

The study of dielectric relaxation in propylene glycol–poly(propylene glycol) mixtures

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Received 23 April 2001; received in revised form 2 July 2001; accepted 20 August 2001

Abstract

Dielectric complex permittivity of propylene glycol (PG), poly(propylene glycol) (PPG-2000) and their mixtures with concentration of 25, 50 and 75 vol% of PG were measured in the frequency range 10 MHz–4 GHz at 25°C using time domain reflectometry (TDR). For these molecules and their mixtures, only one frequency independent dielectric loss peak was observed. The relaxation for these systems is described by a single relaxation time using Debye model. The large value of observed relaxation time for PG molecules shows the formation of molecular clusters. It is found that the relaxation time for PG–PPG mixtures is smaller in comparison to the relaxation times of PG and PPG molecules, and it linearly increases with the concentration of the PG in the mixtures. The values of relaxation times of PG–PPG mixtures are discussed particularly with respect to the solvent (PG) behaviour, which can be assigned to unaffected, loosely affected and tightly bound solvent and also with respect to the PPG chain coiling. As a peculiar feature the observed relaxation time is direct evidence of the interchange of solvent–solvent to solvent–polymer interaction. © 2001 Published by Elsevier Science Ltd.

Keywords: Propylene glycol–poly(propylene glycol) mixtures; Dielectric relaxation behaviour; Molecular conformations

1. Introduction

Recently [1–10], dielectric relaxation behaviour of mixtures of polar molecules (small and macromolecules) under varying conditions of composition have evoked considerable interest, because, it helps in formulating adequate models of liquid relaxation and also in obtaining information about the relaxation processes in mixtures. For ordinary mixtures there exist theoretical tools that allow one to deal with specific interactions in a rather satisfactory way. When the mixture contains components that can associate, (e.g. through hydrogen bonding) the situation becomes complicated. In case of associating polymer systems [3–10], the situation is further complicated because the chain character of the components linked by hydrogen bonds leads to association complexes that are three-dimensional in character, and the degree of theoretical development is less satisfactory.

In recent years glass-forming H-bonded propylene glycol (PG) [HO–CH(CH₃)CH₂–OH] and poly(propylene glycol)s [H{O–CH(CH₃)CH₂}]_n–OH] (PPG) liquids have received considerable attention. The four sites available

for H-bonding in a PG molecule (it can be viewed as a dihydric anisotropic alcohol molecule) promote a set of transient crosslinks between neighbouring molecules. Similarly PPG can form both inter- and intramolecular hydrogen bonds. Recently [11,12], broad-band dielectric spectroscopy (10⁻²–10⁹ Hz) is employed to study the molecular dynamics of PG molecules confined to porous sol–gel glasses. Carini et al. [13] investigated the reorientational dynamics of neat liquid PG molecules and compared with that of confined molecules in 2.5 and 7.5 nm pores of a sol–gel porous glass by means of depolarised light-scattering spectroscopy, and confirmed that the neat PG, characterised by intermolecular crosslink effects imposed by H bonding, and by intramolecular links between the two OH end groups. More recently Leon et al. [14] studied the low frequency dielectric relaxation on PG and oligomers having different number of repeat units ($n = 2, 3$ and 69) and established the relationship between the primary and secondary dielectric relaxation processes. They suggested that there is an increase in intermolecular cooperativity with increasing number of repeat units in these oligomer molecules.

The measurements of dielectric relaxation time of the associating macromolecules are interesting in understanding the molecular flexibility and coiling in the molecular chain, the mobility of polymer segments, internal group

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rotations, steric hindrance to the internal rotations and also the effect of solvent environment because it depends upon the molecular size, shape, intra- and intermolecular interactions. Earlier [15], we have studied the dielectric relaxation of poly(propylene glycol)-2000 in dilute solutions of benzene, decaline, cyclohexane and carbon tetrachloride solvent and it was observed that the relaxation times corresponding to overall rotations of the molecules and segmental motion depends strongly on the density of the solvent while the relaxation time corresponding the group rotations is found independent of the solvent environment. The study of PPG in associating polar solvents is very interesting. Colin et al. [16–19] have extensively studied the formation of hydrogen bonds in the mixtures of PPG + water, PPG + ethanol, PPG + PEG + water and PEG + PPG + PEG over whole concentration range to display very complex phase diagrams of these extremely challenging systems by measuring the P - V - T data.

