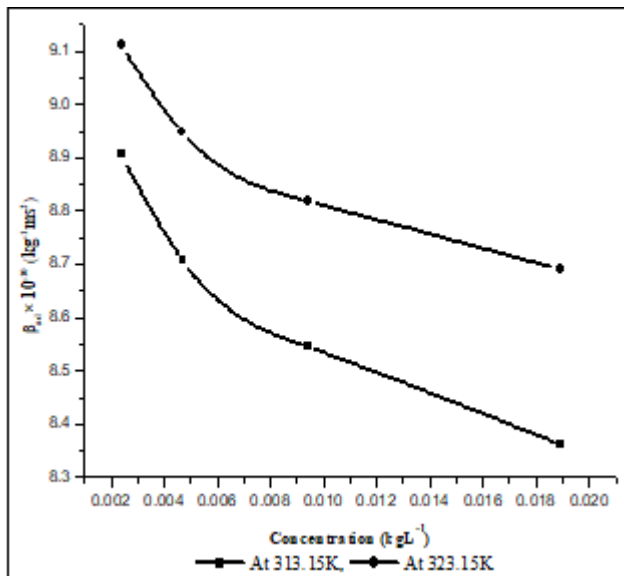
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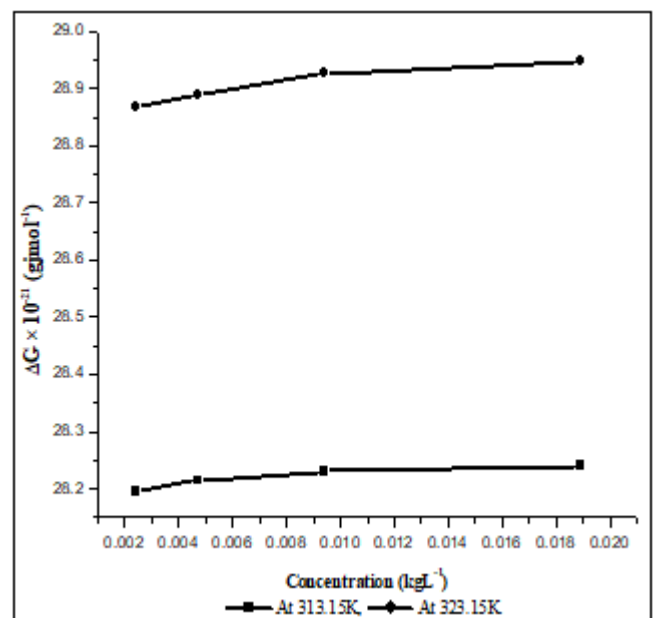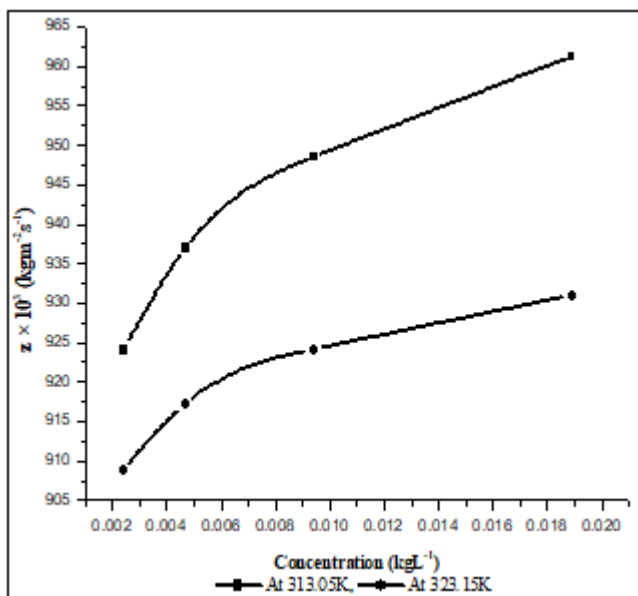
Figure 2: β_{ad} vs Concentration

