# The Supercooled State and Its Applications

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## 1 Characteristic of the supercooled state

The supercooled state means the physical phase in which a liquid exists without crystallizing at the temperatures below the melting point. The most remarkable characteristic of the supercooled state is that the viscosity of the liquid increases suddenly and rapidly with lowering the temperature to reach $10^{13}$ poise at the glass transition temperature($T_g$). We can call the state below $T_g$ as amorphous solid and glassy state (vitreous state). All organic and inorganic substances have the proper tendency for supercooling with various stableness. But their specific temperature dependency of viscosity can be expressed uniformly by W. L. F. Equation[1)] (the relationship between the viscosity and the temperature in the supercooled state). This specific increase of viscosity in the supercooled systems gives the possibilities for various applications. The supercooling tendency can be estimated and anticipated[2] by evaluating the values of $T_m$-$T_g$ ($T_m$: melting point ) and $T_m$-$T_c$ ($T_c$: cooling temperature). We can get a map for supercooling tendency by plotting those values and drawing a boundary curve between supercooled systems and non-supercooled systems. The relationship between the supercooling tendency and the chemical structure has not been clarified so clearly and systematically. But it was found that most organic esters and ethers having hydrogen bonding or bulky groups were supercooled stably. The binary systems showed the increased supercooling tendency than the single substances.

## 2 Polymerization in the supercooled state

Many acrylic and methacrylic ester monomers can be supercooled easily. The polymerization of those monomers in the supercooled state can be carried out using radiations such as gamma-ray and electron beam, because the radiation can penetrate through the viscous and solid state to initiate the reaction. It was found that the radiation polymerization was carried out with remarkable higher rate in the supercooled state even at low temperatures in comparison to normal liquid phase polymerization.[3)]. The temperature dependency of the polymerization rate showed a maximum at a certain temperature above and close to $T_g$, as shown in Fig. 1. No polymerization occurred at temperature below $T_g$. The accumulation of radicals was observed in the irradiation at temperatures below $T_g$ and the rapid post-polymerization occurred when the system was warmed up to the temperature above $T_g$ after irradiation below $T_g$. The mechanism for those characteristic features in the polymerizability of supercooled monomer was studied. It was concluded that the maximum polymerization rate (apparent negative activation energy) forms owing to the rapid decrease of termination rate with the sudden in crease of viscosity below $T_m$ and the decrease of propagation reac-

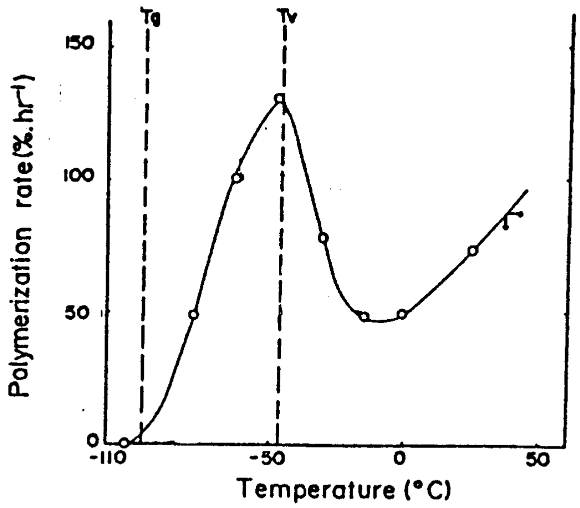


Fig 1: Effect of temperature on the polymerization rate in the polymerization of HEMA induced by $^{60}Co$ $\gamma$-rays, Monomer: HEMA (2-hydroxyethyl methacrylate)

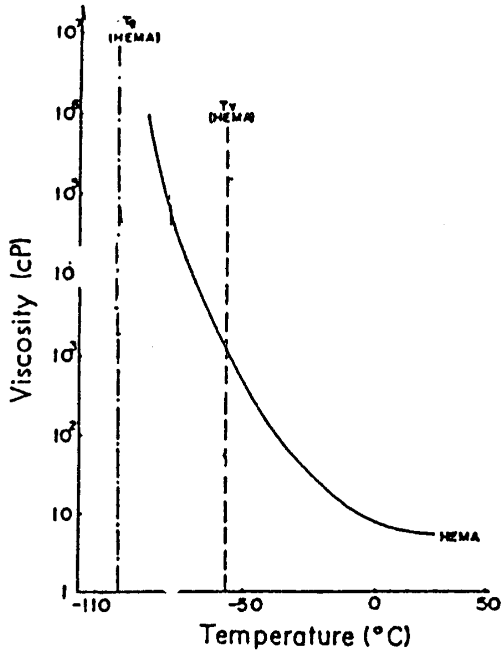


Fig. 2: Relationship between viscosity of monomer and temperature. $T_g$: Glass transition temperature, $T_v$: Temperature of maximum polymerization rate in Fig. 1. Monomer: 2-hydroxyethyl methacrylate.

