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Preparation of Poly(*p*-Phenylene Pyromelliteimide) by Phase Separation during Polymerization

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Introduction Poly(*p*-phenylene pyromelliteimide) (PPPI) has been predicted to exhibit many outstanding properties. However, the infusibility and insolubility derived from the rigid liner structure make it difficult to process. PPPI has been generally prepared by the two-step synthesis including the preparation of the soluble poly(amic acid) precursor and the following imidization. The difficulty of the orientation due to the catenation of *para* and *meta* linkages of poly(amic acid) and the rapid crystallization during imidization prevent to create the desirable morphology. In this paper, the PPPI is prepared by means of the reaction-induced phase separation of oligomers during the solution polymerization of *p*-phenylene diamine (PPDA) and pyromellitic dianhydride (PMDA) to create novel morphology.

Experimental PMDA and liquid paraffin (LPF) or Therm S-1000 (TS10) (a mixture of the isomers of dibenzyltoluene) were placed in a cylindrical flask, and the reaction solution was heated under N_2 atmosphere. When the polymerization temperature reached at the given temperature of 240, 280, and 330°C, PPDA was added into the solution and stirred until it was entirely dissolved. The polymerizations were carried out for 6 hours without stirring at 330°C. Thermal property and crystal structure of the obtained precipitates were measured by using TGA, WAXD and TEM.

Results and discussion The precipitation occurred immediately after the addition of PPDA, and PPPI precipitates were obtained by the one-pot synthesis through the phase separation of oligomers. At the concentration over 0.50%, microspheres were formed in LPF through the liquid-liquid phase separation. In contrast to this, the mixture of star-like aggregates of needle-like (SA) crystals and lozenge-shaped crystals of PPPI were obtained at the concentration lower than 0.25% as shown in Figure 1. At the lower concentration, the molecular weight of supersaturated oligomers must become higher bringing about the elevation of the freezing point of the oligomers. Therefore, the crystallization was induced to form the crystals. On the other hand, when the polymerization was carried out in TS10, SA crystals and lozenge-shaped crystals were obtained at the concentration of 0.50%. The

miscibility between the oligomer and TS10 is higher compared with LPF and the oligomers having higher molecular weight were phase-separated in TS10 to form the crystals. These products showed extremely high crystallinity. The crystallinity of SA and lozenge-shaped crystals were slightly higher than of microspheres.

The temperature at which PPDA was added also influenced the morphology. SA crystals and lozenge-shaped crystals were obtained when PPDA was added at 280 and 330°C. In contrast, microspheres were obtained by the addition at 240°C. In order to explain these results, the degree of imidization (DI) of the products precipitated right after the addition at 240 and 330°C was estimated by the IR spectra..[1] The results are plotted as a function of polymerization time with the polymerization temperature profiles in Figure 2. The value of DI of crystals obtained by the addition at 330°C was higher than ca 80%, and this shows that the oligomers rich in imide moiety were phase-separated and formed crystals due to the higher melting point compared with the oligomers rich in amic acid mioety. On the other hand, the value of DI of the precipitates obtained by the addition at 240°C was ca 40% and increased with time. The oligomers rich in the amic acid moiety were phase-separated to form microspheres. The morphology of the product was quite susceptible to the value of DI of the oligomers.

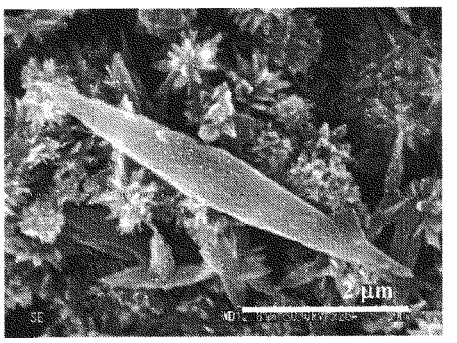

Figure 1. Morphology of PPPI prepared in LPF at 0.15%.

These PPPI products possess very high crystallinity, and the polymer chains of a lozenge-shaped crystal were aligned along the long axis of the crystal. Thermal decomposition temperatures of 10 wt % loss in N_2 were quite high in the range of 681-737°C. The preparation of PPPI by using the other monomers such as *p*-phenylene diisocyanate will be also referred.

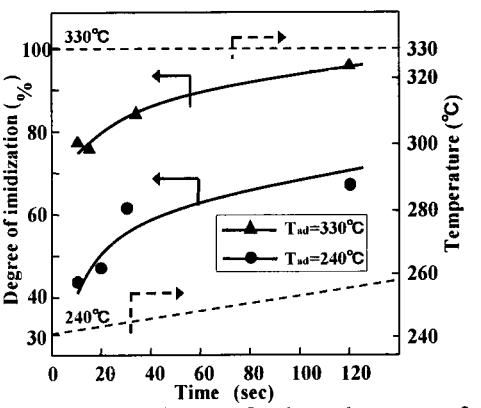

Figure 2. Plots of the degree of imidization of the precipitates and polymerization temperature profiles as a function of polymerization time. Tad stands for the temperature at which PPDA was added.

Reference 1) Hyuck, J.L.; Jongok, W.; Hyun, C. P.; Hoosung, L.; Yong, S. K. *J. Membr. Sci.* **178**, 35 (2000)