CHAPTER I

INTRODUCTION

1.1 Background

The formation of a hydrogen bond in a compound modifies a great many physical and chemical properties. Usually, the properties change sufficiently to require special treatment for associated materials in some correlation of behavior. These changes are not surprising because hydrogen bonding may alter the size, shape and conformation of molecules, as well as the electronic structure of the functional groups [Pimentel and McClellan, 1960].

Many researchers have studied hydrogen bonding in phenolic compounds [Cairns and Eglinton, 1962, 1965; Kovac and Eglinton, 1969]. Through infrared studies of solutions at various concentrations, they found that acyclic tetra-, penta-, and hexa-nuclear novolacs showed the absorption bands in the same manner. These materials formed cyclic intramolecular hydrogen bonds which were concentration independent. Di- and tri-nuclear novolacs, however, demonstrated a concentration dependent absorption, indicating that intermolecular association existed. They also distinguished the OH---O and OH---π intramolecular association and assigned infrared bands to the free hydroxyl stretching as well as both inter and intramolecular hydrogen bonding modes of hydroxyl groups. However, less report dealt with the Infrared study on temperature dependency of hydrogen bonding in phenolic resins.

Recently, benzoxazines, a new class of phenolic materials, were synthesized in our laboratory and unusual properties were observed [Ishida and Allen, in press; Ishida and Low, submitted]. Benzoxazine resins have been found to exhibit a near-zero shrinkage or volumetric expansion upon curing, while traditional thermosetting resins typically undergo a volumetric shrinkage during polymerization in the range from 2 to 6 %. The near-zero shrinkage or expansion of polybenzoxazines makes them ideally be suited for high performance adhesives, sealants, and coatings. This would be advantages for many applications, such as precision casting, dental composites, and high strength composites [Shimbo et al, 1981]. The volumetric expansion of polybenzoxazines have been studied by Ishida and coworkers (in press). They reported that bisphenol-A and aniline-based benzoxazine (hereinafter termed B-a) has polymerized with near-zero shrinkage while bisphenol-A and methylamine-based benzoxazine (hereinafter termed B-m) exhibited the expansion in volume around 3%. They also found that some polybenzoxazines have rather high glass transition temperatures even though they have low crosslink densities which would be expected to give low Tg's.

The polybenzoxazines contain both hydroxyl and amine groups. Despite the fact that these groups have been reported to be the main loci to form hydrogen bonding with water molecules [Danieley and Long, 1981; Carfagna et al, 1982], the polybenzoxazines shows a water content at saturation of only 1.9% for B-a and 1.3% for B-m [Ishida and Allen, in press]. But, it is demonstrated that water bonding would not occur if hydroxyl or amine groups have already formed hydrogen bonding in the system [Bellenger et al, 1989]. Thus, these unusually low water up-takes of polybenzoxazines are suspected to be caused by the strong hydrogen bonding.

Previously, a dilution study on hydrogen bonding in benzoxazine model compound was focused by Dunkers et. al. (submitted). They reported the evidence of the existence of hydrogen bonding in polybenzoxazines. By using molecular modeling, they demonstrated that the strong hydrogen bonding between the phenolic OH and the N atom of the Mannich base could be formed. The conformation of model dimer of 3,5-dimethyl-bis(2-hydroxylbenzyl)-methylamine was also discussed and it was shown that bifurcated hydrogen bonding was preferred. Using Fourier transform infrared spectroscopy (FT-IR), they reported that no free hydroxyl groups existed in crystalline, quenched and molten forms of the model compound. However, by their dilution study, they found that free hydroxyl groups and intramolecular association appeared at the concentration of 3 mM. Upon increasing the concentration, free hydroxyl groups decreased while intermolecular hydrogen bonding appeared and became stronger.

1.2 Objective

The purpose of this work is to study the molecular origin of unusual physical and mechanical properties by studying hydrogen bonding in polybenzoxazines as a function of temperature.