

Broadband Spectroscopy of Slow Dynamics
in Glass Transition

広帯域スペクトロスコピーによるガラス転移の
スローダイナミクスの研究

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ABSTRACT

The study of the relaxation behavior in simple liquid is important to clarify the dynamical properties of more complicated system. Although alcohol has a simple molecular structure, it shows non-Debye type relaxation and the existence of several relaxation modes due to the hydrogen bonding. Alcohols are classified into intermediate liquids from their relaxation behavior. To clarify the roles of the hydrogen bond and the molecular structure of alcohol, the relaxation dynamics was investigated using the broadband dielectric and calorimetric measurements.

Dielectric relaxation was studied by the broadband dielectric spectroscopy using impedance analyzer and time domain reflectometry (TDR) technique. It covers the frequency range of $10^2 - 10^{10}$ Hz. Calorimetric measurement was carried out using the modulated differential scanning calorimetry (MDSC). The complex dielectric permittivity and complex heat capacity of several alcohols were measured in the liquid, supercooled and glass states.

The roles of hydrogen bonding and molecular structure in the relaxation feature are discussed in respect to the number of -OH group (n-propanol, propylene glycol and glycerol), the bonded position of the -OH group (n-propanol and i-propanol) to alkyl group, its substitution by heavy deuterium (n-propanol-d1 and i-propanol-d1) and -OCH₃ group (monomer and two oligomers of propylene glycol monomethyl ether), and the molecular weights (monomer and five oligomers of propylene glycol). The results are discussed mainly on the basis of the two order parameter model, free volume theory and cooperativity models such as Adam-Gibbs theory and Matsuoka's domain model.

By the best fit to the dielectric spectra by Havriliak-Negami function, we determined the information on the relaxation frequency (f_{max}), dielectric strength ($\Delta\epsilon$) and shape parameters (α and γ).

All samples studied show several universal features: (1) The relaxation behavior has a crossover near the melting point. The temperature dependence of the relaxation frequency was well reproduced by the Vogel-Tammann-Fulcher (VTF) law, $f_{max} = f_0 \nu \exp [-B/(T-T_0)]$, in low temperature range and the Arrhenius law, $f_{max} = f_0 \nu \exp (-E/T)$ in high temperature range. (2) The dielectric strength of the main relaxation mode can be well described by the modified Onsager equation, $\Delta\epsilon = -A + B/T$. (3) The parameter β in Kohlrausch-Williams-Watts function is a monotonically increasing function of temperature.

The relaxation behavior of alcohol was explained in terms of the frustration between the density and bond order parameters on the basis of the two order parameter model which was advocated by Tanaka. The attractive potential between molecules is given by the superposition of isotropic and its anisotropic interactions. The former represents the long-range density ordering, while the latter causes local bonds. In alcohol, it seems that the packing effect by alkyl groups influences the density, while the -OH group mainly controls the bond order parameter. The material, which easily forms long chain structure is stronger than that which forms short chain or ring structure. The fragility of alcohol depends on not only the number of -OH groups but also the chain structure. The frustration between the density and bond order parameters described the facts that the fragility and the glass transition temperature depend on both the molecular weight and the number of -OH groups of alcohol.

Both the Adam-Gibbs theory and the Matsuoka's domain model, based on the molecular cooperativity, derived the VTF relation for the thermal and dielectric behaviors. The correlation between calorimetric and dielectric measurements supports the fact that the dielectric relaxation behavior originates from the structural change during the liquid-glass transition. The minimum configurational entropy s^* and temperature dependent domain size are quantitatively determined for the PG monomer and its oligomers by the combination of the Adam-Gibbs theory with the domain model through VTF relation. For poly propylene glycol with 4000 g/mol, the calculated value of minimum configurational entropy per repeat unit is 5.5 cal/K/mol and the domain includes 4.8 repeat units at glass transition temperature. The non-linearity of the relaxation behavior is enhanced as domain size increases.

Three different relaxation processes are found in four kinds of propanol. It is supposed that Debye relaxation originates from the rotation of -OH group in the network structure, α relaxation from the cooperative motion of the molecules as segment around the surface of the domain, and slow β relaxation from the free molecules outside domain.