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Revealing the rich dynamics of glass-forming systems by modification of composition and change of thermodynamic conditions

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ABSTRACT

Secondary relaxations have been classified into two types, depending on whether they are related to the structural α-relaxation in properties or not. Those secondary relaxations that are related to the α-relaxation may have fundamental importance, and are called the Johari–Goldstein (JG) β-relaxations. Two polar molecular glass-formers, one flexible and another rigid, dissolved in apolar host with higher glass transition temperature are studied by broadband dielectric spectroscopy at ambient and elevated pressure. The neat flexible glass-former diethylphthalate (DEP) has a resolved secondary relaxation which, unlike the α-relaxation, is insensitive to pressure and hence is not the JG β-relaxation. In the solution, the JG β-relaxation of DEP shows up in experiment and its relaxation time τ_β is pressure and temperature dependent like τ_α. The result supports the universal presence of the JG β-relaxation in all glass-formers, and the separation between τ_α and τ_β is determined by intermolecular interaction. The rigid glass-former is cyano-benzene (CNBz) and its secondary relaxation involves the entire molecule is necessarily the JG β-relaxation. The dielectric relaxation spectra obtained at a number of combinations of pressure and temperature at constant τ_α show not only unchanged is the frequency dispersion of the α-relaxation but also τ_β. The remarkable results indicate that the JG β-relaxation bears a strong connection to the α-relaxation, and the two relaxations are inseparable when considering the dynamics of glass-forming systems. Experimentally, τ_α has been found to be a function of the product variables, T/ρ^γ, where ρ is the density and γ is a material constant. From the \invariance of the ratio, τ_α/τ_β, to change of thermodynamic conditions seen in our experiment as well in other systems, it follows that τ_β is also a function of T/ρ^γ, with the same γ at least approximately. Since the JG β-relaxation is the precursor of the α-relaxation, causality implies that the T/ρ^γ-dependence originates from the JG β-relaxation and is passed on to the α-relaxation.

1. Introduction

Relaxation dynamics of glass-forming systems presents a complex scenario, characterized by numerous relaxation processes over a very broad frequency window of more than 12 decades. Among these processes manifested over wide temperature or broad frequency range, the structural or α-relaxation process traditionally had been considered as the most important. Therefore research on glass transition was usually centered around this slow α-relaxation process alone, and inadvertently the other faster secondary relaxations are often thought to have no fundamental role. In the early years, secondary relaxation in general were considered as originating from some intramolecular degree of freedom, and hence cannot be related to the intermolecularly cooperative α-relaxation. Historically this is perhaps the primary reason for trivializing the role of secondary relaxations in glass transition.

There are two research developments separated by almost three decades and together they have changed the attitude toward the secondary relaxations. In 1970, Johari and Goldstein shocked the research community by showing the existence of secondary relaxation in a totally rigid small molecular glass-former [1]. Starting from 1998, Ngai [2–4], Ngai and co-workers [5–26], and other workers [27–33] found secondary relaxations belonging to a special class have properties bearing strong connection to the α-relaxation in glass-formers of various chemical and physical compositions. For non-polymeric glass-formers in general that can be flexible or not totally rigid, the secondary relaxation in the special class has to involve the entire molecule or the basic relaxation unit. For polymeric glass-formers, the secondary relaxation in the special class must involve also some motion of the backbone of the repeat unit. This discovery since 1998 was motivated by the Coupling Model (CM) [4,34–37]. The CM is based on the primitive relaxation, which is a local and independent relaxation involving the motion of the entire molecule and acting as the precursor of the cooperative

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α-relaxation. The primitive relaxation time, τ_0, rigorously related to the α-relaxation time, τ_α, given by the time honored equation,

$$\tau_\alpha = \left[t_c^{-n}\tau_0\right]^{1/(1-n)}, \tag{1}$$

where t_c is about 1 to 2 ps for molecular and polymeric glass-formers, and $(1 - n)$ is the fractional exponent in the Kohlrausch correlation function of the α-relaxation,

$$\phi(t) = \exp\left[-(t/\tau_\alpha)^{1-n}\right]. \tag{2}$$

Existence of strong connections in properties and dependencies on variables between the primitive relaxation and the α-relaxation is immediate consequence of Eq. (1). Since by definition secondary relaxation of the special class is also a local and independent process, involving the motion of the entire molecule, and having connections with the cooperative α-relaxation in properties, the approximate relation, $\tau_0 \approx \tau_\beta$, between τ_0 and the relaxation time, τ_β, of the secondary relaxation is expected. On combining this approximate relation with Eq. (1), we have the *approximate* relations

$$\tau_\beta \approx \tau_0 = (t_c)^n(\tau_\alpha)^{1-n}, \tag{3}$$

or the *approximate* relation between τ_α and τ_β

$$\tau_\alpha \approx \left[t_c^{-n}\tau_\beta\right]^{1/(1-n)}. \tag{4}$$

Either Eq. (3) or (4) predicts that not only are the values of τ_α and τ_β related quantitatively, but their dependencies on temperature *T* and pressure *P* or other variables are also related, albeit approximately. The various predictions coming out from these approximate relations have been amply verified in many glass-formers and non-glassformers since the start in 1998 (see Ref. [4] for a comprehensive review).

