결정성 고분자를 포함하는 용액에서의 경쟁적 상분리

이 환 광[†] · Kalle Levon[*]

충남산업대학교 공업화학과, *미국 폴리테크닉대학교 화학과

(1996년 10월 15일 접수)

Competitive Phase Separation in a Crystallizable Polymer Solution

Hwan Kwang Lee[†] and Kalle Levon[*]

Department of Industrial Chemistry, Chungnam Sanup University, #29, Namjang-Ri,

Hongsung-Eub, Hongsung-Gun, Chungnam 350-800, Korea

*Department of Chemistry, Polytechnic University, Six Metrotech Center, Brooklyn, NY 11201, U.S.A.

(Received October 15, 1996)

요 약: i-PP 용액에서 액-액상분리 및 결정화의 경쟁적 발생에 의한 구조형성을 온도 급강하 실험을 통하여 연구하였다. 고분자와 용매 사이의 상호작용을 조절하기 위하여 알킬사슬에서 탄소원자의 개수가 다른 dialkyl phthalate를 사용하였다. 액-액상분리와 결정화를 체계적으로 조절하기 위하여 i-PP 용액에 다양한 냉각조건을 적용시켰다. 결정화 속도가 느리면 형성되는 액적은 구정의 성장방향으로 잡아 늘려진다. 낮은 온도로 급냉시켰을 경우 액-액상분리의 성장은 빠른 속도로 진행되는 결정화에 의하여 멈춰진다. 실험결과로부터 용매 및 온도조건을 적합하게 선정하면 융점 이하에 존재하는 액-액상분리의 진행정도를 성공적으로 조절할 수 있음이 밝혀졌다.

ABSTRACT: The structure formation by liquid-liquid (L-L) phase separation coupled with crystallization in isotactic polypropylene (i-PP) solutions was investigated by 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.

Keywords: *liquid-liquid phase separation, crystallization, competitive phase separation, isotactic polypropylene solution.*

INTRODUCTION

Thermally induced phase separation (TIPS) is one of the major processes to produce polymeric membranes.[1] When a crystallizable polymer is used in the TIPS process, there is a possibility that liquid-liquid (L-L) phase separation is cou-pled with crystallization. The phase diagrams of semicrystalline polymer-solvent mixtures are shown in Fig. 1 with different thermal conditions which can be applied to obtain the competitive phase separations. The upper critical solution temperature (UCST) is located above the equilibrium liquid-solid (L-S) transition in a
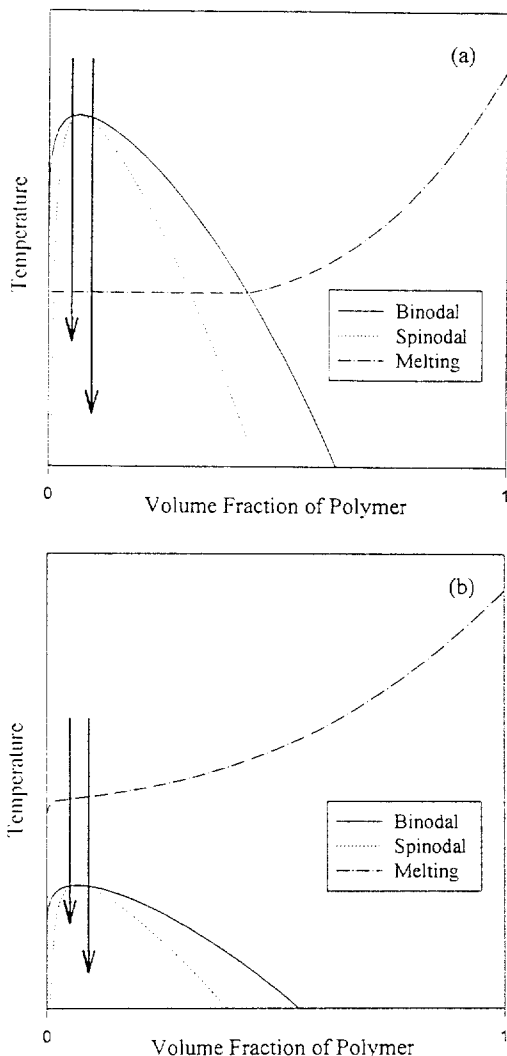
Figure 1. Two possible types of phase diagrams for semicrystalline polymer-solvent mixtures with different thermal conditions to obtain the competitive phase separations in a poor solvent (a) and in a good solvent (b).

