

Solid State Transition of Polyacrylonitrile after hydration

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It is well known that the melting behavior of polyacrylonitrile(PAN) is not observed because its melting temperature is higher than the degradation temperature. As shown in Fig.1, a DSC thermogram of dry PAN shows only a glass transition temperature(T_g) around at 100°C , but wet PAN containing water exhibits a conspicuous endothermic peak at 184°C in the first heating under the sealed state. This endotherm is attributed to the hydration of nitrile group which results in the solid-melt transition of PAN. In the second heating, double peaks are observed: A new and small peak at about 160°C in addition to the intense 184°C endotherm appears. During cooling from the melt, double exothermic peaks are also observed. Frushour, who reported this phenomenon first, mentioned that the new peak must be associated with an unknown structure.

Moreover, we realized that a novel endothermic peak around 160°C appeared in heating the sample which experienced hydration and then was dried sufficiently by heating up to 200°C with the cap of the sample capsule opened, as shown in Fig.2. An exothermic peak was also observed around 143°C during cooling the sample from above 160°C . These phenomena were reproducible with each additional cycle.

It was attempted to confirm the supposition that this is not a solid-melt transition, but a solid-state transition. Since PAN is a semicrystalline polymer which has not 3-dimensional crystal structure, the possibility of a transition between different crystal structures is excluded.

This solid-state transition temperature and peak area is nearly coincide with those of secondary peak appeared in hydrated samples as mentioned above. Therefore, the two peaks are assumed to be related each other.

In order to investigate the origin of the solid-state transition, the comonomer effect was studied. A comonomer would reduce the dipole-dipole interaction between nitrile groups. As shown in Fig. 2, the novel peak shifts to the lower position and the area decreases with increasing of the comonomer content. Therefore, it is safe to say that the novel endothermic peak results from the weakening of dipole-dipole interaction. If all of the interaction would disappear, the solid state is probably no more maintained. Thus, it is conclusive that the origin of the peak attributed mainly to the dissociation of the interchain attraction.

Although Frushour tentatively related the double melting and crystallization phenomenon to two distinct crystalline variants, we conclude that the secondary peak is not associated with melting or crystallization behavior, but it is a kind of a solid-state transition.

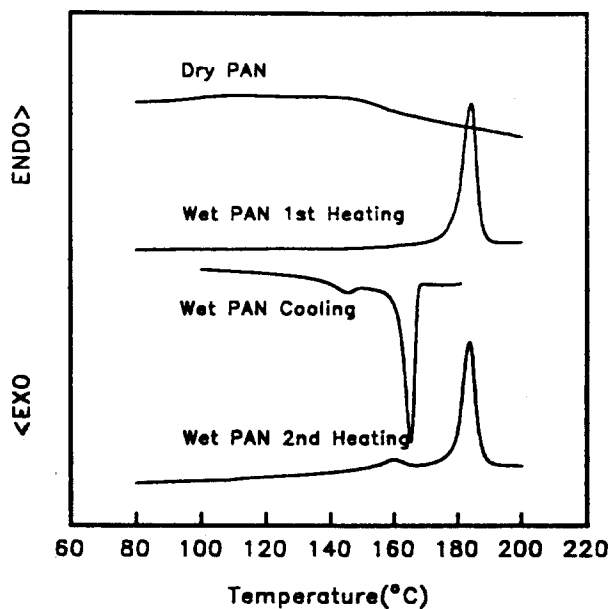


Fig. 1. Melting and crystallization peaks of polyacrylonitrile-water mixture (100% water)

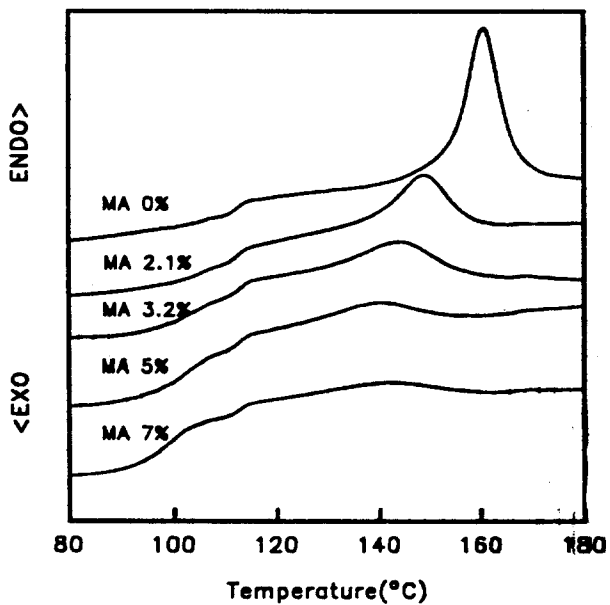


Fig.2. The change of solid state thermal transitions of polyacrylonitrile with comonomer content. (MA: methyl acrylate)