Figure 5: ΔG vs Concentration

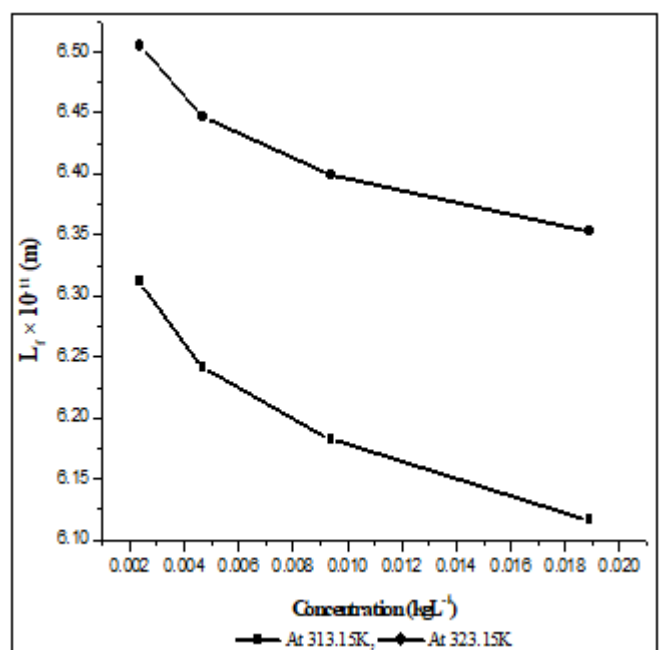**Figure 3: z** vs Concentration

Figure 6: L_f vs Concentration

Figure 4: τ vs Concentration
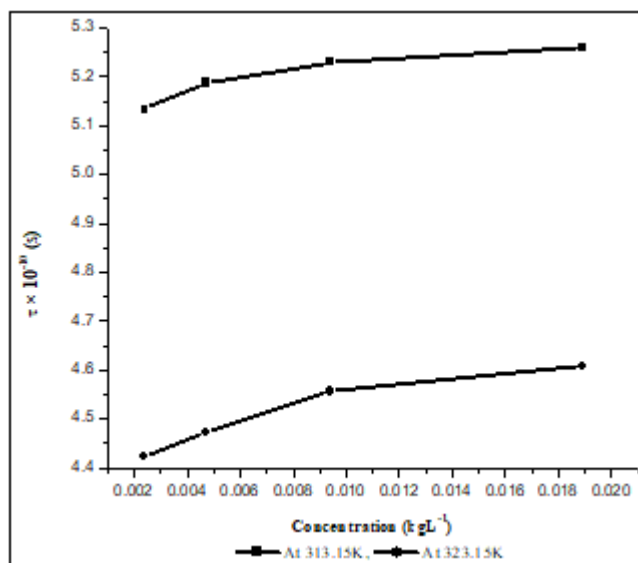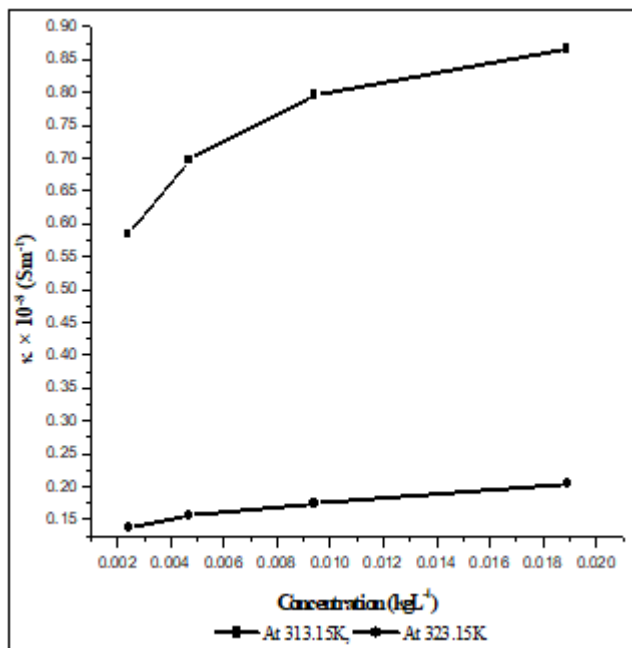
Figure 7: κ vs Concentration

In this study, the thermo-physical and acoustical properties of non-aqueous solutions of polystyrene + toluene for different concentrations at temperatures of (313.15 ± 0.1) K and (323.15 ± 0.1) K were investigated. The results show that the viscosity of the solution increases with an increase in molar concentration, but decreases with an increase in temperature, due to the maximum frictional force produced between the solution layers. The density of the solution also increases with the addition of solute content because the number of polymer chains increases and is added to the solution with an increase in the concentration of the polymer solution, which can be attributed to the larger molecular weight of polystyrene compared to toluene. The ultrasonic velocity (u) of the polymer solution generally increases with concentration, indicating a strong solute-solvent interaction. However, at higher temperatures, there is a decrease in ultrasonic velocity, suggesting that thermal energy exceeds the repulsive forces between polymer chains. Adiabatic compressibility decreases with an increase in polymer concentration, indicating closed packing of molecules or attractive molecular interactions, and shows lesser ionic repulsion. The increase in adiabatic compressibility with rising temperature indicates the strengthening of intermolecular forces among polymeric molecules, suggesting the onset of segmental motion. Acoustic impedance increases gradually with increasing concentration, yet decreases with rising temperature, suggesting a strong intermolecular association between polymeric and toluene molecules. There is no indication of complex formation, but rather, the existence of solute-solute interactions, possibly due to H-bonding between solute-solvent and solvent-solvent molecules. The increase in polymeric concentration is accompanied by an increase in viscous relaxation time (τ), indicating that viscous forces play a dominant role in the relaxation process. Free energy (ΔG) increases with increasing concentration of the polymeric solution, suggesting that thermo-physical properties are affected by several types of molecular interactions, such as molecular reorganization, H-bonding, etc., and also indicating a longer time for rearrangement of molecules. The hindrance of segmental motion of the polymeric chain causes an increase in free energy, attributed to a specific type of molecular interaction between the polymeric chain and solvent molecules. Intermolecular free length (L_f) follows the same trend as adiabatic compressibility, decreasing with increasing concentration and increasing with temperature, indicative of the presence of strong molecular interactions at a higher temperature. The decrease in intermolecular free length indicates the presence of significant interactions occurring between the molecules of polystyrene and toluene in the form of a hydrogen bond. Finally, the specific conductance (κ) of the polymeric solution increases with an increase in concentration, yet decreases with the rising temperature of the system. This confirms that association takes place between the polymeric chain, increasing the density of the polymeric chain, and subsequently increasing the electrical conductivity of the polymeric solution. The decrease in electrical conductivity with increasing temperature can be attributed to the dominant repulsive forces over attractive forces, causing a decrease in density.

^{1}H-NMR Spectroscopy Study
In order to identify molecular interactions, spectra parameters such as chemical shift displacement of ^{1}H-NMR signals can be obtained. These signals provide information about the electronic environment of different protons of the polystyrene + toluene systems at different concentrations. Obtaining such measurements is important because it allows for more accurate determination of the protons involved in molecular interactions [12]. The ^{1}H-NMR spectra of the polymeric solution with toluene are presented in Figs. 8-11, which show the variations in chemical shift for various protons as a function of concentration. The chemical shift values and their deviations for the polymeric solution over different concentrations of polystyrene in toluene are listed in Tables 2 and 3.