poor solvent (Fig. 1(a)) and below the L-S transition in a good solvent (Fig. 1(b)). The relation between L-L phase separation and L-S phase transition can be altered since the binodal curve is remarkably influenced by the solvent quality while the crystal melting transition is slightly.[2,3] 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 processing. L-L phase separation would be able to precede crystallization upon rapid quenching due to the high nucleation barrier to polymer crystallization.

Although these coupled phenomena are expected to occur in crystallizable polymer solutions, the influences of the competitive phase separation on the formed morphologies were not studied extensively. Inaba et al.[4,5] found that the crystallization process could lock-in the modulated structure obtained by L-L phase separation in polymer blends. Schaaf et al.[6] observed globule-like morphologies resulting from L-L phase separation in polyethylene solutions.

In this article we investigate the competitive phase separations and resulting morphologies in solutions of isotactic polypropylene (i-PP) and dialkyl phthalate by applying temperature-jump experiment. The variation of the number of carbon atoms in the alkyl substituent of phthalate was utilized to control the interaction between polymer and solvent. Thermal quench conditions were varied in order to control systematically the extents of L-L phase separation and crystallization.

EXPERIMENTAL

Materials. An i-PP with M_w 3.1×10^5 and M_w/M_n 3.4 was obtained from Himont R & D Center. The solvents supplied by Exxon were 1, 2-dialkyl phthalates with a different number of carbon atoms in the alkyl chain designated as C6, C7, C8, C9 and C10. Molecular characteristics such as the type of alkyl group and molecular mass, and boiling point are summarized in Table 1. All the solvents were used as received without purification. An atactic polypropylene (a-PP) (M_w 3.8×10^5 and M_w/M_n 1.1) obtained

Table 1. Molecular Characteristics and Boiling Point of Phthalates Used

symbol	alkyl group	molecular mass	boiling point[a]
C6	hexyl	334	210 ℃
C7	heptyl	362	220 ℃
C8	octyl	391	230 ℃
C9	nonyl	419	252 ℃
C10	decyl	447	256 ℃

[a] The value at 5 mmHg and the information provided by the supplier.

from Exxon was also used with the same solvent system to explore L-L phase separation of a strongly interacting system excluding interference by crystallization.

Methods. Observation of phase transition temperatures was followed by optical microscopy (OM) with a hot stage under nitrogen purge. The experimental details are described elsewhere.[3] The L-L phase separation temperature (T_{L-L}) observed by phase-contrast microscopy was assigned to the temperature at which fine droplet structures start to appear during cooling at a rate of 2 ℃/min. The value of melting temperature (T_m) by polarized light microscopy was the temperature at which the last traces of crystallinity disappear between crossed polarizers on the reheating cycle at the same rate.

The morphology was examined by OM (Nikon HFX II) with temperature-jump experiment and by scanning electron microscopy (SEM). The three different modes of OM (transmitted light, phase-contrast, and polarized light) were applied to take advantage of OM fully. A phase-contrast microscopy employed in this work (Hoffman modulation contrast) allows observation of a three-dimensional image in the surface region of the specimen, and transmitted light microscopy usually conveys structural features through the whole thickness. The structure of spherulites can be observed by polarized light microscopy since crystalline materials are able

to rotate the plane of polarized light.

For OM sample preparation mixtures of a thin i-PP film and solvent were weighed to obtain a known concentration in flatcavity microslides. A cover glass was placed over the sample and sealed in position with Conap Easypoxy Resin (Conap Inc., Olean, NY) in a nitrogen atmosphere. The weighed mixtures were slowly heated to 15 ℃ above the higher value of either T_m or T_{L-L} and heating was continued for 10 min to ensure the complete dissolution. The samples were quickly transferred to a preset temperature in a Metter hot stage. The time for equilibrating the specimen at the experimental temperature varied from 30 to 240 s depending on the quench depths. Condensation of the solvents during quenching was negligible for C8, C9 and C10. In the case of C6 phthalate the bulk concentration of the solution was destroyed by the quenching process and the discussion of structure formation in C6 solvent is omitted.