It is also worthwhile to study the PPG in PG solvent because both liquids exhibits pronounced self-association. Moreover the chemical structure of PG molecules is almost the same as that of the repeat unit of PPG, so that PPG-PG hetero interactions are likely to be similar to the self-interactions. Further the investigations of dielectric properties of PG-PPG solutions in particularly important and interesting to clarify how the structure of PG changes or is broken by adding little amount of its to the PPG.

In the present paper an attempt has been made to study the molecular interactions between self-associating PG and PPG molecules and also in their mixtures of different concentrations by evaluating the permittivity and dielectric relaxation times. Complex permittivities of these systems were made in the frequency range 10 MHz–4 GHz at 25°C, by employing the TDR measurements. The measurements in the frequency range 10 MHz–4 GHz are interesting because the dielectric dispersion of these molecules occurs in the same frequency range. Further the frequency dependent complex permittivity measurements using TDR are more reliable because it is a powerful technique and a single measurement covers a wide frequency range in a very short time.

2. Experimental

Measurements of the complex permittivity i.e. ϵ' and ϵ'' were carried out over a frequency range 10 MHz–4 GHz by employing the TDR at 25°C. The maximum errors in the evaluated values of ϵ' and ϵ'' are ± 2 and $\pm 3\%$, respectively. The detailed explanations of the apparatus and the procedures of the system have been previously reported [2].

PG of AR grade was obtained from s.d. fine-chem. Pvt. Ltd, India while poly(propylene glycol) average molecular weight 2000 (PPG-2000) was obtained from BDH of LR grade, supplied by Ms Asses Chemical Works, Jodhpur and used as received. The solutions

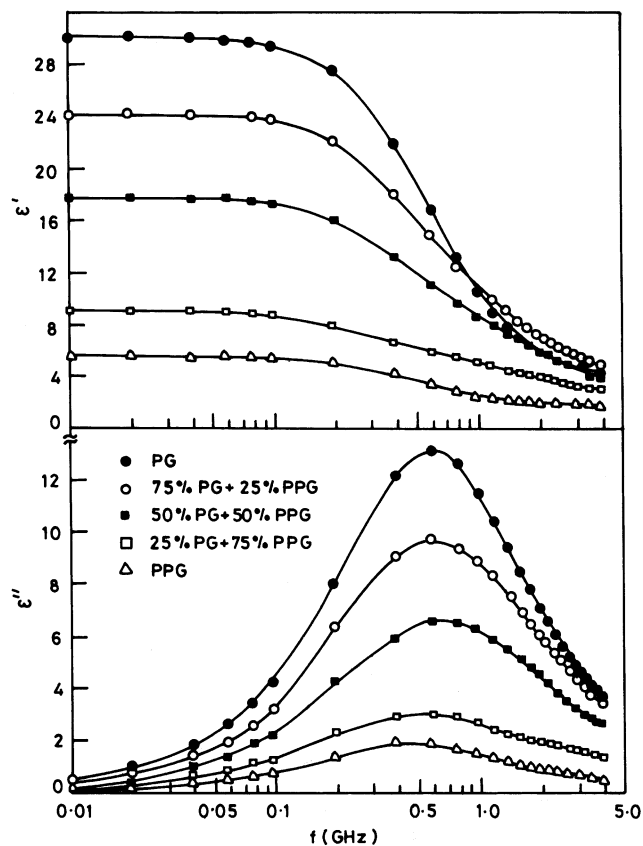


Fig. 1. Frequency dependent of dielectric constant ϵ' and absorption ϵ'' curves for PG, PPG and their mixtures at 25°C.

were prepared at different volume percentages of PPG in PG at room temperature.

3. Results and discussion

Frequency dependence of dielectric dispersion (ϵ') and absorption (ϵ'') curves for PG, PPG and PG-PPG mixtures with 25, 50 and 75 vol% of PG at 25°C are depicted in Fig. 1. To evaluate various dielectric parameters, the frequency dependent experimental complex permittivity data were fitted with the Debye expression [19]

$$\epsilon^*(\omega) = \epsilon_\infty + [(\epsilon_0 - \epsilon_\infty)/(1 + j\omega\tau_0)] \quad (1)$$

with ϵ_0 , ϵ_∞ and τ_0 as fitting parameters. In Eq. (1), ϵ_0 is the static dielectric constant, ϵ_∞ is the high-frequency dielectric constant, ω is the angular frequency, and τ_0 is the average relaxation time. It has been found that the complex dielectric data of pure PG, PPG and PG-PPG systems obey the Debye dispersion model faithfully. These Debye type complex plane plots (ϵ'' vs. ϵ') of these systems are also shown in Fig. 2. The values of dielectric parameters ϵ_0 , ϵ_∞ and τ_0 obtained from fitting into the Eq. (1) for PG, PPG and PG-PPG mixtures with volume percentage of PG are recorded in Table 1. The evaluated values of τ_0 are within the $\pm 3\%$ error.

