

## 특별강연 III

### Competitive Phase Separation in a Crystallizable Polymer Solution

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**ABSTRACT:** The structure formation by liquid-liquid(L-L) phase separation coupled with crystallization in isotactic polypropylene(i-PP) solutions was investigated by a temperature jump experiment. A series of dialkyl phthalates with a different number of carbon atoms in the alkyl chain was used to control the interaction between polymer and solvent. Various thermal quench conditions were applied to the i-PP solutions to control systematically L-L phase separation and crystallization. A slow crystallization elongates the liquid droplets in the radial direction of a spherulite. A rapid crystallization under the deep quench locks-in the growth of L-L phase separation. These results indicate that the extent of L-L phase separation which exists below melting point can be successfully controlled through the proper selection of solvent and thermal conditions.

#### Introduction

Thermally induced phase separation(TIPS) is one of the major processes to produce polymeric membranes<sup>1</sup>. When a crystallizable polymer is used in the TIPS process, there is a possibility that liquid-liquid(L-L) phase separation is coupled with crystallization. The phase diagrams of semicrystalline polymer-solvent mixtures are presented in Figure 1 with different thermal conditions which can be applied to obtain the competitive phase separation. The upper critical solution temperature(UCST) is located above or below the equilibrium liquid-solid(L-S) transition depending upon solvent quality. The relation between L-L phase separation and L-S phase separation can be altered since the binodal curve is remarkably influenced by the solvent quality while the crystal melting transition is slightly<sup>2,3</sup>. When the binodal exists below the melting point, the L-L phase separation has no equilibrium significance, but it may significantly affect the final morphology in membrane forming processes. L-L phase separation would be able to precede crystallization upon rapid quenching due to high nucleation barrier to polymer crystallization.

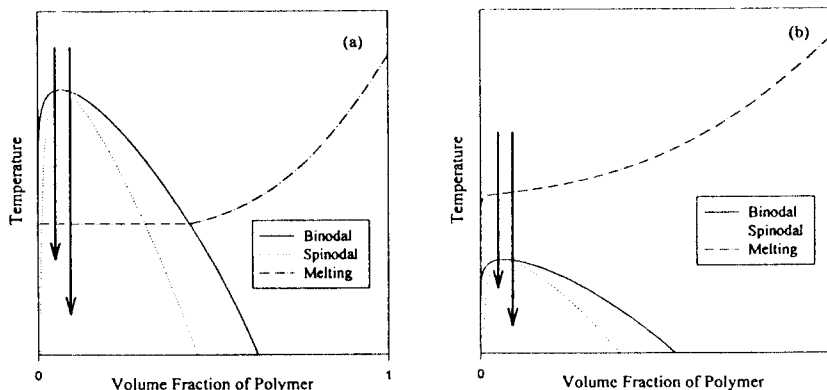


Figure 1. Two possible types of phase diagrams for semicrystalline polymer-solvent mixtures with different thermal conditions to obtain the competitive phase separation in a poor solvent(a) and in a good solvent(b).

In this presentation we investigate the competitive phase separation and resulting morphologies in solutions of isotactic polypropylene(i-PP) and dialkyl phthalates by applying a temperature jump

experiment. The variation of the number of carbon atoms in the alkyl substituent of phthalate was utilized to control the solvent power. Thermal quench conditions were varied in order to control systematically the extents of L-L phase separation and crystallization as denoted schematically in Figure 1.

### Experimental

An i-PP ( $M_w$   $3.1 \times 10^5$  and  $M_w/M_n$  3.4) and a series of dialkyl phthalates designated as C6(hexyl), C7(heptyl), C8(octyl), C9(nonyl) and C10(decyl) were used to control systematically the interaction between polymer and solvent. An atactic polypropylene(a-PP) ( $M_w$   $3.8 \times 10^5$  and  $M_w/M_n$  1.1) was also used with the same solvent system to explore L-L phase separation of a strongly interacting system excluding interference by crystallization. Observation of phase transition temperatures was followed by optical microscopy(OM) with a hot stage. The morphology was examined by OM with temperature-jump experiment and by scanning electron microscopy(SEM). For OM sample preparation the weighed mixtures were slowly heated to  $15^\circ\text{C}$  above the higher value of either melting point or L-L phase separation temperature and heating was continued for 10 min to ensure the complete dissolution. The samples were quickly transferred to a preset temperature in a Mettler hot stage.