The specimen for SEM were prepared by using DSC (Perkin Elmer DSC-7). The weighed mixtures of i-PP and solvent were dissolved at 170 ℃ for 10 min. The specimen was cooled at a nominal rate of 200 ℃/min to a set temperature and held for 5 min to give rise to phase separation. Evaporation of solvent was negligible during DSC running. The sample was immersed in hexane for 48 hrs to extract the solvent at a room temperature. The solvent-free samples were dried in a vacuum oven for more than 2 days. The final sample was fractured in liquid nitrogen. The fractured surface was vacuum metallized with platinum using a sputter coater (Model3, PELCO) and observed through a scanning electron microscope (Model 1200, AMR). Magnification ranged from 100× to 3000 × depending on the purpose of viewing.

RESULTS AND DISCUSSION

Experimental Scheme to Control Phase Separations. 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.[7] 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 in order to obtain SD the specimen were prepared with the critical concentration, which was found to be around 2.5 wt % i-PP with the various phthalates.[3]

It was shown in the previous study[3] that an a-PP can be used to probe non-equilibrium L-L phase separation of i-PP solutions which exists below crystallization temperature (T_{cry}). L-L phase separation of an a-PP solution does not interfere with crystallization when the a-PP used is purely amorphous. Fig. 2 shows T_{L-L} of a-PP and i-PP solutions and T_m of i-PP solutions for 2.5 wt% polymer concentration 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 °C/min. When the interaction between polymer and solvent becomes more favorable, T_m decreases negligibly but T_{L-L} does in a great amount as expected. The L-L phase decomposition may also reflect the molecular weight of polymer. The T_{L-L} of the a-PP (M_w 3.8×10^5) solution is *ca.* 3.0 °C greater than that of the i-PP (M_w 3.1×10^5) solution in the same solvent at the given concentration in Fig. 2. Applying an analogy to better solvents in which T_{L-L} cannot be determined in situ due to crystallization oc-

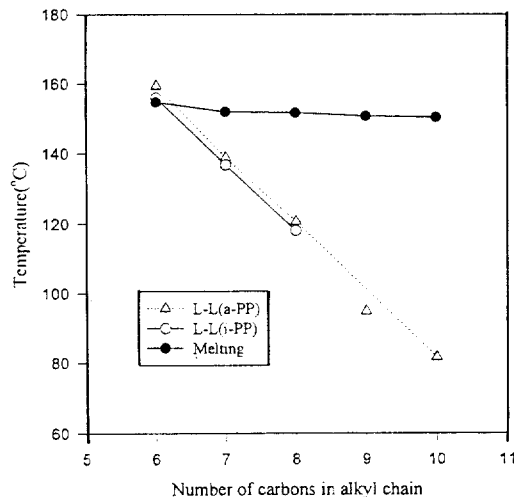**Figure 2.** Liquid-liquid phase separation temperatures of a-PP (M_w 3.8×10^5) and i-PP (M_w 3.1×10^5) solutions and melting tiemperatures of i-PP solutions for 2.5 wt% polymer concentration as a function of solvent quality (number of carbons in the alkyl chain of phthalate) determined by optical microscopy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

Table 2. $\Delta T_{L-L}{}^a$ and $\Delta T_{L-L}{}^b$ Values in Celsius Applied for 2.5 wt% i-PP solutions in a Series of Phthalates as a Function of Quenching Temperature

	C7		C8		C9		C10	
	ΔT_{L-L}	ΔT_{cry}	ΔT_{L-L}	ΔT_{cry}	ΔT_{L-L}	ΔT_{cry}	ΔT_{L-L}	ΔT_{cry}
121 °C	16	31						
113 °C			5	39				
110 °C			18	52				
70 °C	67	82	48	82	22	81	9	81
0 °C					92	151	79	151

[a] ΔT_{L-L} = L-L phase separation temperature – quenching temperature.
[b] ΔT_{cry} = Melting point – quenching temperature.

curring prior to L-L phase separation during cooling, one can estimate the T_{L-L} of the i-PP solution with C9 phthalate and that with C10 phthalate to be 92 °C and 79 °C, respectively.

