

Thermal Stability of Acrylonitrile Polymer Melt

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Melting point(T_m) of the acrylonitrile polymer which is the material for a commercial acrylic fiber was depressed from 272 °C to 153 °C due to hydration with water. This melting point depression makes it possible to prepare acrylic fiber through melt spinning process.

Since acrylonitrile polymer is very sensitive to heat, we investigated stability of acrylonitrile polymer in melt state.

Observed differences between acrylonitrile polymer before and after melting were discoloration and lower solubility. It was observed in DSC measurement that the melting peak shifted to higher temperature and the heat of fusion (ΔH_f) decreased as the resident time in melt state increased. These changes were more sensitive to temperature than the amount of water in hydrated melt. Since ΔH_f represents the quantity of coupled nitrile groups, the reduction of ΔH_f signifies that the amount of nitrile groups decreased with increasing of the time in melt state. On the other hand, the entropy of fusion (ΔS_f) decreased with increasing of time in melt state, which means that the molecular chain became more rigid. From the reduction of nitrile groups and an increase in chain rigidity, it is conclusive that a cyclizing reaction of nitrile side groups takes place to form naphthyridines in melt state.

The conjugate bonds in naphthyridines are seemed to be the main reason of discoloration. Chemical transformation during melt could not be monitored by IR spectra, but it was found that the extent of visible discoloration is consistent with the absorptivity of UV at 255 nm. UV absorptivity at 255 nm which seems to be originated from naphthyridines was linearly increased with time and temperature in melt state but was almost independent on the amount of water in hydrated melt. Another interesting phenomenon is that UV absorptivity of the

specimen obtained through the melt state is greater than that of dry specimen at the same temperature and time. Therefore, it is considered that, in hydrated melt, hydrolysis of nitrile groups would occur and that this initiates or accelerates a cyclizing reaction.

From the results of relatively lower UV absorptivity of the specimen sampled in nitrogen atmosphere, it was also concluded that oxygen in air has a significant effect on thermally induced discoloration during melt of acrylonitrile polymer.

Molecular weight from viscometry showed a tendency of slight decrease with time in the melt.

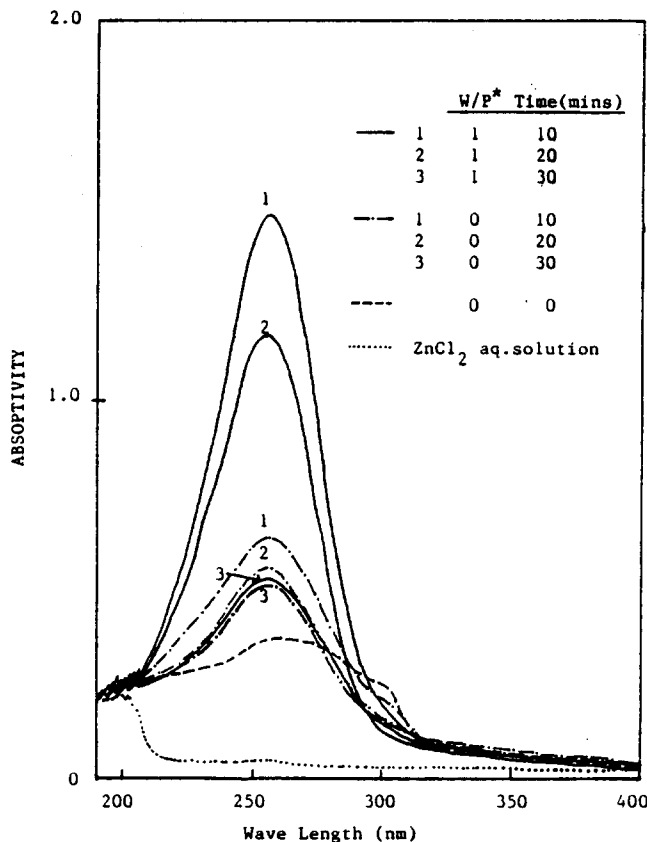


FIG.1 Ultraviolet Spectrum of Acrylonitrile polymers in 65% ZnCl₂ aqueous solution before and after heat treatment.

* W/P=ratio of water to polymer