### Results and Discussion

While the mechanism of crystallization is nucleation and growth(NG), for L-L phase separation the mechanism depends on the thermodynamic stability of the system. In the unstable region the phase separation occurs according to spinodal decomposition(SD) and in the metastable region according to NG<sup>4</sup>. Since the binodal curve merges with the spinodal at the critical point in the phase diagram of a binary system one can avoid the NG mechanism for L-L phase separation during cooling at the critical composition. Hence the specimen for the observation of the competitive phase separation were prepared with the critical concentration, which was found to be around 2.5 wt% i-PP with the various phthalates<sup>3</sup>.

It was shown in the previous study<sup>3</sup> that a-PP can be used to probe non-equilibrium L-L phase separation temperature of i-PP solutions which exists below crystallization temperature. L-L phase separation of an a-PP solution does not interfere with crystallization when the a-PP used is purely amorphous. Figure 2 shows L-L phase separation temperatures of a-PP and i-PP solutions and melting temperature of i-PP solutions for 2.5 wt% concentration of polymer as a function of solvent quality (number of carbon atoms in the alkyl chain of phthalate) determined by optical microscopy at a scanning rate of  $2^\circ\text{C}/\text{min}$ . When the interaction between polymer and solvent becomes more favorable the melting temperature decreases negligibly but L-L phase separation temperature does in a great amount as expected. The L-L phase decomposition also reflects the molecular weight

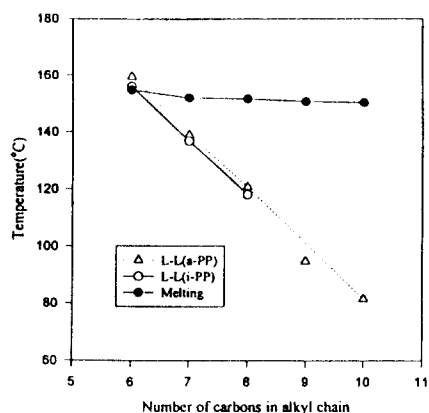


Figure 2. Liquid-liquid phase separation temperatures of a-PP( $M_w$   $3.8 \times 10^5$ ) and i-PP( $M_w$   $3.1 \times 10^5$ ) solutions and melting temperature of i-PP solutions for 2.5 wt% concentration of polymer as a function of solvent quality (number of carbons in the alkyl chain of phthalate) determined by optical microscopy at a scanning rate of  $2^\circ\text{C}/\text{min}$ .

of polymer. Thus the L-L phase separation temperature of the a-PP( $M_w 3.8 \times 10^5$ ) solution is  $\alpha. 3.0$  °C greater than that of the i-PP( $M_w 3.1 \times 10^5$ ) solution in the same solvent at a given concentration in Figure 2. Applying an analogy to better solvents in which L-L phase separation temperature can not be determined in situ due to crystallization occurring prior to L-L phase separation during cooling, one can estimate the L-L phase separation temperatures of the i-PP solution with C9 and C10 phthalates to be 92 °C and 79 °C, respectively.

When crystallization is coupled with liquid demixing, the various structures are created by the competition between the two non-equilibrium processes and the final structures are strongly dependent on their dynamics. Figure 3 gives the optical micrographs for 2.5 wt% i-PP solution in C8 phthalate quenched to 100 °C, which corresponds to an experimental driving force for crystallization ( $\Delta T_{\text{crv}} = \text{melting point} - \text{quenching temperature}$ ) of 52 °C and that for L-L phase separation ( $\Delta T_{\text{L-L}} = \text{L-L phase separation temperature} - \text{quenching temperature}$ ) of 18 °C, respectively. Interestingly the modulated structure due to SD and a ribbon-like elongated droplet appear in the spherulite. Observation through OM revealed that the modulated structure and the droplet formation were frozen-in by the spherulitic crystallization. It is understood that the droplets are formed by concentration fluctuation in the thermodynamically unstable state and subsequently split into the radial direction by a growing crystal. The region at which the ribbon-like structure exists possesses a higher light intensity under crossed polars as can be observed in Figure 3, in which both pictures were taken on the same field of the sample, suggesting that crystallization is enhanced by the droplet formation or vice versa. It is interpreted that the solvent molecules rejected preferentially by growing crystals are piled up in the droplet region<sup>5</sup>. This result was supported by scanning electron microscopy as will be discussed. The ribbon-like structure observed after extracting the solvent occupied the vacant site oriented in the radial direction of a spherulite. In the view point of L-L phase separation, since a droplet would be formed by coarsening of SD, the concentration of polymer should be higher in the boundary of droplets formed and a greater degree of crystallization is expected.