In order to understand the competitive phase separation, it is necessary to control L-L phase separation and crystallization systematically. An approach to study this problem is to control the

thermodynamic conditions through selection of solvent while keeping thermal conditions constant. The magnitude of the driving force for L-L phase separation can be varied without changing significantly that for crystallization because the liquid-crystal equilibrium is not sensitive to solvent quality. Table 2 represents the thermal conditions applied to the i-PP solutions to change systematically the extents of L-L phase separation and crystallization, where $\Delta T_{L\text{-}L}$ stands for an experimental driving force for L-L phase separation which is the difference between $T_{L\text{-}L}$ and the quenching temperature and ΔT_{cry} stands for that for crystallization which is the difference between T_m and the quenching temperature. One can change $\Delta T_{L\text{-}L}$ without changing ΔT_{cry} too much at a certain temperature by selecting a proper phthalate. Both $\Delta T_{L\text{-}L}$ and ΔT_{cry} are increased by decreasing the experimental temperature in a given solvent. Combination of solvent selection and the proper experimental temperature may allow the variation of ΔT_{cry} keeping $\Delta T_{L\text{-}L}$ constant.

Optical Microscopy with Temperature-Jump Experiment. 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. We investigate first the effects of a small extent of L-L phase separation on the spherulitic formation by optical microscopy in the i-PP/C8 system quenched to 113 ℃. The thermal condition corresponds to a deep queching for crystallization ($T_{cry} = 39$ ℃) and a shallow quenching for L-L phase separation ($T_{L\text{-}L} = 5$ ℃). It is expected that the phase transition should be dominated by crystallization. The droplets formed due to L-L phase separation are elongated to the radial direction of the spherulite as shown in Fig. 3. The droplets are ob-
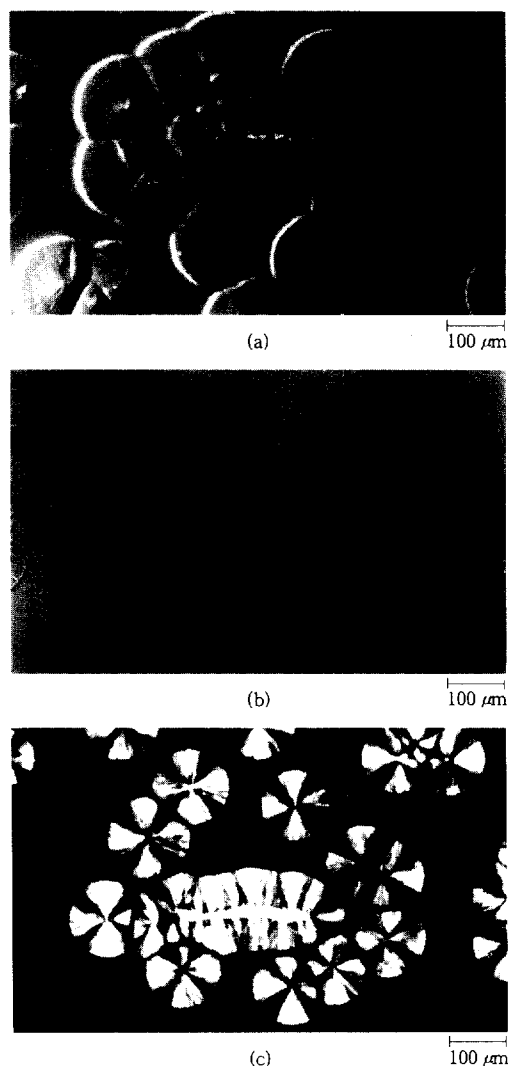

(a)   100 μm

(b)   100 μm

(c)   100 μm

Figure 3. Phase-contrast micrograph (a), transmitted light micrograph (b), and polarized light micrograph (c) for 2.5 wt% i-PP solution in C8 phthalate quenched to 113℃. All pictures were taken on the same field of the specimen.