Table 2: Chemical shifts (δ) and their variations (Δδ) for ^{1}H NMR of –CH$_3$ at different concentrations of polymeric solution (Polystyrene + Toluene)

| S.N.	Conc. (kgL^{-1})	δ (ppm)	Δδ (ppm)
^{1}H NMR for –CH$_3$
1.	0	2.69	0
2.	0.0024	2.729	-0.039
3.	0.0047	2.623	+0.067
4.	0.0094	2.772	-0.082
5.	0.0189	3.1895	-0.499

Table 3: Chemical shifts (δ) and their variations (Δδ) for ^{1}H NMR of –CH at different concentrations of polymeric solution (Polystyrene + Toluene)

^{1}H NMR for -CH				
δ ppm (0 kgL[-1])	δ ppm (0.0024 kgL[-1])	δ ppm (0.0047 kgL[-1])	δ ppm (0.0094 kgL[-1])	δ ppm (0.0189 kgL[-1])
7.06	7.540	7.430	7.583	8.035
7.06	7.563	7.455	7.606	8.061
7.07	7.614	7.504	7.658	8.071
7.14	7.626	7.528	7.681	8.095
7.14	7.636	7.552	7.706	8.138
--	7.663	--	--	8.163
--	--	--	--	8.186
Δδ ppm (0 kgL[-1])	Δδ ppm (0.0024 kgL[-1])	Δδ ppm (0.0047 kgL[-1])	Δδ ppm (0.0094 kgL[-1])	Δδ ppm (0.0189 kgL[-1])
0	-0.48	-0.37	-0.523	-0.975
0	-0.503	-0.395	-0.546	-1.001
0	-0.544	-0.435	-0.588	-1.001
0	-0.486	-0.388	-0.541	-0.955
0	-0.496	-0.412	-0.566	-0.998

In this study, the chemical shift displacement of ^{1}H-NMR signals was used as a tool to identify molecular interactions. The ^{1}H-NMR spectra of the polymeric solution with toluene were analyzed, and it was observed that the δCH3, δCH2, and δCH signals shifted upfield with increasing polystyrene concentration. This upfield shift suggests an increase in electron density around the H nuclei, which is likely due to the breaking of intermolecular hydrogen bonding and weak interactions of the hydrogen bonding type between toluene and polystyrene. Additionally, the deviation of the chemical shift (Δδ) can be used to study the strength of molecular interactions, including hydrogen bonding. The magnitude of Δδ is directly proportional to the strength of molecular interaction and concentration of the polymeric solution. Overall, the chemical shift displacement of ^{1}H-NMR signals provides valuable information about the electronic environment and molecular interactions of different protons in the polystyrene + toluene system.
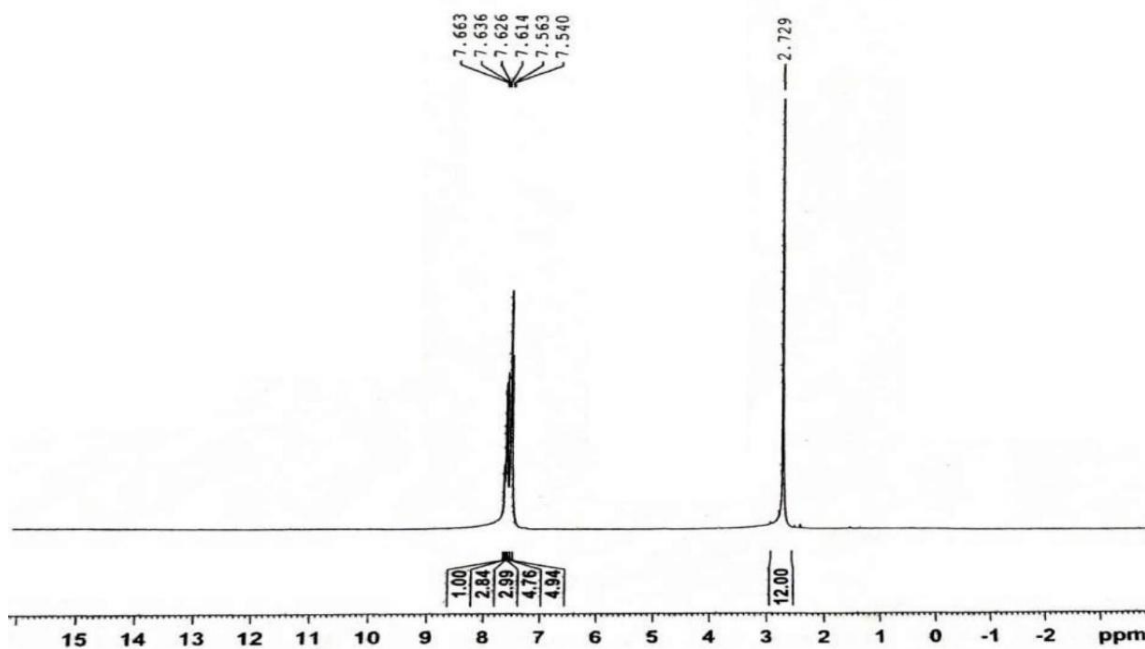
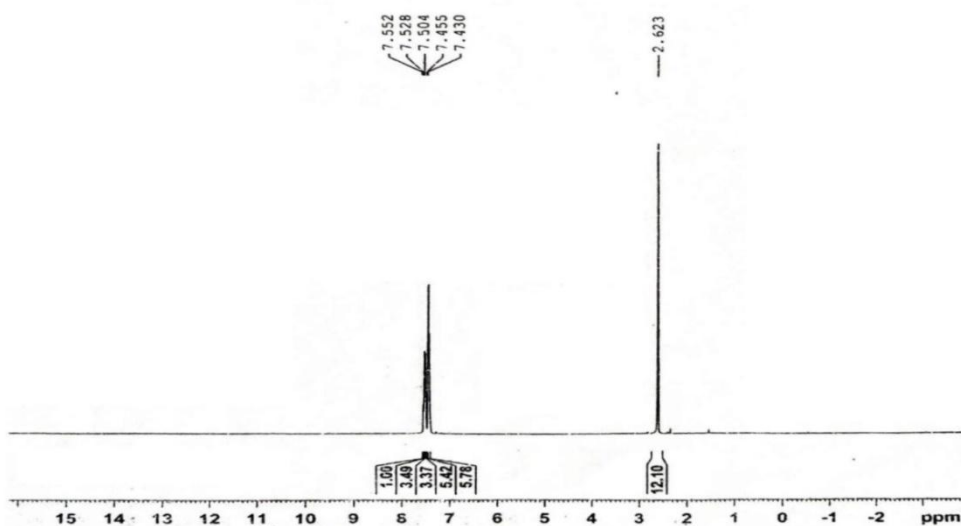**Figure 8:** 1D ^{1}H NMR spectrum of polystyrene + toluene at 0.0024kgL[-1]

