

특별강연 I

Coarsening Effects on the Formation of Microporous Membranes

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The microstructure of polymer membranes produced via thermally induced phase separation (TIPS) of polymer solutions is a strong function of both the early-stage (by spinodal decomposition or nucleation & growth) and the late-stage phase separation (referred to in general as coarsening). In the case of early stage effects, the membrane morphology resulting from a nucleation & growth mechanism is either a poorly interconnected, stringy, beady structure which is mechanically fragile or a well interconnected structure with highly nonuniform pore sizes. In contrast, spinodal decomposition results in a well interconnected, mechanically strong membrane with highly uniform pore sizes. Here I describe recent quantitative studies of the coarsening effects on the microstructure of membranes produced via TIPS process. The dependence of microstructure on coarsening time, quench depth, solution viscosity, and polymer molecular weight was investigated in order to distinguish among three possible coarsening mechanisms, Ostwald ripening, coalescence, and hydrodynamic flow, which may be responsible for structural evolution after the early-stage phase separation (spinodal decomposition or nucleation & growth).

The theory of Ostwald ripening[1][2] was developed by examining the case of widely spaced domains of a second phase

growing and shrinking in a matrix. The domains are predicted to have a growth rate proportional to the 1/3 power of the coarsening time, t . In the coalescence mechanism[3], coarsening occurs by two or more droplets impinging on each other by translational diffusion and forming a single droplet, also is predicted to have a growth rate proportional to $t^{1/3}$. In contrast, in the hydrodynamic flow mechanism, in which coarsening results from the viscous flow caused by the interfacial tension, the growth rate is linear in t . It is believed that the dominant coarsening mechanism should be a function of coarsening time. Siggia[4], who considered theoretically a general two component system undergoing phase separation, took into account both diffusive coalescence and hydrodynamic flow effects in order to explain the accelerated growth rate beyond the initial stage. He estimated that the domain growth proceeds in three stages:

(i) initial stage (including coalescence)

$$d \sim \left(\frac{k_B T \Psi}{\eta} \right)^{\frac{1}{3}} t^{\frac{1}{3}} \quad \xi < d \leq \left(\frac{k_B T}{\sigma} \right)^{\frac{1}{2}} \quad (1)$$

(ii) flow stage

$$d \sim \left(\frac{\sigma}{\eta} \right) t \quad \left(\frac{k_B T}{\sigma} \right)^{\frac{1}{2}} \leq d \leq \left(\frac{\sigma}{g \Delta \rho} \right)^{\frac{1}{2}} \quad (2)$$

(iii) gravity-dominated stage

where d is the average domain size, k_B is the Boltzmann constant, T is the separation temperature, Ψ is the total volume fraction of droplets, η is the viscosity, ξ is the correlation length, σ is the surface tension, $\Delta \rho$ is the density difference between the two phases, and g is the gravitational constant.

In the case of polymer systems, the evolution of coarsening from one mechanism to another have been demonstrated for the case of polymer blends[5][6]. In blends, coarsening, which has been

characterized by time-resolved light scattering, has been interpreted to be initially dominated by Ostwald ripening followed by a gradual transition to hydrodynamic flow. Very recently, the evolution of the coarsening mechanism in polymer solution systems has been described based on the evidence of membrane microstructure as well as the characterization of coarsening in solution[7][8][9]. In order to study coarsening in polymer solutions in the absence of significant effects of gravity and hence macroscopic phase separation, a nearly *isopycnic* system of polystyrene-diethyl malonate was chosen for study. Effects of gravity and solution viscosity were studied employing polystyrene-cyclohexane and polystyrene-cyclohexanol solutions. Cell size determined in membranes by SEM and mercury intrusion porosimetry and in solution by *in situ* optical microscopy agree within 10%, implying that the method of preparing the membranes from solutions, including freezing the solutions and extracting solvent with supercritical CO₂, does not significantly impact the microstructure of membranes.