served only inside spherulites suggesting that the droplet formation plays a role in nucleation for crystal growth. It is understood that the droplets are formed by concentration fluctuation in the thermodynamically unstable or metastable states and subsequently split into the radial direction by a growing crystal.
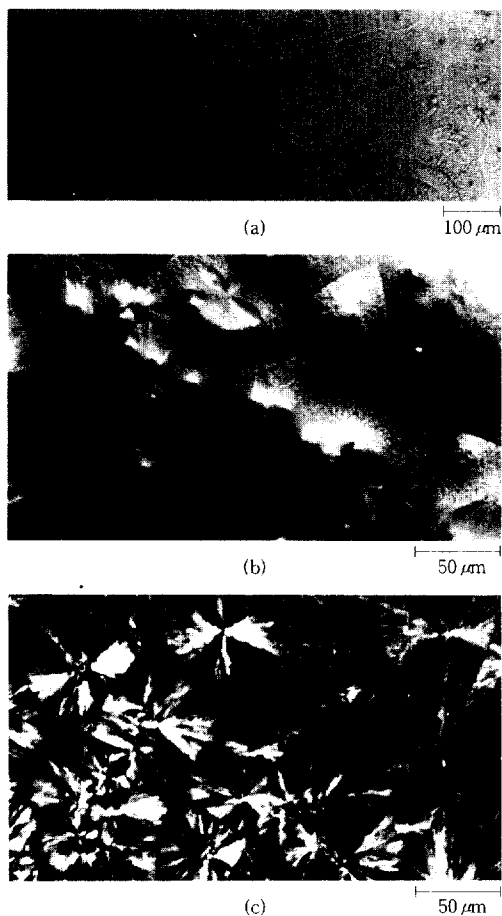
(a)   100 μm

(b)   50 μm

(c)   50 μm
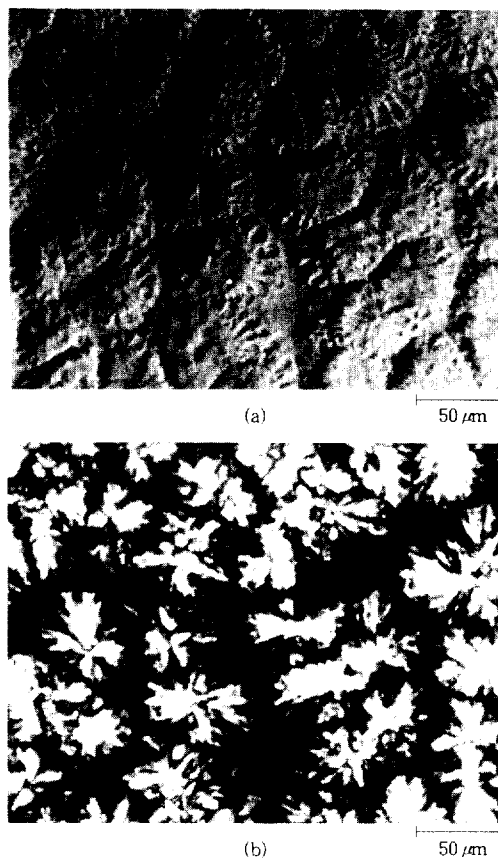
Figure 4. Transmitted light micrograph (a), phase-contrast micrograph (b), and polarized light micrograph (c) for 2.5 wt% i-PP solution in C8 phthalate quenched to 100 ℃. The pictures (b) and (c) were taken on the same field of the specimen.

When the queching temperature is lowered to 100 ℃ with the i-PP/C8 solution in which $\Delta T_{L.L.}$ =18 ℃ and ΔT_{cry}=52 ℃, the ribbon-like elongated structure is ubiquitous and the modulated structure produced by SD appears as shown in Fig. 4. According to the linearized theory of SD,[8,9] the wavelength of concentration fluctuation decreases with the increased undercooling for SD and the period at which the linearized theory is valid becomes short, i.e. rapid coarsening. Thus the modulated structure is obtained with the in-

(a)   50 μm

(b)   50 μm

Figure 5. Phase-contrast micrograph (a) and polarized light micrograph (b) for 2.5 wt% i-PP solution in C7 phthalate quenched to 121 ℃. Both pictures were taken on the same field of the specimen.