Figure 9: ^{1}D ^{1}H NMR spectrum of polystyrene + toluene at 0.0047kgL^{-1}

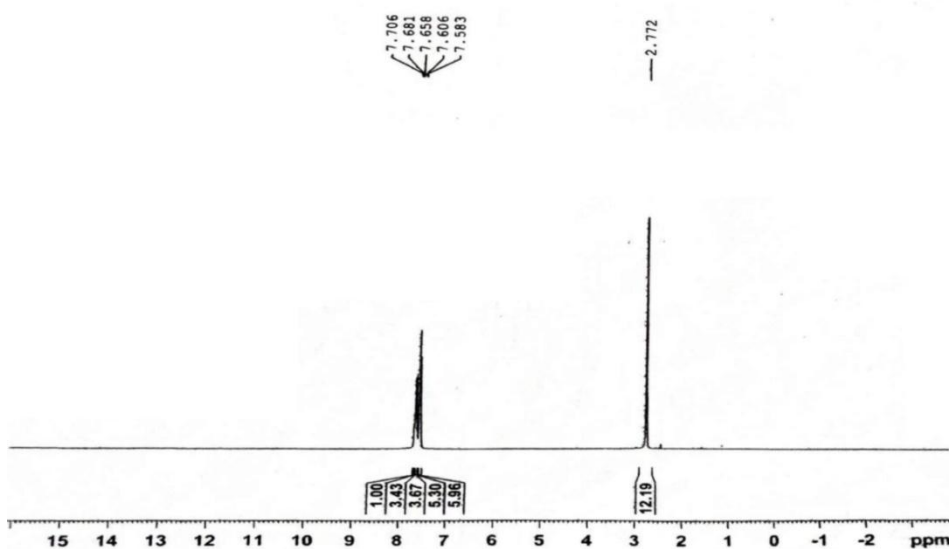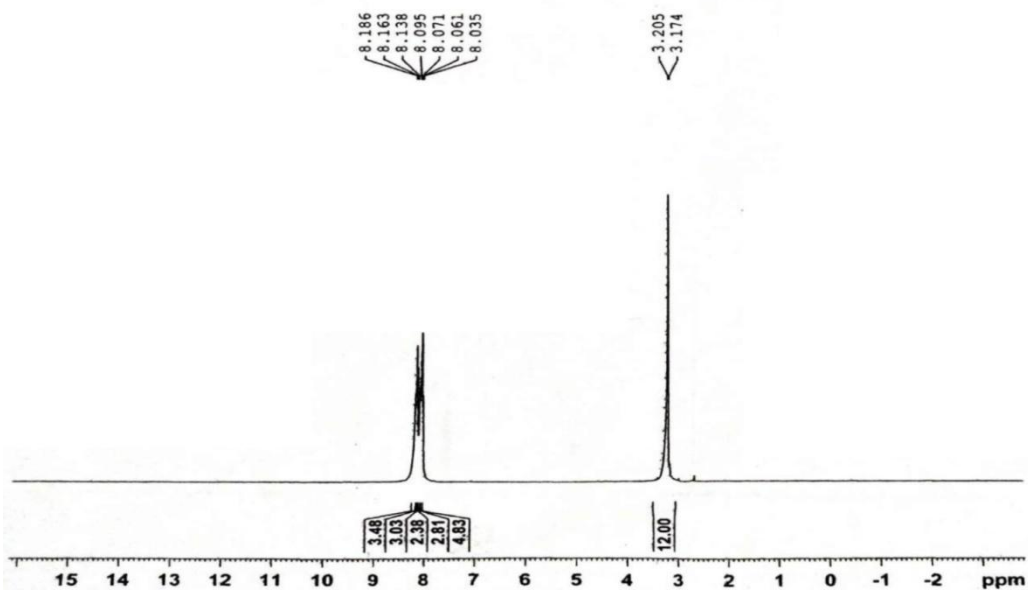**Figure 10:** ^{1}D ^{1}H NMR spectrum of polystyrene + toluene at 0.0094kgL^{-1}

Figure 11: ^{1}D ^{1}H NMR spectrum of polystyrene + toluene at 0.0198kgL^{-1}

In the investigated polymeric solutions of polystyrene and toluene, negative $\Delta\delta$ (1HNMR) values were observed for CH3 and C-H of both components, except for the concentration of 0.0047kgL-1, which exhibited a very weak type of molecular interaction. The minima in $\Delta\delta$ values indicate the point of maximum interaction between polystyrene and toluene for different selected concentrations. Negative $\Delta\delta$ values suggest that a strong molecular interaction is present in the polymeric solution. As the concentration of polystyrene in toluene increased, a greater change in chemical shift was observed for the different protons of polystyrene and toluene, with the highest change at higher concentrations and the minimum change at lower concentrations. However, line broadening was observed for CH3 and C-H protons in the solution due to the environmental effect, causing nuclei to transfer rapidly from one magnetization condition to another, or due to the disorganizing effect that leads to line broadening. The disorganizing effect was also reflected in signal multiplicity, showing merged peaks of polystyrene and toluene protons, such as quartet and doublet at 0.0024 - 0.0094kgL-1, and triplet and quartet at 0.0189kgL-1. The strong interaction between polystyrene and toluene at higher concentrations causes the disorganizing effect. Therefore, it can be suggested that the addition of polystyrene to toluene disrupts their self-associate structure and stabilizes the molecular structure based on the observed experimental data, spectral evidence, and literature information. The investigation indicates that lower and higher concentrations are more effective in creating a strong molecular interaction than the mid-range of concentration.