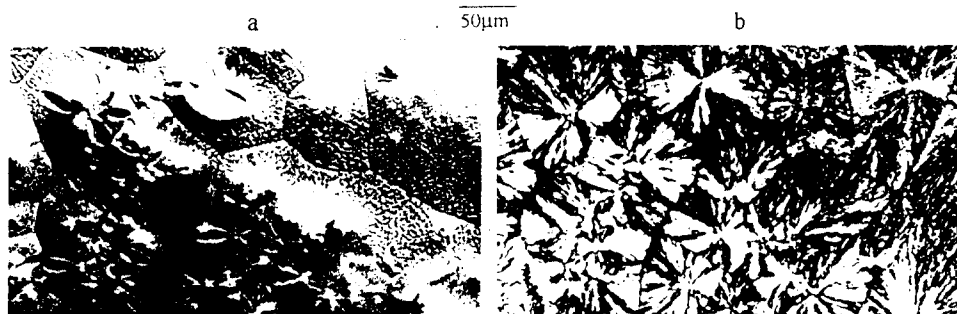


Figure 3. Modulation contrast micrograph(a) and polarized light micrograph(b) for 2.5 wt% i-PP solution in C8 phthalate quenched to 100 °C. Both pictures were taken on the same field of the specimen.

The optical micrographs for the i-PP/C10 and i-PP/C9 pairs quenched to 0 °C are shown in Figure 4. A uniform network structure was produced on quenching and frozen-in immediately. While the size of the spherulite was not clearly recognized from the polarized optical micrographs, the author was able to determine the size of the domains due to L-L phase separation and that of spherulites from the light scattering pattern<sup>6</sup>. The structure formed consisted of small spherulites(about 10  $\mu\text{m}$ ) and large liquid phase separated domains(about 30  $\mu\text{m}$ ) in the i-PP/C10 solution quenched to 0 °C.

The size of liquid droplets is greater in i-PP/C9 ( $\Delta T_{L-L} = 92\text{ }^{\circ}\text{C}$ ) than in i-PP/C10 ( $\Delta T_{L-L} = 79\text{ }^{\circ}\text{C}$ ) as seen in Figure 4. Thus the droplet size is increased with a greater extent of L-L phase separation under the same supercooling for crystallization ( $\Delta T_{\text{cry}} = 151\text{ }^{\circ}\text{C}$ ). The observed morphology is resulted from the rapid liquid demixing and locking-in the structure by crystallization. Although both types of non-equilibrium processes are extremely rapid, the coarsening rate of L-L phase separation is high enough to produce a larger domain due to L-L phase separation than the size of a spherulite which is determined by competition between nucleation and subsequent crystal growth. This is manifested from the fact that the droplet size in i-PP/C9 is greater than in i-PP/C10.

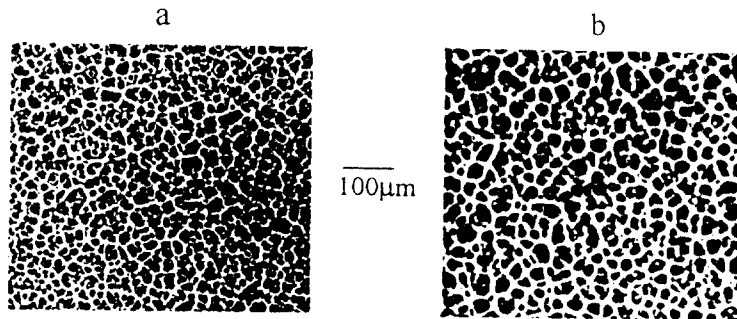


Figure 4. Transmitted light micrographs for 2.5 wt% i-PP solutions in C10 phthalate(a) and in C9 phthalate(b) quenched to  $0\text{ }^{\circ}\text{C}$ .

