Microwave dielectric relaxation study of poly (methyl methacrylate) and polysulphone in dilute solutions

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Received 23 January 2006; revised 3 April 2006; accepted 17 April 2006

Dielectric relaxation studies of poly (methyl methacrylate) in dilute solutions of benzene and 1,4-dioxane and polysulphone in dilute solutions of 1,4-dioxane have been carried out at 8.92 GHz and temperatures 30, 40, 50, 60ºC, respectively. Average relaxation time $\tau_0$, and relaxation times corresponding to group rotation $\tau (1)$, segmental motion $\tau (2)$ and dipole moment $\mu$ have been determined. The results have been interpreted by the internal and hindered rotation of ester group and sulphone unit for PMMA and polysulphone, respectively. The study reveals the existence of both, the intramolecular and overall orientations in PMMA and polysulphone. Thermodynamic parameters, viz. free energy, enthalpy and entropy of activation have been calculated using the dielectric data. Thermodynamic parameters indicate existence of cooperative orientation in the molecule resulting from the dipole-dipole interaction.

Keywords: Dielectric relaxation, Poly (methyl methacrylate), Polysulphone, Dipole-dipole interaction

IPC Code: G01R27/26

1 Introduction

The dielectric behaviour and relaxation studies of polymers have been investigated due to its basic and applied aspects like applications of polymers in microelectronics and optical waveguide systems for their isolation, insulation and passivation properties in the past. The dielectric studies of small polar molecules and polymers in pure liquid state and dilute solutions at microwave frequencies provide vital information on the molecular configuration of a system. Polymer solutions show very complex behaviour, as a consequence of the combination of free volume and energetic contributions of the constituent components. Conformational changes originating in macromolecules as a consequence of their interaction with solvent have been the subject of large number of investigations. Micro-Brownian motion of polymer chain is one of the most important subject in polymer physics. Microwave dielectric relaxation studies in non-polar solvents are very useful in determining the flexibility of chains, mobility of the polymer segment, internal group rotation and steric hindrance to the internal rotation due to hydrogen bonding.

Sengwa et al have studied dielectric behaviour of four series of ethylene oxide condensation products in dilute solutions of carbon tetrachloride and inferred that the extensive inter and intra H-bonding exists in the molecules of monoalkyl ethers of ethylene glycol and diethylene glycol in dilute solutions of carbon-tetrachloride. Murthy et al have reported the dielectric constant $\varepsilon'$ and loss factor $\varepsilon''$ of poly (butyl acrylate), poly (butyl methacrylate) and poly (isobutyl methacrylate) in dilute solutions and determined the relaxation times from the Cole-Cole arc plots on three acrylates. Iwasa et al carried out dielectric measurements on dilute solutions of isotactic and syndiotactic poly (methyl methacrylate) in toluene and dioxane in the frequency range 1-150 MHz over a wide range of temperature.

In the present paper, a type C polymer i.e. poly (methyl methacrylate) and a type B polymer i.e. polysulphone have been selected. The dielectric relaxation of polysulphone in dilute solutions at microwave frequencies has not been reported so far. The dilute solutions of PMMA were prepared in benzene and 1,4-dioxane whereas dilute solutions of polysulphone were prepared in 1,4-dioxane and dielectric relaxation studies were done at 8.92 GHz and at temperatures 30, 40, 50 and 60ºC.

2 Experimental Details

The polymers polysulphone (PSU), molecular weight 125000, supplied by Gharda Chemicals Ltd.
Bharuch, Gujarat and poly (methyl methacrylate) or PMMA, molecular weight 15000, supplied by HiMedia Laboratories Pvt. Ltd., Mumbai were used for the study. Benzene and 1,4-dioxane, both of AR grade were procured from E Merck Ltd, Bombay. Benzene and 1,4-dioxane were distilled twice before use. The wavelength and voltage standing wave ratio were measured in the dielectric at a fixed frequency of 8.92 GHz, employing a slotted waveguide and a short circuited plunger. The permittivity $\varepsilon'$ and dielectric loss $\varepsilon''$ at four different concentrations of solute in dilute solutions of benzene and 1,4-dioxane at 8.92 GHz microwave frequency were determined by the method described by Heston et al.\textsuperscript{13}. The values of $\varepsilon'$ and $\varepsilon''$ so obtained are accurate within ±1 and ±5%, respectively. The static permittivity ($\varepsilon_0$) at 100 kHz was measured using a dipole meter by directly measuring the capacitance and calibrating it for standard liquids. The accuracy of this measurement is 0.1%. The optical permittivity ($\varepsilon_\infty$) was obtained by squaring the refractive indices of the sodium D-lines, measured with the help of an Abbe's refractometer. The accuracy of measurement of refractive indices for sodium light is about 0.03%. All these measurements were made at four temperatures 30, 40, 50 and 60°C using a temperature regulating system and constant temperature water bath. Temperature was controlled electronically within ±0.5°C.