^{13}C Spectroscopy Study

Table 4: Chemical shift (δ) and their variation ($\Delta\delta$) for ^{13}C of –CH$_3$ at different concentrations of polymeric solution (Polystyrene + Toluene)

S.N.	Conc. (kgL^{-1})	δ (ppm)	$\Delta\delta$ (ppm)
	^{13}C for –CH$_3$		
1.	0	20.9	0
2.	0.0024	21.55	-0.65
3.	0.0047	21.60	-0.70
4.	0.0094	21.54	-0.64
5.	0.0189	21.17	-0.27

Table 5: Chemical shift (δ) and their variation ($\Delta\delta$) for ^{13}C of –CH at different concentrations of polymeric solution (Polystyrene + Toluene)

^{13}C NMR for -CH				
δ ppm (0 kgL^{-1})	δ ppm (0.0024 kgL^{-1})	δ ppm (0.0047 kgL^{-1})	δ ppm (0.0094 kgL^{-1})	δ ppm (0.0189 kgL^{-1})
137.7	137.92	137.99	137.91	137.54
129.2	129.53	129.22	129.20	129.03
129.2	129.19	--	--	--
128.4	128.78	128.42	128.40	128.22
128.4	128.59	--	--	--
125.5	128.39	--	--	--
--	125.48	125.50	125.49	125.36
$\Delta\delta$ ppm (0 kgL^{-1})	$\Delta\delta$ ppm (0.0024 kgL^{-1})	$\Delta\delta$ ppm (0.0047 kgL^{-1})	$\Delta\delta$ ppm (0.0094 kgL^{-1})	$\Delta\delta$ ppm (0.0189 kgL^{-1})
0	-0.22	-0.29	-0.21	+0.16
0	-0.33	-0.02	0	+0.17
0	+0.01	--	--	--
0	-0.38	-0.02	0	+0.18
0	+0.01	--	--	--
0	+0.02	--	--	--

Table 6: Chemical shift (δ) and their variation ($\Delta\delta$) for ^{13}C of –CH$_2$ at different concentrations of polymeric solution (Polystyrene + Toluene)

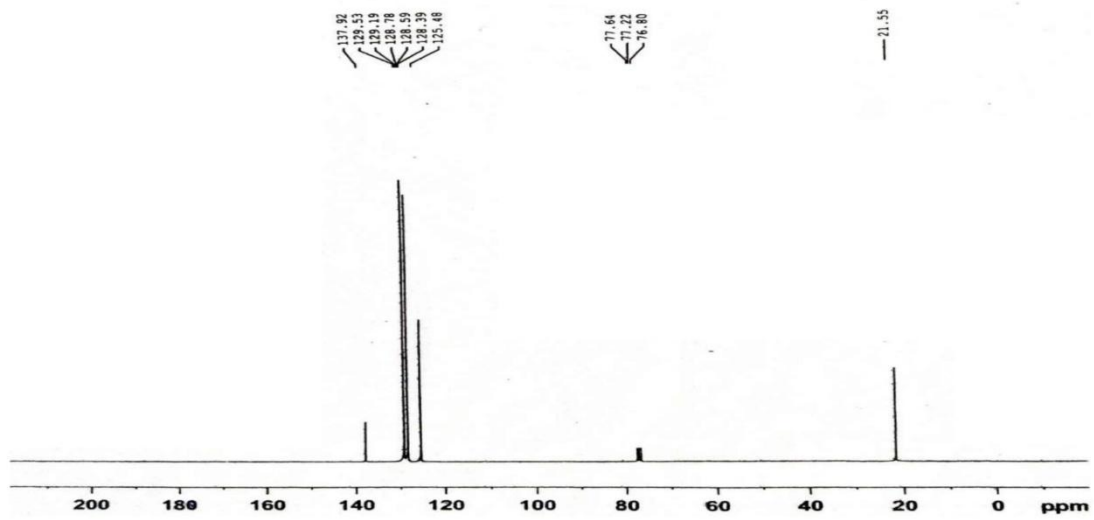| ^{13}C NMR for -CH$_2$				
δ ppm (0 kgL^{-1})	δ ppm (0.0024 kgL^{-1})	δ ppm (0.0047 kgL^{-1})	δ ppm (0.0094 kgL^{-1})	δ ppm (0.0189 kgL^{-1})
	77.64	77.65	77.66	77.66
77.5	77.22	77.23	77.24	77.23
	76.80	76.81	76.81	76.81
$\Delta\delta$ ppm (0 kgL^{-1})	$\Delta\delta$ ppm (0.0024 kgL^{-1})	$\Delta\delta$ ppm (0.0047 kgL^{-1})	$\Delta\delta$ ppm (0.0094 kgL^{-1})	$\Delta\delta$ ppm (0.0189 kgL^{-1})
	-0.14	-0.15	-0.16	-0.16
0	+0.28	+0.27	+0.26	+0.27
	+0.7	+069	+69	+0.69