creased undercooling and subsequently frozen-in by the spherulitic crystallization prior to coarsening. The region at which the ribbon-like structure exists possesses a higher light intensity under crossed polars as can be observed in Fig. 4 (b) and (c), in which both pictures were taken on the same field of the sample, suggesting that crystallization is enhanced by droplet formation or vice versa. It is interpreted that the solvent molecules rejected preferentially by growing crystals are piled up in the droplet region.[10,11] This result was supported by scanning electron microscopy as will be discussed. The
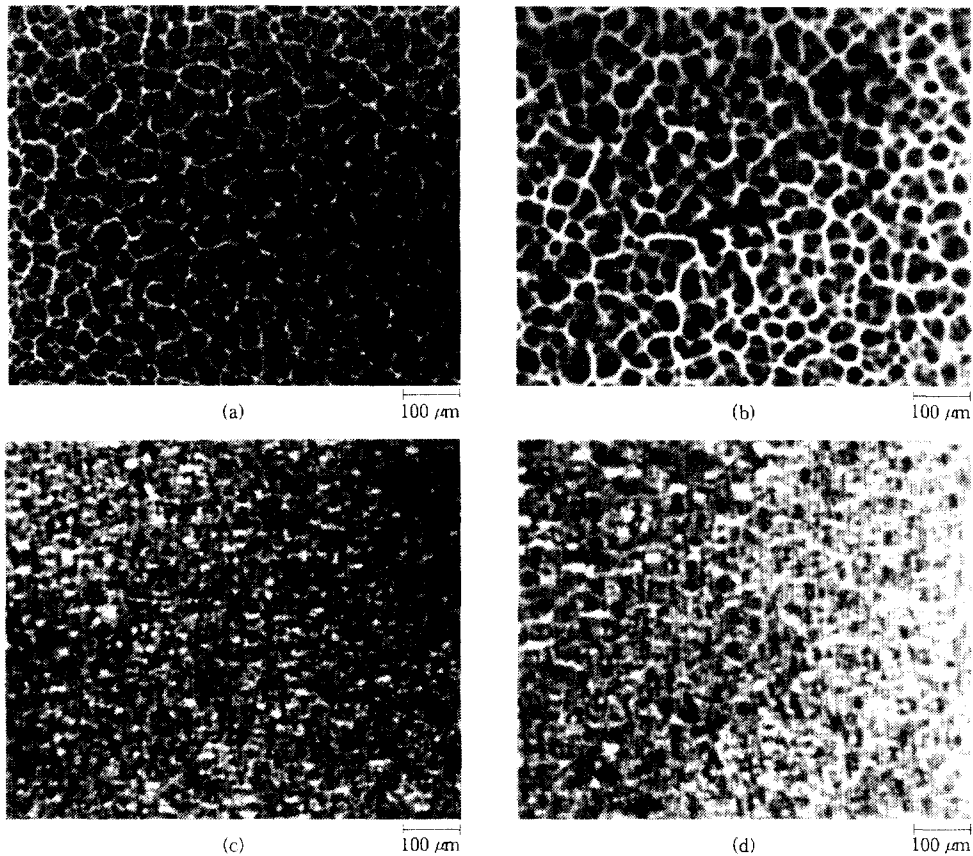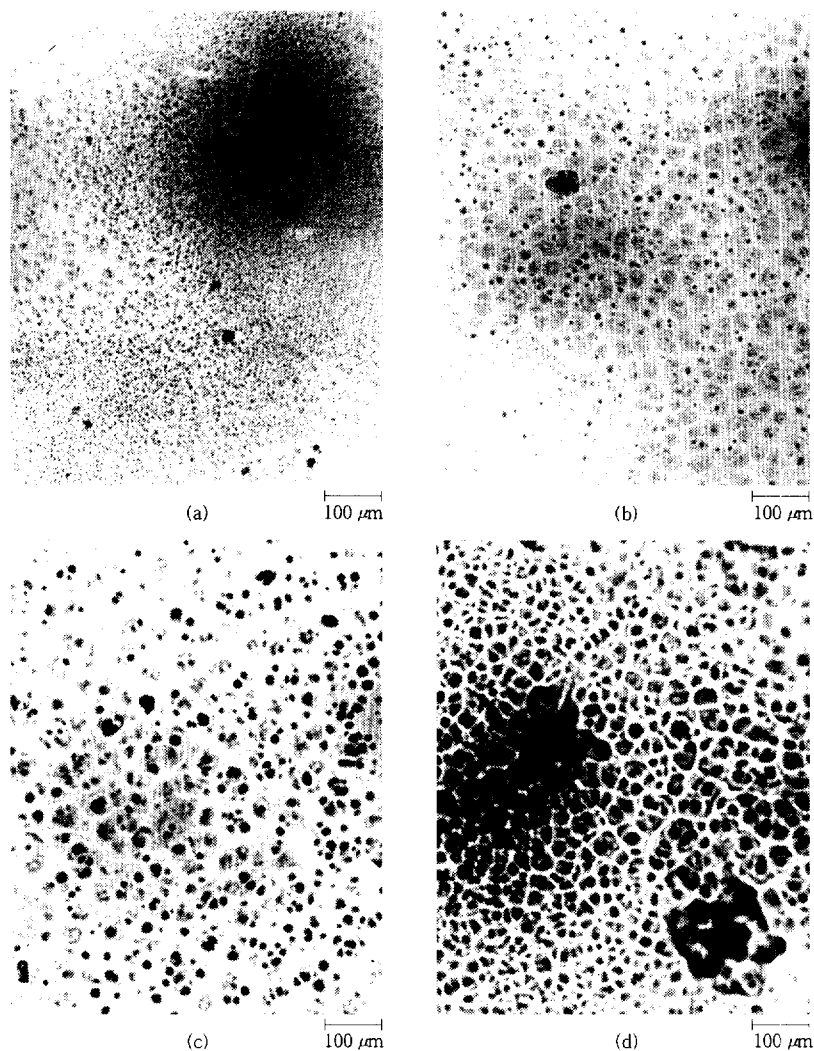
Figure 7. Transmitted light micrographs for 2.5 wt% i-PP solutions in C10 phthalate (a), in C9 phthalate (b), in C8 phthalate (c), and in C7 phthalate (d) quenched to 70 ℃.