3 Theory

It has been observed that the static permittivity $\varepsilon_0$, $\varepsilon'$, $\varepsilon''$ and the high frequency permittivity $\varepsilon_\infty$ are linear functions of concentration. The linear slopes $a_0$, $a'$, $a''$ and $a_\infty$ corresponding to $\varepsilon_0$, $\varepsilon'$, $\varepsilon''$ and $\varepsilon_\infty$ versus weight fraction of solute at different concentrations have been used for the determination of the relaxation times and molecular dipole moments. The average relaxation time $\tau_0$ and distribution parameter, $\alpha$, were calculated by Higasi's\textsuperscript{14} single frequency measurement equations:

$$\tau_0 = \frac{1}{\omega} \left[ \frac{A^2 + B^2}{C^2} \right]^{(\frac{1}{\omega-a})} \text{ and } 1-a = \left( \frac{2}{\pi} \right) \tan^{-1} \left( \frac{A}{B} \right) \ldots (1)$$

where $\omega$ is the angular frequency selected for the measurement and

$$A = a'\alpha (a_0-a_\infty), \quad B = (a_0-a') (a' - a_\infty) - a''^2 \quad \text{and} \quad C = (a' - a_\infty)^2 + a''^2 \ldots (2)$$

The relaxation times corresponding to group rotations $\tau (1)$ and segmental reorientation $\tau (2)$ were calculated using the equations of Higasi et al.\textsuperscript{15} proposed for dilute solutions

$$\tau (1) = \frac{a''}{\omega(a'-a_\infty)} \ldots (3)$$

and

$$\tau (2) = \frac{a_0-a'}{\omega a''} \ldots (4)$$

Higasi et al.\textsuperscript{15} have proved that:

$$\tau (2) = \tau_1 \quad \ldots (5)$$

and

$$\tau (1) = \tau_1 (1-c) + \tau_2 c \quad \ldots (6)$$

where $\tau_1$ is the molecular relaxation time for overall rotation while $\tau_2$ arises from internal rotation of a polar group in a molecule. This shows that $\tau(2)$ would correspond to the dielectric relaxation time for overall or molecular orientation and $\tau(1)$ is the explicit function of $\tau_1$ and $c$, the weight fraction of intramolecular relaxation mechanism.

The molecular dipole moments of these molecules have been calculated using the Koga et al.\textsuperscript{16} equation:

$$\mu^2 = \frac{27kTM_1}{4\pi Nd_1(\varepsilon_0+2)^2} \ldots (7)$$

where $\varepsilon_0$ is the relative permittivity of the solvent, $k$ the Boltzmann constant, $T$ the absolute temperature of the material, $N$ the Avogadro number, $M_1$ the molecular weight of the solute and $d_1$ is the density of the solvent. The specific dipole moment $\mu_{sp}$ is evaluated by the relation $\mu_{sp} = \left( \frac{\mu^2}{n} \right)^{\frac{1}{2}}$, where $n$ is the degree of polymerization. The thermodynamic parameter, free energy ($\Delta F_e$), enthalpy ($\Delta H_e$) and the entropy of activation ($\Delta S_e$) were calculated using Eyring's\textsuperscript{17} equations. The calculated values of $\tau_0$, $\tau (1)$, $\tau (2)$, $\alpha$, $\mu$ and $\mu_{sp}$ in 1,4-dioxane solutions of PMMA and polysulphone are reported in Table 1 and in benzene solutions of PMMA are reported in Table 2. The calculated values of $\Delta F_e$, $\Delta H_e$ and $\Delta S_e$ are reported in Table 3.