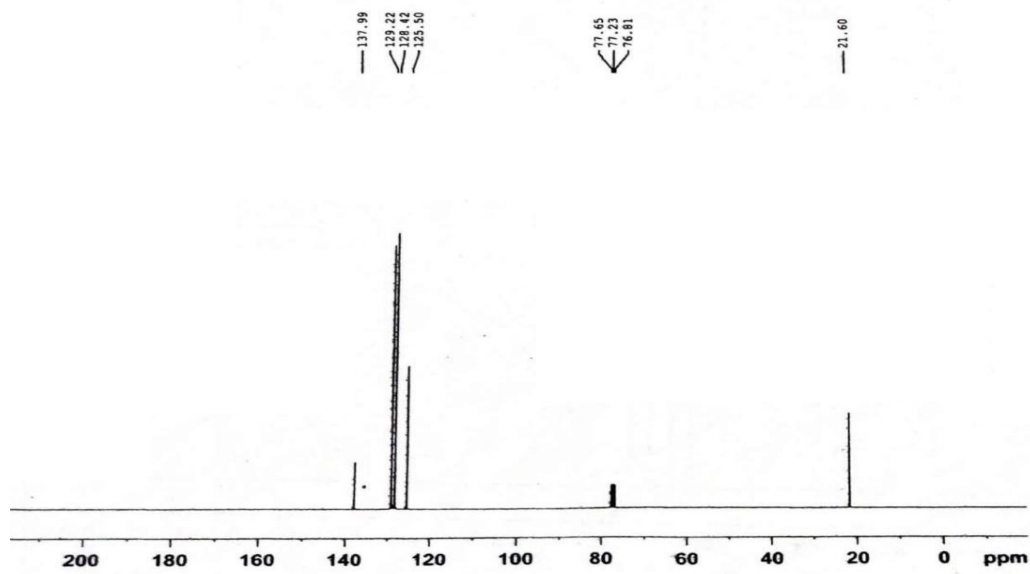**Figure 12:** ^{1}D ^{13}C spectrum of polystyrene + toluene at 0.0024kgL^{-1}

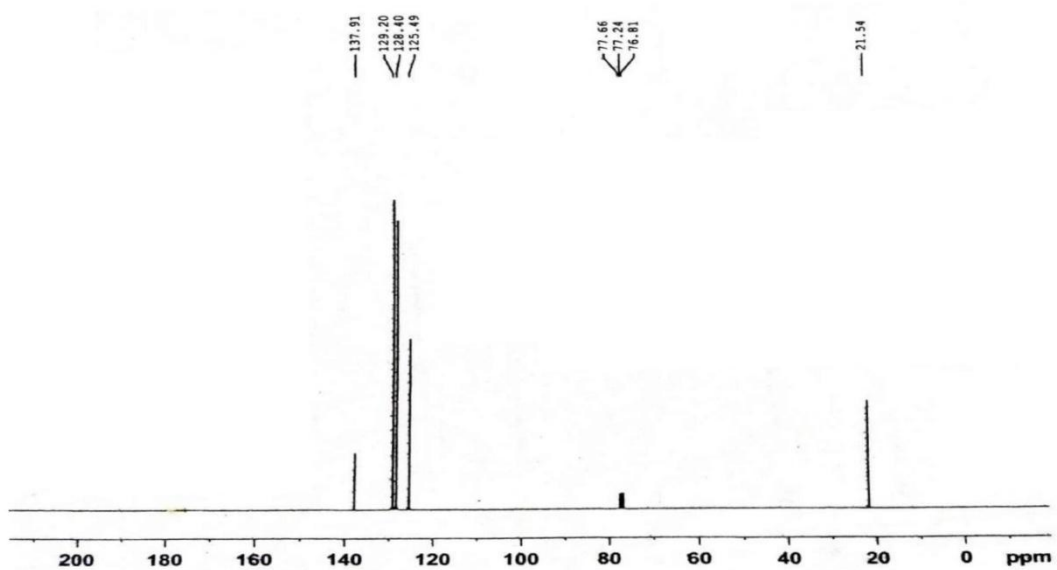**Figure 13:** 1D ^{13}C spectrum of polystyrene + toluene at 0.0047kgL^{-1}

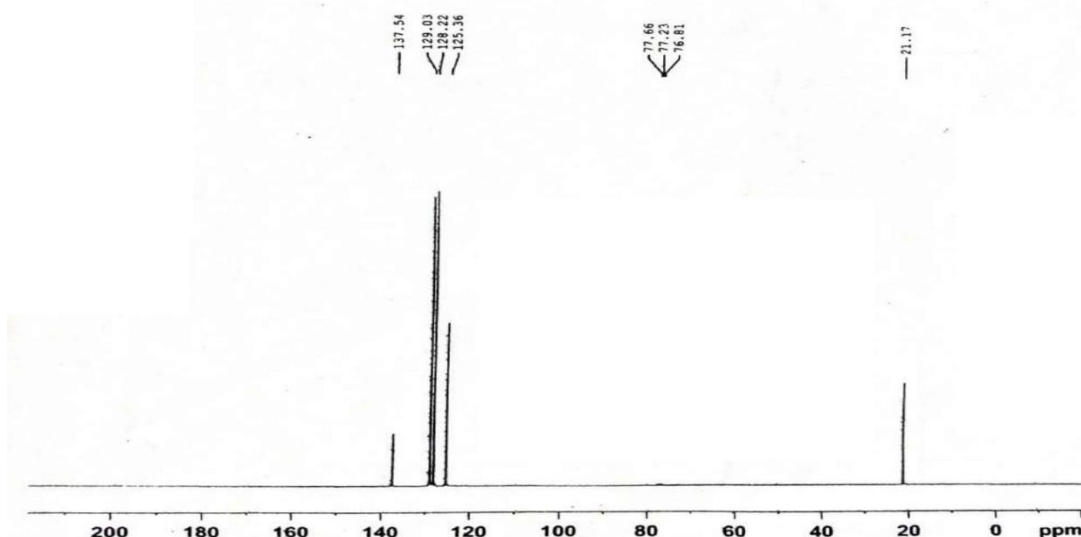**Figure 14:** ^{1}D ^{13}C spectrum of polystyrene + toluene at 0.0094kgL^{-1}

Figure 15:[1]D ^{13}C spectrum of polystyrene + toluene at 0.0189kgL[-1]