Certainly, all totally rigid molecular glass-formers investigated by Johari and Goldstein (JG) belong to this special class because there is only one secondary relaxation, and it necessarily involves the entire rigid molecule. With the intent to honor JG for their important findings three decades ago, the glass-formers belonging to the special class are summarily called the JG β-relaxations by Ngai and co-workers [2–26]. This usage of the term has to be distinguished from some workers in the field who still refer to any secondary relaxation as JG β-relaxation, irrespective of whether it has connection to the α-relaxation or not. Moreover, secondary relaxation of this special class is universal and found in all kinds of glassformers, organic molecular, polymeric, metallic, inorganic, ionic, colloidal, and plastic crystalline [4]. Most remarkable is the finding of the secondary relaxation in metallic glasses [38, 39], which are atomic particles devoid of rotational degree of freedom, and in plastic crystals which have no translational degree of freedom [40–42].

In the earlier years, relations (3) and (4) have been mainly the criteria used to verify whether the secondary relaxation is the JG β-relaxation or not. If the approximate relations (3) or (4) are satisfied, the connection between τ_β and τ_α becomes obvious. Not only the value of τ_β approximately predicted by (3) is verified quantitatively, but also the dependence of τ_α on any variable λ, including temperature *T* and pressure *P*, are related to the corresponding dependence of τ_β on λ. An example is that τ_β of JG β-relaxation has to be pressure dependent because τ_α is invariably pressure dependent. These expanded criteria for JG β-relaxation were summarized in the paper of 2004 [6] as one of the methods to classify secondary relaxations. An important advance was made by Böhmer and co-workers in 2006 [27,28]. Using spin–lattice relaxation weighted stimulated-echo spectroscopy, they were able to suppress the contributions of some sub-ensembles of the JG β-relaxation above the glass transition temperature in ortho-terphenyl, D-sorbitol, and cresolphthaleindimethylether, and it was found that the α-relaxation is modified. The findings provide direct experimental support for the strong connection between the α- and the JG β-relaxation.

The advance of broadband dielectric relaxation spectroscopy in making measurements at elevated pressure up to 2 GPa and compensated by increasing temperature has helped immensely to bring out the strong connection of the JG β-relaxation to the α-relaxation, and hence its fundamental importance was not appreciated before. This experimental advance is complemented by elegant molecular dynamics simulations of polymers [33]. Another research trend of recent years is the study of the modification of the relation between the JG β-relaxation and the α-relaxation of a glass-former by mixing with another glass-former having significantly different T_g [14,25,32,43]. The presence of the other component alters the coupling parameter *n* of the α-relaxation, and in turn the approximate relation between τ_α and τ_β according to relation (4). By combining the two new research trends (i.e. studying the dynamics of a component in binary mixtures under elevated pressure), deeper insight is gained into the fundamental role played by the JG in the dynamics of glass-formers and in glass transition. In this paper we present new results from such combined experimental study of component dynamics of novel binary mixtures at ambient and elevated pressure. The far reaching implications of the results on the physics of the dynamics of glass-forming systems as well as the impact on other current research efforts are brought out.

2. Experimental section

Mixing polar aromatic molecules with oligomers of styrene is an ideal strategy to have very good glass-formers with a good miscibility range. The presence of aromatic rings, in fact, improves the solubility of the polar probes in the apolar oligo-styrene system due to the affinity of the π–π interactions. The study of the dielectric response of such binary mixtures can selectively reveal the rotational dynamics of the polar component alone, even when the polar component is dilute. Actually the permanent dipole moment of the styrene repeating unit ($\mu = 0.2$ D) is very small compared to the strong permanent dipole moment of the solute (in our case μ is in the range between 2.5 and 5 D). Since the dielectric strength, i.e. the intensity of the loss peak, scales as $N\mu^2$ (where N is the number of dipoles per unit volume and μ is the permanent dipole moment), we can affirm that the dynamics of the polar component dominates the dielectric response of the mixtures presented in this paper, having a molar concentration of the polar component of $X_M = 0.1$.

Cyanobenzene (CNBz, $M_W = 103$ g/mol) and diethylphthalate (DEP, $M_W = 222.2$ g/mol) were purchased at high purity grade from Sigma-Aldrich and used as received. CNBz was mixed at mole fraction $X_M = 0.1$ with tristyrene (PS370) ($T_g = 234$ K, $M_W = 370$ g/mol, obtained from Polymer Standard Service). DEP was mixed at mole fraction $X_M = 0.1$ with oligostyrene of $M_W = 820$ g/mol, $M_W/M_n = 1.01$, (PS800) ($T_g = 282$ K, obtained from Scientific Polymer Product). All samples were stored and handled in a dry nitrogen atmosphere.

Novocontrol Alpha-Analyzer was used for dielectric measurements, both at atmospheric and at high pressure, in the frequency interval from 10 mHz to 10 MHz. The sample cell consisted in a parallel plate capacitor separated by a quartz spacer (empty capacitance ~90 pF) and filled by the sample in the liquid state. For atmospheric pressure measurements the temperature was controlled using a dry nitrogen-flow Quatro cryostat ($T = 100$–360 K) with a temperature accuracy of better than 0.1 K. For high pressure measurements, a sample-holder multi-layer capacitor (empty capacitance ~ 30 pF) was separated from the pressurizing fluid (silicon oil) by a Teflon membrane. The high pressure chamber (Cu–Be alloy), provided by UNIPRESS, was connected to a hydraulic pump able to reach 700 MPa and controlled in the interval 195–360 K within 0.1 K by means of a thermally conditioned liquid flow.