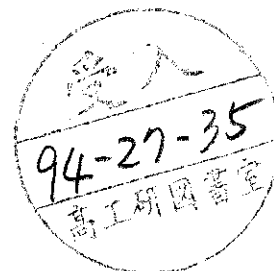# Polymerization of Bisphenol A Dicyanate Studied by Positron Annihilation

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POLYMERIZATION OF BISPHENOL A DICYANATE STUDIED

BY POSITRON ANNIHILATION

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ABSTRACT

A polymerization process of Bisphenol-A dicyanate (BADCy) has
been studied by a positron annihilation lifetime (PAL) technique.
In the process, BADCy was cured through triazine ring formation
by heating; the state changed from a powder at room temperature,
through a liquid above the melting point, to a solid after curing
at high temperatures. It has been shown that PAL is a powerful
technique for studying microscopic structure changes and the
state transition of the continuous polymerization process.

INTRODUCTION

Thermosetting resins are widely used for engineering products.
Especially, many types of epoxy resins are utilized for integral
circuits (ICs) and multilayer printed wiring boards as indispen-
sable materials for the long-term reliable operation of computers
and electronics devices [1]. The physical properties of thermo-
setting resins, such as the refractive index, viscosity, elastic-
ity, mechanical strength and glass transition temperature [2],
are influenced by the polymerization process. Hence, investiga-
tions of the process are important so as to apply it to both ICs
and devices for advanced technologies.

The polymerization process involves transition through
several states [3]: a liquid at room temperature, a solid after
polymerization at the curing temperature, and a mixture of solid
and liquid between the two states. From the view point of free
volumes, PAL can suggest the change of state, the gel time, the
development of three-dimensional networks and the glass
transition temperatures (Tg).

In this study, a polymerization process of BADCy, which is
used as multilayer printed wiring boards, has been followed
through the powder, liquid, and solid states by PAL at several
curing temperatures.

EXPERIMENTAL

The experimental set-up was the same as that in Ref.[3]. The system time resolution was 0.27 ns at the full-width at half maximum. A positron source was prepared by depositing and drying about 30μCi of aqueous ^{22}NaCl on a 7 μm thick kapton film having an area of 10×10 mm^2, which was then covered with the same size of film.

The curing reaction of BADCy (Fig.1) is exothermic, and the time required for polymerization differs depending on the curing temperature. Since it takes 1 hour to obtain one PAL spectrum, it is necessary to control the reaction so as to proceed slowly. Without a catalyst, it must be kept at a high curing temperature in order to accelerate the polymerization and to obtain fully developed three-dimensional networks. It was found that the polymerization reaction took more than 10 hours when the curing temperature was set at 120°C.

The temperature control for the polymerization process was conducted as shown in Figure 2. After this curing process was finished, PA in the solidified sample was performed again, while it was heated from 30 to 300°C at a rate of 5°C/hour, then kept for 1 hour at 300°C, and finally cooled to 30°C at the same rate.

The PAL spectra were automatically recorded every hour, collecting about 1.5 million events in one spectrum. The spectra were analyzed by a POSITRON FIT [4] with three components.

RESULTS and DISCUSSION

BADCy is a powder at room temperature; the chemical structure of monomers is shown in Figure 1, which indicates that it has cyanate groups (-OCN) at both ends. It has a melting point (Tm) at 79°C and cures by itself at high temperature without any catalyst, resulting in triazine (or cyanurate) ring formation.

Below Tm, PA occurred in a powder (or solid) of BADCy, which is described by the first three-hour data in Figure 2. These data correspond to PA in a monomer state; there was no change in I_3, but a large increase in τ_3. The results show that I_3 was quite small due to a suppression of positronium (Ps) formation, as expected from the large electron affinity of the -OCN group. Passing through Tm, I_3 greatly increased from 3 to 11%, and then became constant for the next 5 h, while τ_3 showed only a slight increase from 2.4 ns to 2.5 ns. There was no observed change in either I_3 or τ_3 between 105°C (5h data) and 120°C (6h data), suggesting a small temperature dependence in the liquid state. It has been clarified that Ps formation in a powder is much smaller than in a liquid; the scavenger effect of the -OCN groups in a powder is efficient. In a liquid, Ps formation process is considered to be different from the case in a powder and, through bubble formation, the electron affinity of the -OCN groups seems to become weaker.

While samples are kept at the curing temperature, these monomers start to undergo chemical reactions; the number of unreacted monomers decreases, resulting in a mixture state of

solid and liquid. Finally, these become solid after the gel time. During the process of BADCY polymerization, PA is considered to be affected by chemical and/or structural effects: (1) I_3 is expected to increase with decreasing monomers due to a reduction in the number of $-OCN$ groups; (2) with the propagation of polymer networks, it is expected that I_3 increases and τ_3 decreases. From this information, the curing mechanism and the relative extent of conversion of monomers to polymers can be analyzed.

Commonly, the gel time is understood as the time at which the largest changing rate of the exothermic reaction is attained; it can be determined by the temperature variation of samples. In PAL measurements, the gel time may be defined at the point of the largest changing rate of τ_3 or I_3. Although the time determined by these two changing rates should be consistent with each other, as presented in the case of epoxy resins [3], these values for BADCy were found to be as different as ca. 14h from I_3 and ca. 20h from τ_3.