The proton decoupled 13C spectrum reveals a weak peak of ipso carbon due to its long molecular relaxation time. The spectrum also displays two larger peaks for the doubled ortho and meta-carbons, and two medium-sized peaks for the para-carbons. Additionally, the methylene group (CH_2) of polystyrene shows a very small peak at 77.22 ppm due to environmental effects, as shown in Figs. 12-15. As the concentration of the polymeric solution increases, this peak diminishes and finally disappears in Fig. 15. These observations confirm the occurrence of very strong molecular interactions at higher concentrations, which stabilize the molecular structure of polystyrene with toluene, as evidenced by longer relaxation times. Tables 4-6 reveal that negative and positive deviations in the values of chemical shift ($\Delta\delta$) indicate both strong and weak types of molecular interactions at different concentrations. Overall, the results suggest that the addition of polystyrene disrupts the self-associate structure of toluene and stabilizes the molecular structure of the resulting polymeric solution, especially at lower and higher concentrations. The line broadening observed for CH_3 and C-H protons in the solution is attributed to the transfer of the nucleus from one magnetization condition to another and the disorganization effect. This disorganization effect is also reflected in signal multiplicity and shows merged peaks of protons of polystyrene and toluene, such as a quartet and doublet at 0.0024 - 0.0094 kg/L and a triplet and quartet at 0.0189 kg/L.

Infrared Spectroscopy Study

Table 1: Absorption Frequency (ν cm^{-1}) and their variation ($\Delta\nu$ cm[-1]) for IR of –CHsp[3] and sp[2] at different concentration of polymeric solution (Polystyrene + Toluene)

IR Spectra for –CH (sp³)				
ν cm^{-1} (0 kgL[-1])	ν cm^{-1} (0.0024 kgL[-1])	ν cm^{-1} (0.0047 kgL[-1])	ν cm^{-1} (0.0094 kgL[-1])	ν cm^{-1} (0.0189 kgL[-1])
3180	3180	3180	3180	3180
$\Delta\nu$ cm[-1] (0 kgL[-1])	$\Delta\nu$ cm[-1] (0.0024 kgL[-1])	$\Delta\nu$ cm[-1] (0.0047 kgL[-1])	$\Delta\nu$ cm[-1] (0.0094 kgL[-1])	$\Delta\nu$ cm[-1] (0.0189 kgL[-1])
0	0	0	0	0
IR Spectra for –CH (sp²)				
ν cm^{-1} (0 kgL[-1])	ν cm^{-1} (0.0024 kgL[-1])	ν cm^{-1} (0.0047 kgL[-1])	ν cm^{-1} (0.0094 kgL[-1])	ν cm^{-1} (0.0189 kgL[-1])
3275	3300	3285	3280	3277
$\Delta\nu$ cm[-1] (0 kgL[-1])	$\Delta\nu$ cm[-1] (0.0024 kgL[-1])	$\Delta\nu$ cm[-1] (0.0047 kgL[-1])	$\Delta\nu$ cm[-1] (0.0094 kgL[-1])	$\Delta\nu$ cm[-1] (0.0189 kgL[-1])
0	-25	-10	-5	-2

Figure 16: [1]D IR spectrum of polystyrene + toluene at $0.0024 kgL^{-1}$
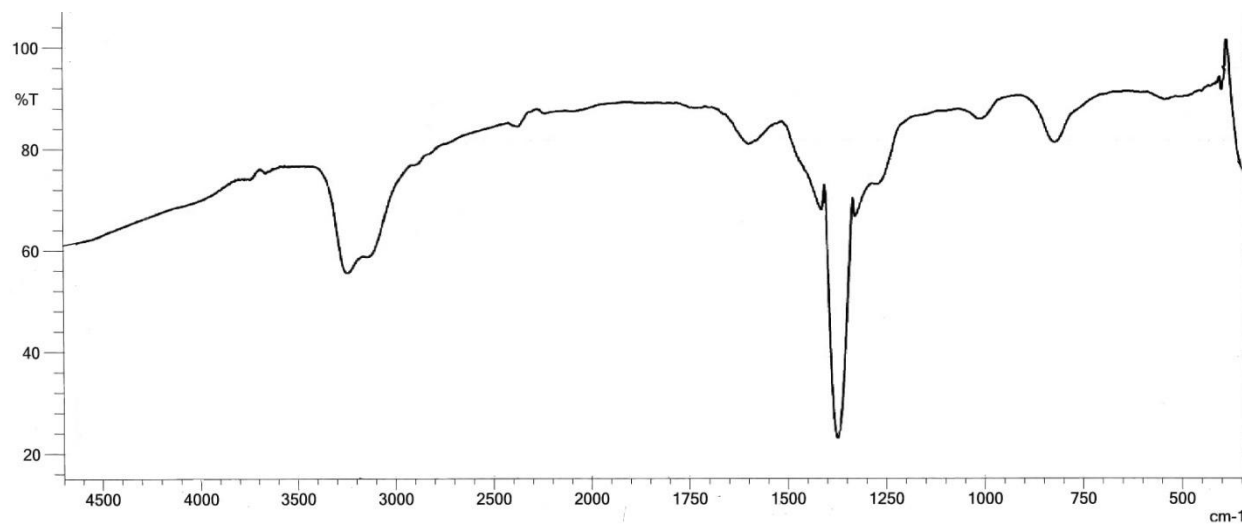
Figure 17: [1]D IR spectrum of polystyrene + toluene at $0.0047 kgL^{-1}$
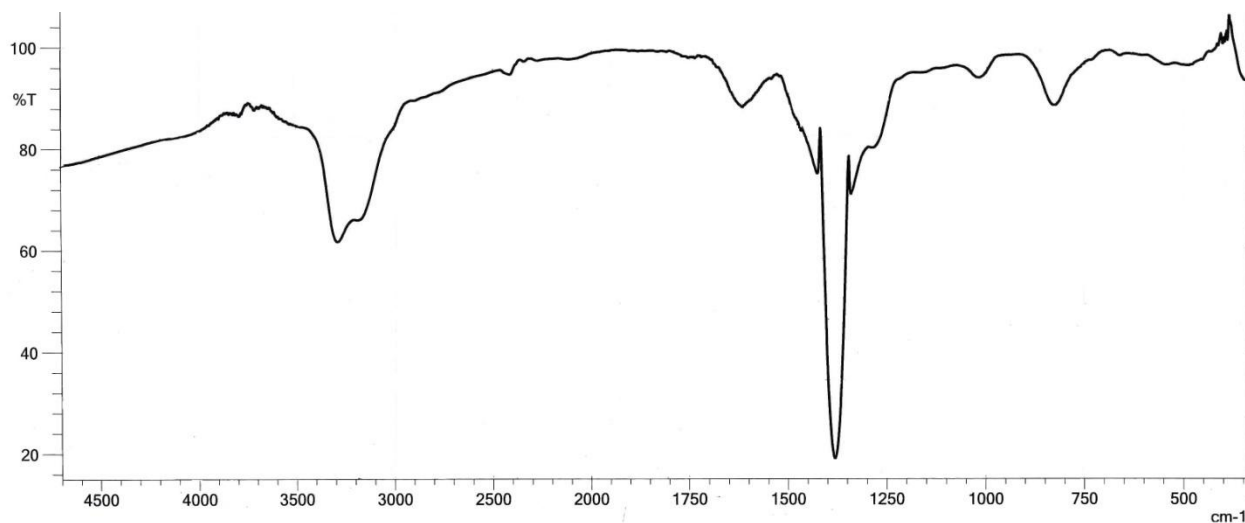