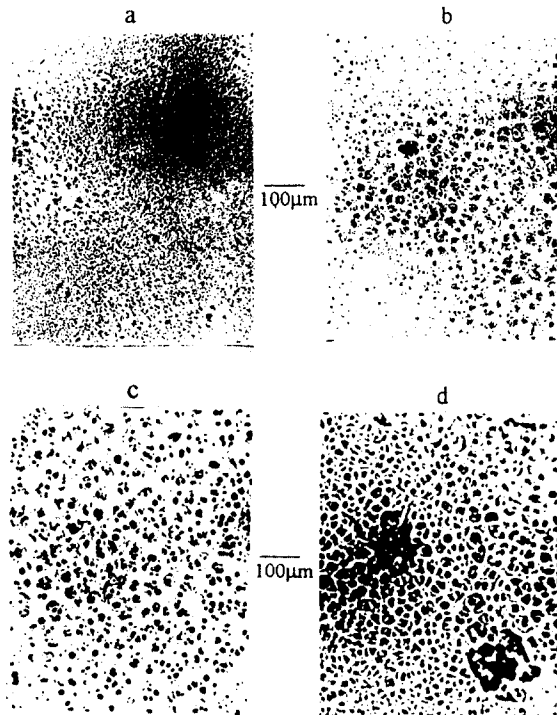


Figure 5. Transmitted light micrographs for 2.5 wt% i-PP solutions in C10 phthalate(a), in C9 phthalate(b), in C8 phthalate(c) and in C7 phthalate(d) quenched to  $70\text{ }^{\circ}\text{C}$ .

A similar trend was followed for i-PP solutions in the series of phthalates when crystallized at different temperatures. Figure 5 shows the structures formed at 70 °C for i-PP/C10 ( $\Delta T_{L-L} = 9$  °C), i-PP/C9 ( $\Delta T_{L-L} = 22$  °C), iPP/C8 ( $\Delta T_{L-L} = 48$  °C) and i-PP/C7 ( $\Delta T_{L-L} = 67$  °C). The size resulting from L-L phase separation increases with the increased undercooling for liquid demixing under the same supercooling for crystallization. Note the liquid-crystal equilibrium is not sensitive to solvent power as shown in Figure 2. The results indicate that the extent of L-L phase separation is controlled through the proper selection of solvent and the resulting structure is locked-in by crystallization. The effects of temperature on the structure formation in the same solvent system can be found in Figure 4 (a) and (b) at 0 °C, and Figure 5 (a) and (b) at 70 °C for the i-PP/C10 and i-PP/C9 pairs. The size of a domain increases at a lower temperature (with increased  $\Delta T_{L-L}$ ) in both systems.

The morphology formed was also studied by SEM. The specimens for SEM were prepared by differential scanning calorimetry(DSC). The samples were cooled from 170 °C to a set temperature (0 °C and 70 °C) at a nominal rate of 200 °C/min and held for 5 min to give rise to phase separation. Since the specimen of 2.5 wt% i-PP solutions tended to collapse during the solvent extraction process, 10 wt% i-PP solutions were also prepared for comparison. Figure 6 shows scanning electron micrographs for 2.5 wt% i-PP solution in C8 phthalate cooled to 0 °C. The fine lacy structure (about 3  $\mu m$ ) and spherulites (about 100  $\mu m$ ) are observed indicating that spinodal decomposition occurred during cooling. It is clearly seen in the high magnification that the interwoven structure and the void are bicontinuous and comprised of a small bead and a few ten micron entity resulting from the coarsening process. The spherulite size is much larger than that observed in optical microscopy suggesting that the spherulites were formed before the temperature reached 0 °C during DSC run.

The morphology of the C8 system cooled to 70 °C of 10 wt% polymer concentration shows the perforated spherulites in Figure 7. The peculiar structure is attributed to the L-L phase separation coupled with crystallization. The liquid droplets are formed by L-L phase separation on cooling and subsequently elongated in the radial direction of a spherulite by growing crystals. The droplets would grow by joining the solvent rejected by crystallization. This feature can be interpreted in conjunction with the ribbon-like structure formation observed with optical microscopy. The cellular structure observed with the high magnification in figure 7 (d) indicates that L-L phase separation occurred during cooling according to NG regime since the concentration of the specimen is in the off-critical region.