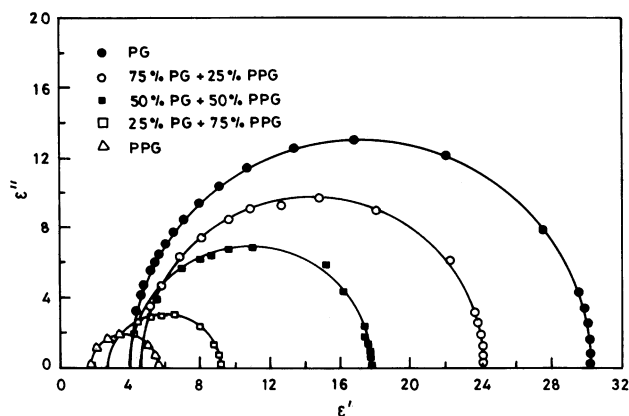


Fig. 2. Complex plane plots of ϵ'' vs. ϵ' for PG, PPG and their mixtures at 25°C.

In Fig. 1, only one relaxation peak is observed for PG, PPG and PG–PPG mixtures. The dielectric loss peaks for these molecules and their mixtures are found in the frequency range from approximately 0.4 to 0.8 GHz. The change in loss peak at constant temperature with mixture concentration variation may be due to the local reorientation of the individual dipole moments perpendicular to the backbone and located on the C–O–C segments of the PPG molecules in the PG–PPG mixtures. Such a relaxation would involve the cooperative motion of a number of monomer units. Further in case of PG molecules the observed Debye type dielectric dispersion behaviour is not surprising. Recently, Carini et al. [13] also confirmed the Debye dielectric dispersion behaviour of PG molecules by means of depolarised light-scattering spectroscopy. The Debye type relaxation in these molecules and their mixtures reflects the behaviour of hydrogen bonded clusters of molecules as large species. Further, the Debye process in case of pure polar liquids also suggests the cooperative process involving the relaxation of the structure. Furthermore, it seems that in the mixture of these associating liquids, the individual principal relaxation processes of the components coalesce, and hence the mixture exhibits a single relaxation time.

In case of PG molecules, the observed relaxation time

Table 1

Values of static dielectric constant ϵ_0 , high frequency limiting dielectric constant ϵ_∞ , dielectric relaxation strength $\Delta\epsilon$ and dielectric relaxation time τ_0 (ps) of PG, PPG and their mixture at 25°C

Volume percent of PG in PG–PPG mixture	ϵ_0	ϵ_∞	$\Delta\epsilon$	τ_0
0	5.59	1.78	3.81	329.3
25	9.11	2.67	6.44	201.7
50	17.72	3.58	14.14	218.9
75	24.04	4.60	19.44	232.6
100	30.20	3.97	26.23	268.8

($\tau_0 = 268.8$ ps) is very large which suggests that primary relaxation of the PG molecules is due to a co-operative process of multimers (i.e. cluster of PG molecules) with (O–H···O) linkage. The evaluated value of Kirkwood correlation factor $g = 2.05$ also confirms the formation of multimers in PG molecules. Further the presence of the methyl side group also produces the steric hindrance to the molecular reorientation, and hence the observed τ_0 value of PG molecules is very large.