Figure 18: [1]D IR spectrum of polystyrene + toluene at $0.0094 kgL^{-1}$
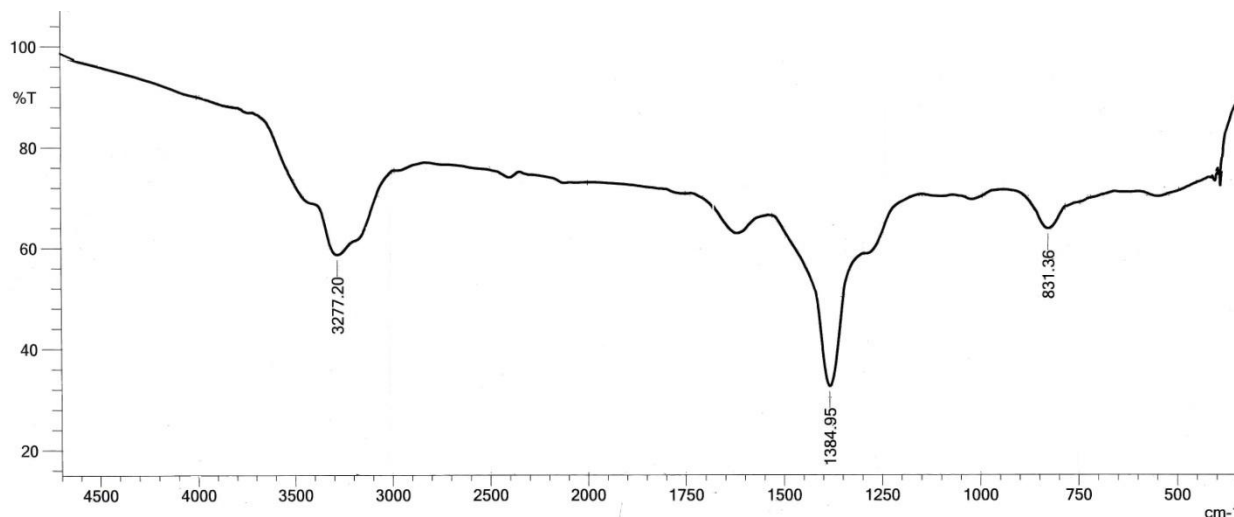
Figure 19: [1]D IR spectrum of polystyrene + toluene at $0.0189 kgL^{-1}$

The infrared (IR) spectra presented in Figs 16-19 show characteristic peaks for the polymeric solution of polystyrene and toluene. The absorption frequency for C-H str. (sp3) at 3180 cm-1 is present for all concentrations, but its intensity decreases with increasing concentration. For C-H str. (sp2), the absorption frequency at 3300 cm-1 is observed at a concentration of 0.0024 kgL-1 and decreases gradually to 3277 cm-1 at 0.0189 kgL-1. The variation in absorption frequencies (Δv) is -25, -10, -5, and -2 cm-1, indicating that the specific nature of molecular interaction involves lower as well as higher concentrations compared to the mid-range of concentration. The observed decrease in absorption frequency is attributed to the reduction in molecular motion and intermolecular interactions between polystyrene and toluene. The data in Table 7 summarize the spectral information of absorption frequencies (cm-1) for the polymeric solution.

4. Conclusion

The experimental findings, as well as the acoustical and spectral data, suggest that the interactions between the solute and solvent molecules are favored in the polymeric solution of polystyrene and toluene. As a result of the association among the polymeric chains of polystyrene, the density, viscosity, and ultrasonic velocities increase with increasing concentration. The observed deviation in the values of the chemical shift of ^{1}H NMR and ^{13}C as well as absorption peaks with respect to concentration suggests the presence of strong polymer-solvent interactions at higher concentrations. It was also found that the lower and higher concentration ranges are more effective than the mid-range of selected concentration in favoring molecular interaction. At this concentration, a specific nature of molecular interactions was observed due to the segmental motion and chain stiffness of the polymer.

Supporting Information
The molecular structure and structural interaction information of polystyrene with toluene can be accessed for free on the internet at http://pubs.acs.org.

Footnotes
Molecular interactions; Effect of segmental motion and chain stiffness of polystyrene with toluene on the molecular structural and thermo-dynamical properties of polymeric solution at different temperatures.

ConflictofInterests
We have no conflicts of interest to disclose. All authors declare that they have no conflicts of interest.

Author's contributions statement
Preeti Yadav involved in the preparation of manuscript, data collection, interpretation, Jaya Tripathi helped in the manuscript preparation. Indu Saxena supervision granted final permission to thepublishedversion.

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