4 Results and Discussion

The values of different relaxation times $\tau_0$, $\tau (1)$ and $\tau (2)$, dipole moment ($\mu$), $\mu_{sp}$ and the distribution parameter ($\alpha$) for PMMA and polysulphone at
Different temperatures in dilute solutions of 1,4-dioxane are reported in Table 1 and all these parameters for PMMA at different temperatures in dilute solution in benzene are reported in Table 2. The various thermodynamical parameters $\Delta F$, $\Delta H$ and $\Delta S$ for the dielectric relaxation process are reported in Table 3.

Non-zero values of $\alpha$ are obtained for dilute solutions of PMMA in benzene and 1,4-dioxane which indicate that besides the overall rotation, there is a large contribution of segment reorientation and group rotation to the relaxation processes. Hence, more than one relaxation process is present in the molecules. This is further confirmed by the values of different relaxation times. As seen from Table 1, the values of $\tau (1)$ and $\tau (2)$ are different which indicate the existence of an intramolecular relaxation process in addition to the overall relaxation process.

It has been observed that the average relaxation time $\tau_0$ for PMMA is small in benzene solution compared with $\tau_0$ for PMMA in 1,4-dioxane solutions. Small values of $\tau_0$ suggest that the chain of this macromolecule is flexible. The variation of $\tau_0$ values for the same polymer in benzene and 1,4-dioxane solvents indicates that the solvent environment affects the average relaxation time of this polymer. Higher values of $\tau_0$ in 1,4-dioxane solution of PMMA may be because of large hindrance offered by 1,4-dioxane molecules to reorientation of polymer molecules as compared to the benzene molecules.

The relaxation time $\tau (1)$, which arises from internal rotation of polar groups in the molecules, is associated with the ester group in PMMA and it is
found to be lower than \( \tau (2) \) in both the solvents. \( \tau (1) \) depends on the energy barriers to rotation at the side group site. It is independent of molecular weight and the value\(^1\) of (glass transition temperature \( T_g \)). The higher values of \( \tau (1) \) in 1,4-dioxane in comparison to values in benzene solutions may be due to larger hindrance to intramolecular rotation offered by 1,4-dioxane.

In both solvents, it has been observed that \( \tau (2) \) is usually higher than the corresponding average relaxation time \( \tau_0 \) (Table 1). The higher values of the segmental relaxation time \( \tau (2) \) in comparison with the average relaxation time \( \tau_0 \) suggest that intramolecular H-bonding exist in the folded structure of the chains of these molecules in dilute solutions. The relaxation time \( \tau (2) \) is found to be solvent density dependent. The conformational energy of a polymer chain depends, among other factors, i.e. on the presence of side groups, steric interactions between side groups and/or between side groups and the main polymer chain are reflected to some extent in the backbone flexibility. The higher \( \tau (2) \) values of PMMA also confirm that the presence of side groups increases hindrance to the segmental reorientation to a greater extent.

In dilute solution, the molecule exists in quasi-isolated state; because of the coiling of the chain there is much intramolecular H-bonding in dilute solutions in addition to intermolecular H-bonding. The observed values of relaxation times in 1,4-dioxane confirm that the steric hindrance to the reorientation motion of PMMA structure increases due to formation of H-bonds between the ester group of PMMA monomer and 1,4-dioxane molecules (Fig. 1). Moreover, it seems that H-bonding with benzene (Fig. 1) is weak in comparison to H-bonding of PMMA monomers with 1,4-dioxane molecules. Hence, increased hindrance in 1,4-dioxane results in higher values of relaxation times in dioxane solutions.

From Table 1, we find finite values of \( \alpha \), for polysulphone in 1,4-dioxane, which suggest the presence of more than one relaxation process in dilute solutions of polysulphone in 1,4-dioxane. The different values of \( \tau (1) \) and \( \tau (2) \) indicate the existence of an intramolecular relaxation process in addition to the over all relaxation process. Large values of \( \tau_0 \) suggest that the chain of this macromolecule is not highly flexible. In general, the value of \( \tau_0 \) increases with increase in the size of molecules of oligomers\(^1\), as it is evident from \( \tau_0 \) values of polysulphone and PMMA in 1,4-dioxane.