Earlier, Schönhal and Stauga [20] investigated the molecular dynamics of oligomeric poly(propylene glycol) liquids ($M_w = 1200, 2000$ and 4000 g/mol) confined to porous glasses using dielectric spectroscopy and confirmed that in these molecules, besides the α -relaxation there is dynamics of whole chain or larger part of it. Recently, we have also studied the dielectric relaxation [15] in PPG-2000 in dilute solutions of four different non-polar solvents. Three different relaxation times for PPG molecules corresponding to the rotation of a molecule as whole (τ_0), segmental motion (τ_1) and group rotation (τ_2) were determined. The observed τ_0 values of PPG molecules in cyclohexane, decaline, benzene and carbon tetrachloride solvents were 25.8, 45.3, 59.5 and 97.3 ps, respectively. From the observed values of τ_0 , τ_1 and τ_2 in dilute solutions it was concluded that τ_0 and τ_1 are strongly dependent on the density of the solvent while τ_2 was found independent of the solvent environment. Further, it was suggested that the variation in τ_0 value in the different non-polar solvents is due to the change in the overall chainlength of the PPG molecules. Larger the coiling in the chain due to the intramolecular interactions reduces the τ_0 value. The significant low τ_0 values of PPG molecules in non-polar solvents in comparison to its τ_0 value ($\tau_0 = 329.3$ ps) in pure liquid state confirms that in pure liquid state there is less coiling in the molecular chain and also larger the intermolecular interactions. These intermolecular interactions increase molecular chain length and produce more hindrance to the molecular reorientation as a whole in comparison to the reorientation in dilute solutions.

The molecules of PG and PPG has methyl side group/s. Due to which there is greater steric hindrance to the molecular reorientation of both the molecules and hence their τ_0 values must be larger in comparison to the τ_0 values of linear chain EG and PEG molecules. In comparison to the τ_0 value of PG molecules, it is expected that the τ_0 value of PPG molecules should be very large because of the presence of 34 monomer units in PPG 2000 molecules. Although the observed τ_0 value of PPG molecules is higher in comparison to the τ_0 value of PG molecules but not very large, which suggests that the primary relaxation of PG molecules is due to a cooperative process of their multimers, and hence its τ_0 value increases. But in PPG molecules, the coiling of chain length cannot be ruled out due to intramolecular interactions and hence the observed τ_0 value is low from the higher expectation. Earlier, in case of self associating low molecular weight poly (ethylene glycol)s [21], (PEG) the τ_0

values in their pure liquid state were found around 100 ps confirms that there is coiling in the molecular chain which starts when the monomer units in the molecular chain are greater than two. The chain coiling in PPG molecules is less in comparison to PEG molecules because of the presence of methyl side group in the PPG chain. Therefore the observed τ_0 value of the PPG molecules is much larger in comparison to the PEG molecules.

In case of PG–PPG mixtures of different volume percentage, the observed τ_0 value is significantly low in comparison to the τ_0 values of pure PG and PPG molecules. This finding is really very interesting and can be understood as follows. Alig and coworkers [22–25] have investigated the molecular dynamics of PPG molecules of different mass by ultrasonic, NMR, light scattering and theoretical, and concluded that the hydrogen bonding causes a dynamic network (called ‘transient entanglement’ or temporary network) due to the transient hydrogen bond structure of PPG molecules. In case of PPG molecules from earlier studies [11–13] and this study it is confirmed that the PG molecules always form clusters in their pure liquid state. When PG is mixed with PPG, three types of cooperative domains (CDs) may take place in the PG–PPG mixtures due to the transient structure of PPG molecules and also due to the breaking of PG clusters. In these CDs, CD_{PG} includes PG molecules only, CD_{PPG} includes PPG molecules only, and CD_{PG-PPG} includes both PG and PPG molecules. Such type of the formation of the co-operative domains has also been suggested by Shinyashiki and Yagihara [8] in poly(vinyl pyrrolidone) (PVP)–water mixtures using the microwave dielectric studies which were carried out by a time domain reflectometry (TDR) method. Further the ratio of these different CDs can vary with the concentration of the constituents of the mixtures. The evaluated τ_0 values in mixtures of PG–PPG, provides the direct evidence of the interchange of solvent–solvent to solvent–polymer interactions. It is inferred from the observed low τ_0 values of PG–PPG systems in comparison to the pure PG and PPG molecules that the structure of pure PG (i.e. clusters of PG molecules) changes or is broken by adding it into the PPG. It also seems that the PG molecules, those are separated from their parent clusters interact with PPG chain thereby increasing the chain coiling and hence the observed τ_0 values of the mixtures are lower in comparison to the τ_0 values of pure PG and PPG. Further, the breaking of homogeneous intermolecular hydrogen bonds and formation of heterogeneous CDs reduces the steric hindrance to the overall rotations of the system, which also reduces the τ_0 values of the PG–PPG systems. It is also seen from Fig. 3 that the τ_0 value of the PG–PPG mixtures increases linearly with the increase in concentration of PG only in the 25–75% volume region. Above 75% volume concentration of PG region the τ_0 value curvedly increases. With increase in the concentration of PG in the PG–PPG mixture, the number of added PG clusters in the mixture increases. Due to this it seems that there are PG clusters those are unaffected or loosely affected