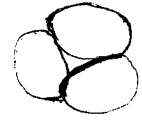
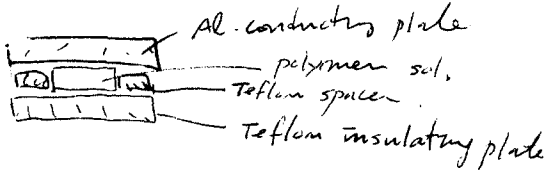
Figure 1 clearly shows the transition in coarsening from the initial stage to the flow stage. The combination of short and long time coarsening (allowed by the *isopycnic* nature of the solution) confirms the transition from one mechanism to another as predicted by Siggia and observed in other systems (non-polymer solution). In Figure 1, cell size was measured as a function of coarsening time for different quench temperatures. In all cases, the growth rate of cell size follows the power law and the growth rate is faster at deeper quench depth until the transition. At shorter coarsening times before the transition, this system exhibits $d \sim t^a$, where "a" $\leq 1/3$; the exponent depends on quench

depth ("a" increases with quench depth). At long coarsening times after the transition, this system exhibits $d \sim t$ in all cases within the experimental error range, that is, every growth rate has same exponent of 1 after the transition (about 1 hr in this system) implying that hydrodynamic flow mechanism controls the rate of growth of cell size in this stage.

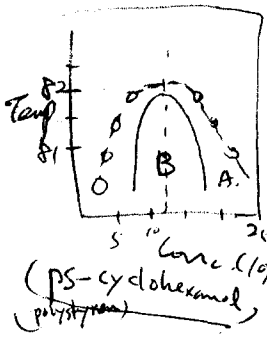
Studies are currently under way to determine whether the effects of coarsening on the microstructure of membranes produced via TIPS have any analogy in the microstructure formation of membranes produced via the nonsolvent induced phase inversion process.

References

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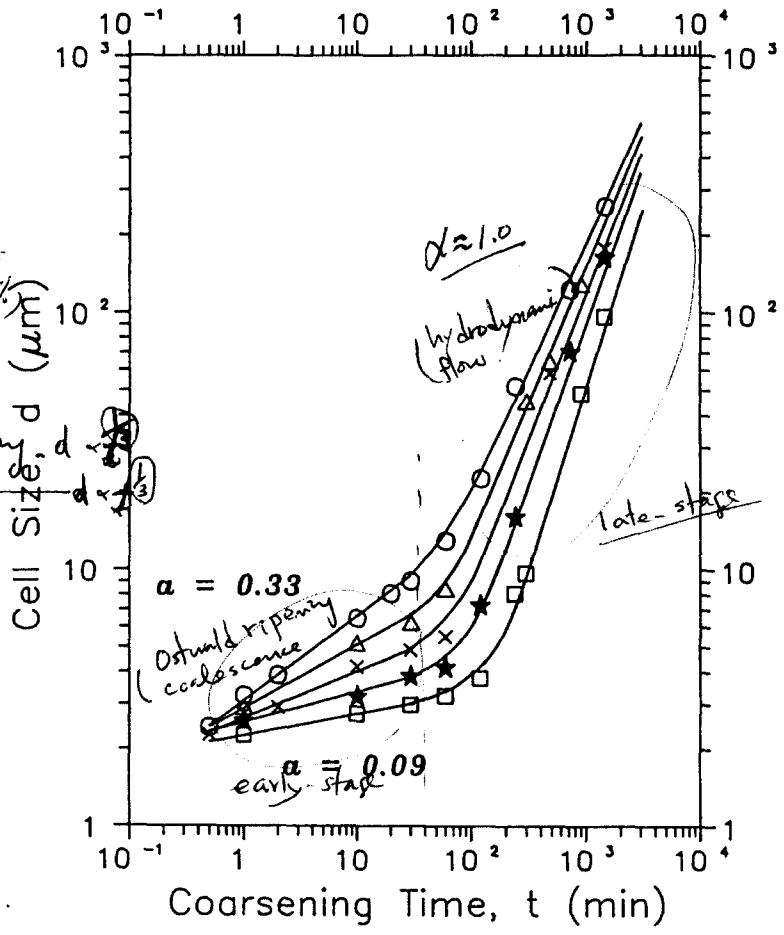
interconnected



* Coarsening

- i) Ostwald ripening
- ii) Coalescence
- iii) hydrodynamic flow

$$d \propto t^a$$



* shallow quench
 deep quench.

Fig. 1. Coarsening time dependence of cell size for the 5 wt% of polystyrene-diethyl malonate system ($M_w = 1.9 \times 10^6$) at various separation temperatures; (O) 20 °C, (Δ) 23 °C, (X) 25 °C, (\star) 27 °C, (\square) 28 °C. The cloud point determined by turbidimetry was 28.6 °C for this system. Note that, in the initial stage of coarsening, the slope was changed from 0.09 to 0.33 as the quench depth increased.

TIPS NIPI (non-solvent induced phase inversion)