The relaxation time \( \tau (1) \) for polysulphone arises from internal rotation of polar group which is also found to be higher than \( \tau (1) \) values of PMMA in 1,4-dioxane. It is because the dipole in polysulphone is in the main chain in the sulphone unit (\(-\text{C}_6\text{H}_4\text{SO}_2\text{C}_6\text{H}_4-\)) and hindered rotation of polar group affects the relaxation time \( \tau (1) \). The dipole in polysulphone experiences more hindrance to rotation as compared to dipole in PMMA which lies in the side chain and experience less hindrance to rotation. The segmental relaxation time \( \tau (2) \) is found to be higher than average relaxation time \( \tau_0 \). This suggests that intramolecular hydrogen bonding exists in dilute solutions of polysulphone in 1,4-dioxane. Large values of \( \tau (2) \) show that higher rigidity in the chains of these molecules offers greater steric hindrance for segmental reorientation which may be attributed to increase in intramolecular hydrogen bonding and the probability of formation of intermolecular hydrogen bonds between adjacent chains.

Hydrogen on the isopropylidene unit in polysulphone may interact with oxygen in 1,4-dioxane (Fig. 2). This intermolecular hydrogen
bonding results in hindrance towards segmental reorientation giving rise to higher values of relaxation time $\tau \ (2)$. In dilute solutions of polysulphone, oxygen of SO$_2$ group in sulphone unit may form bond with hydrogen of 1,4-dioxane (Fig. 2). Intermolecular H-bonding gives rise to hindered rotation which results in increased values of relaxation times.

The distribution parameter $\alpha$ decrease with increasing temperature and the relaxation time also decrease with increasing temperature (Table 1). The decrease in relaxation time with increasing temperature may be explained on the basis of the fact that there is probably greater uniformity in the energy barriers hindering the dipolar or molecular orientations in the solutions$^2$. The increase in dipole moment ($\mu_{\text{sp}}$) with temperature may be attributed to lengthening of the dipoles with increase in temperature.

The $\Delta F_e$ values in dilute solutions of PMMA and PSU increases with increase in temperature (Table 3). This may be attributed to the decreasing viscosity of the medium with rise in temperature. When we compare the molar enthalpy of activation ($\Delta H_e$) values for dilute solutions of PMMA and PSU with corresponding free energy ($\Delta F_e$) values, they are found to be less. Lesser values of $\Delta H_e$ than the corresponding $\Delta F_e$ values which result in the negative molar entropy of activation ($\Delta S_e$). The negative values of $\Delta S_e$ show that the activated state is more ordered as compared to the normal state due to better alignment of dipoles in the activated state. Further, it is the indication of existence of cooperative orientation in the molecules resulting from the dipole-dipole interaction in the molecules of PMMA and PSU.

5 Conclusions

It is observed that the intramolecular and overall orientation are present giving rise to different values of $\tau \ (1)$ and $\tau \ (2)$. The relaxation times $\tau_0$, $\tau \ (1)$ and $\tau \ (2)$ are higher for dilute solutions of PSU in 1,4-dioxane than those for dilute solutions of PMMA in 1,4-dioxane at each temperature. It is inferred that the dipole moment of PSU is higher when compared to PMMA at each temperature. In dilute solutions of PSU and PMMA in 1,4-dioxane with dipole moment does not change with temperature but for PMMA in benzene the dipole moment increases with increase in temperature. $\Delta F_e$ and $\Delta H_e$ values for PSU are found to be higher when compared with the corresponding values for PMMA. Intermolecular and intramolecular H-bonding affects the relaxation times for both the polymers. The solute-solvent interactions are present in dilute solutions of PSU and PMMA in 1,4-dioxane and dilute solutions of PMMA in benzene.

Acknowledgement

One of the authors (AT) would like to thank UGC, Bhopal, for awarding a teacher research fellowship and Dr A Raja, Gardha Chemicals Ltd, Bharuch, Gujarat, for fruitful discussion. The authors are also grateful to the Principal, M S J College, Bharatpur, for providing experimental facilities.

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