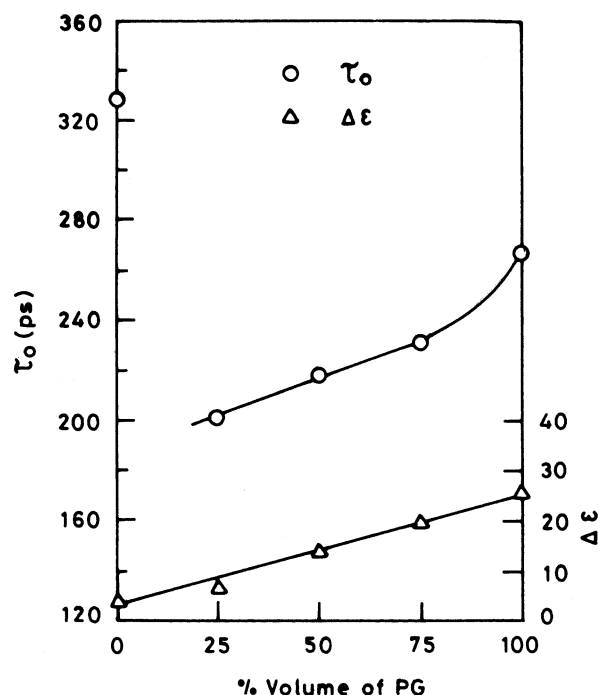


Fig. 3. Plots of τ_0 and $\Delta\epsilon$ vs. concentration of PG for PG–PPG mixtures at 25°C.

by the PPG. These unaffected or loosely affected PG clusters are CD_{PG} . The increase in CD_{PG} in comparison to CD_{PG-PPG} in the PG–PPG mixture increases the resultant relaxation time of the system with increase in PG concentration. The non-linear increase in the τ_0 above 75% volume concentration is expected due to large increase in CD_{PG} and also the strong intermolecular hydrogen bonding in the PG molecules. Further, from Fig. 3 it can be predicted that the homogeneous PG and PPG species vanishes simultaneously under the influence of the PPG when the amount of added PG in PPG is very small and therefore in the PG–PPG mixture, there is large number of CD_{PG-PPG} in comparison to the CD_{PG} and CD_{PPG} in the lower % volume of PG. Due to the formation of such large number of heterogeneous CDs, the τ_0 value abruptly reduces by adding small amount of PG in PPG. Similar conclusions has also been drawn using the dielectric relaxation times in pyrrolidone–poly (vinyl pyrrolidone) (Py–PVP) mixtures [4] and also in case of poly(acrylic acid) in different polar solvents [5]. The earlier P–V–T study [16,17] of PPG–ethanol and PPG–water also confirmed that the increasing ability of the solvents to form intermolecular hydrogen-bonds with PPG, with concomitant breaking of hydrogen-bonds between the pure components. Besides the three different type of CDs and their reorientation motion in the PG–PPG mixtures, the observed Debye type relaxation behaviour of these PG–PPG polar molecules are interesting. Such Debye type relaxation behaviour corresponding to single relaxation also confirms that there is highly cooperative reorientation motion of different CDs. The degree of cooperativity is characterised by defining the CD in which all dipoles

must relax simultaneously. Stronger interaction among the moving units can yield larger CD, and hence the observed relaxation behaviour of these molecules and their mixtures obey the Debye type relaxation behaviour.

Fig. 3 also depicts the plot of dielectric relaxation strength $\Delta\epsilon$ against the volume percentage of PG in the PG–PPG mixture. Further, the increase in the dielectric relaxation strength with the increase in volume percentage of PG in PG–PPG mixtures is due to the decrease in number of carbon atoms in the mixtures in comparison to the number of carbon atoms in pure PPG liquid. This is the general characteristics behaviour of homologous series [21,26]. The almost linear increase in $\Delta\epsilon$ with the volume percentage of PG in the mixtures of two molecules of homologous series i.e. PG and PPG also suggests that the mixing is uniform.

Acknowledgements

One of the authors (SCM) is thankful to the Department of Science and Technology (DST), New Delhi, India for financial support.

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