tion with the further increase of viscosity near $T_g$ as shown in Fig. 2. That is, the viscosity increase first affects on the diffusion of polymeric growing chain and then the further viscosity increase causes the difficulty of monomer diffusion. As at temperatures below $T_g$ no monomer molecule can diffuse and no polymerization occurs. The various characteristics in polymerizability of supercooled monomers were studied systematically and in details using gamma-ray, because the radiation can carried out the reaction in the very broad conditions such as temperatures, phases, viscosities, dose rates and monomer concentrations. The result have been summarized and published.

# 3 Applications of radiation polymerization of supercooled monomers

The supercooled monomer has the characteristic: (1) very high polymerizability, (2) high viscosity or almost amorphous solid state, (3) high polymerizability at low temperatures, and (4)relatively small change in volume and density during the polymerization. Those characteristic were applied to the two fields, (1)cast polymerization of organic glass, and (2)immobilization of biofunctional components. The cast polymerization process to produce organic glass such as glazing materials, optical lenses and other transparent articles requires the severe control of temperature and dimension exactness of the product. The advantages of supercooling polymerization (1)-(4) as described above can fit to the requested conditions for casting process. The result of application has been successful. It was found that the optical articles can be obtained in a much shorter time cycle without formation of optical strain and significant dimensional error. The second application has been studied on the immobilization of various biofunctional components such as enzymes, antibodies, proteins, organella, microbial cells, yeasts, tissue cells, hormones, anticancer drugs and various physiologically active substances. As those components require relatively low temperature and mild conditions for the immobilization, the supercooling polymerization was expected to be effective and convenient for the purpose. It was proved that the various biofunctional components from small molecules to polymeric molecules and living bodies can be entrapped and attached effectively on the various polymerized materials. The products have been used for biomass conversion, cell culture, biosensor, immunodiagnosis, drug delivery system and artificial organ.

# 4 Other kinds of applications

The supercooled state has the broad possibilities to be applied in various scientific and technological fields. We can mention some of the possible applications other than the polymerization.

## 4.1 Studies on the chemistry of short life chemical species

As the supercooled system has the very high viscosity at temperatures near and below $T_g$, the diffusion and mobility of the molecule is very limited or almost inhibited. This state is advantageous to prolong the chemical life of unstable species. Therefore, the study on the short life species and the chemical process has been carried out using flash-photolysis and pulse-radiolysis techniques with the supercooled compound and solvent. This kind of technical method has contributed greatly to the basic researches in radiation chemistry and photo-chemistry.

## 4.2 Studies and applications to prevention of freezing in biological species.

The living cells contain and combine with water indispensably for the life. Therefore, the living bodies like animals and insects might have the special protecting mechanism for freezing of water at low temperatures and any kind of supercooling substance might contribute to the mechanism. The supercooling systems have contributed to the protection and reserve of biological species such as sperm, vaccine and tissue cells in an artificial storage system. The supercooling systems has been used for the prevention of freezing in plants also. Those research and application area is called the Low Temperature Biology. This field is extending further with the progress of low temperature and supercooling techniques and the increase of biological needs.

## 4.3 Studies and applications to amorphous metals and inorganics

With the development of material science and the related technology, the research interest in amorphous metals and inorganics is increasing steadily. One of the key techniques for the preparation of amorphous materials is obviously the supercooling technique. The quick cooling of the melt in the cooled rolls is well known supercooling technique. The deposition of the vapor on the cooled surface is another important method. The deposition combined with ion implantation would be also interesting. The supercooling under no gravity and thermal stream as in space environment is a unknown region. As well known, the trial to prepare a large perfect single crystal in the space environment has been carried out. The lack of diffusion due to the thermal stream and gravity might contribute to the quite different features of supercooling and possibly the more advantageous supercooling. The different kinds and compositions in the amorphous materials would be expected with the new technology of supercooling in the future.

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