It is thus suggested that, while several monomers were reacting rapidly during the first period of curing, i.e. I_3 was increasing sharply ($\sim$16h), τ_3 showed only a small increase; the chemical effect was larger than the structural effect. After the sharp increase in I_3, τ_3 started to decrease and the largest decreasing rate was attained at ca. 20h; the structural effect became larger. The difference between epoxy resins [3] and BADCy was in the chemical structures, which is responsible for the reduction of Ps formation; the former has carbonyl groups.

CONCLUSION

PAL has been applied to the polymerization of BADCy, which has been developed so as to be utilized for multilayer printed wiring boards. Before polymerization, Ps formation was largely reduced by $-OCN$ groups in powder. However, the inhibition became weak in liquid due to bubble formation, resulting in an increase in I_3. Ps formation during the polymerization process was affected by chemical and structural factors. The reduction in monomers due to polymerization is associated with an increase in I_3, due to a chemical reason. Along with progress in polymerization, τ_3 started to decrease due to a structural change caused by the change in state from liquid to solid, and the development of three-dimensional networks.

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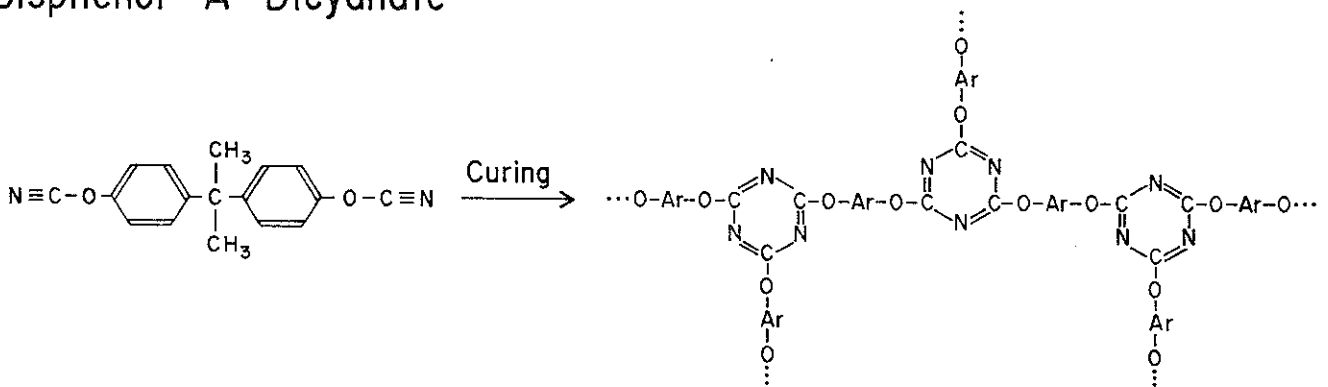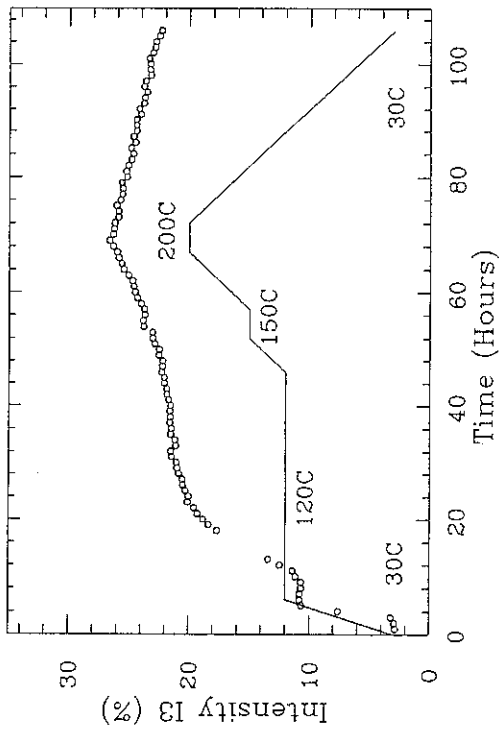[4]P.Kirkegaard and M.Eldrup,Computer communication,3,240(1972)
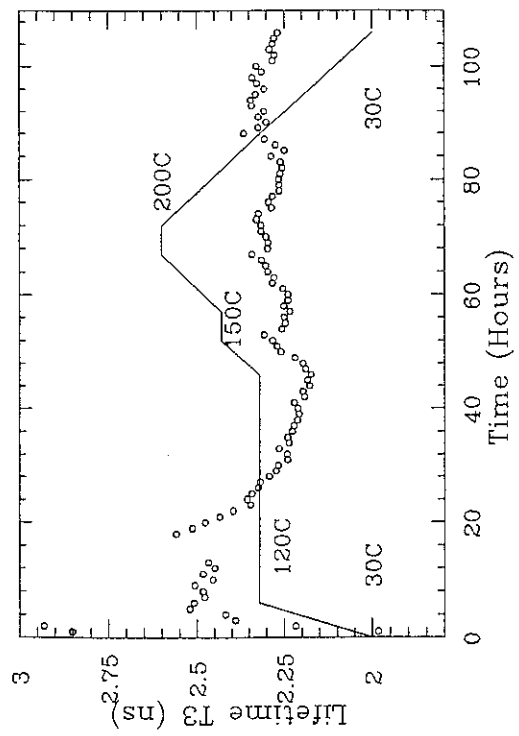
Figure 2. (a) I_3 during the polymerization of BADCY

Figure 2. (b) τ_3 during the polymerization of BADCY

Intensity I3 (%)

Lifetime T3 (ns)

Time (Hours)

Bisphenol A Dicyanate

Curing

Figure 1. Chemical structure of Bisphenol A Dicyanate (BADCy)
and its triazine ring formation