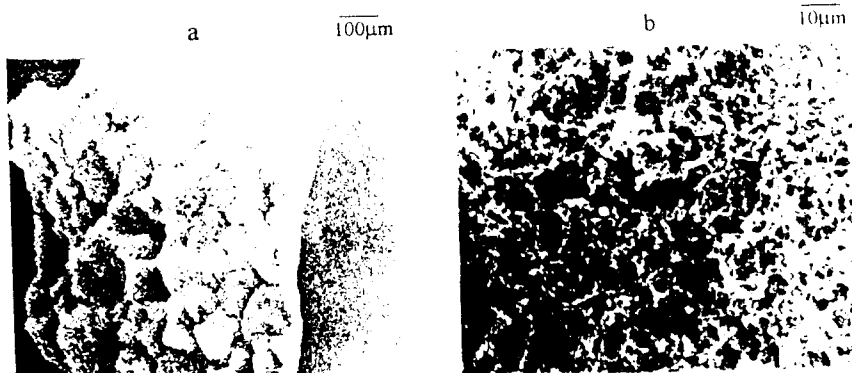


Figure 6. Scanning electron micrographs for 2.5 wt% i-PP solution in C8 phthalate cooled to 0 °C at 200 °C/min and held for 5 min.

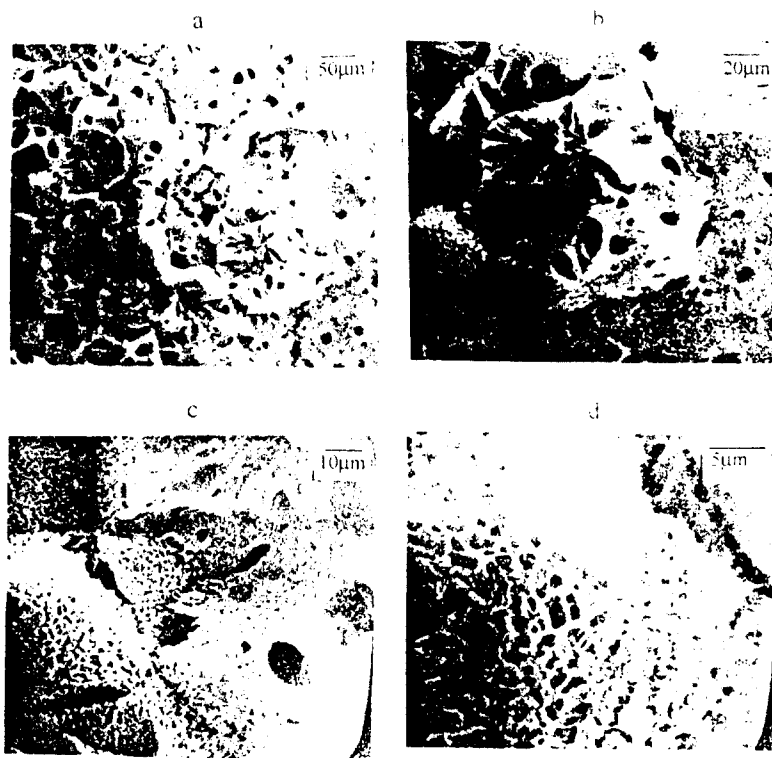


Figure 7. Scanning electron micrographs for 10 wt% i-PP solution in C8 phthalate cooled to 70 °C at 200 °C/min and held for 5 min.

## References

1. R. E. Kesting, *Synthetic Polymeric Membranes: A Structural Perspective*, 2nd ed., Wiley-Interscience, New York, 1985.
2. W. R. Burghardt *Macromolecules* 1989, 22, 2482.
3. H. K. Lee, A. S. Myerson, and K. Levon *Macromolecules* 1992, 25, 4002.
4. J. W. Cahn and J. E. Hilliard *J. Chem. Phys.* 1959, 31, 688.
5. H. D. Keith and F. J., Jr. Padden *J. Appl. Phys.* 1964, 35, 1270.
6. H. K. Lee, Ph. D. Dissertation, Polytechnic University, 1992.