6. An uniform network structure was produced on quenching and frozen-in immediately. Although the size of the spherulite was not clearly recognized from the polarized optical micrographs, we were able to determine the size of the domains due to L-L phase separation and that of spherulites from the light scattering pattern.[14] The structure formed consisted of small spherulites *ca.* 10 μm and large liquid phase-

separated domains *ca.* 30 μm in the i-PP/C10 solution quenched to 0 ℃. The size of liquid droplets is greater in i-PP/C9 ($\Delta T_{L-L}=92$ ℃) than in i-PP/C10 ($\Delta T_{L-L}=79$ ℃) as seen in Fig. 6 (a) and (b). Thus the droplet size is increased with a greater extent of L-L phase separation under the same supercooling for crystallization ($\Delta T_{cry}=151$ ℃). 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.

A similar trend was followed for i-PP solutions in the series of phthalates when crystallized at different temperatures. Fig. 7 shows the structures formed at 70 ℃ for i-PP/C10 ($\Delta T_{L-L}=$ 9 ℃), i-PP/C9 ($\Delta T_{L-L}=22$ ℃), i-PP/C8 ($\Delta T_{L-L}=$ 48 ℃) and i-PP/C7 ($\Delta T_{L-L}=67$ ℃). 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 quality as shown in Fig. 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 by comparing Fig. 6 (a) and (b) at 0 ℃, and Fig. 7 (a) and (b) at 70 ℃ for i-PP/C10 and i-PP/C9 pairs. The size of a domain increases at a lower temperature (with increased ΔT_{L-L}) in both systems.

Scanning Electron Microscopy. The specimens for SEM were prepared by DSC as explained in the experimental part. 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. Fig. 8 shows scanning electron micrographs for 2.5 wt% i-PP solution in C8 phthalate cooled to 0 ℃. The fine lacy structure ca. 3 μm in Fig. 8 (b) and spherulites ca. 100 μm
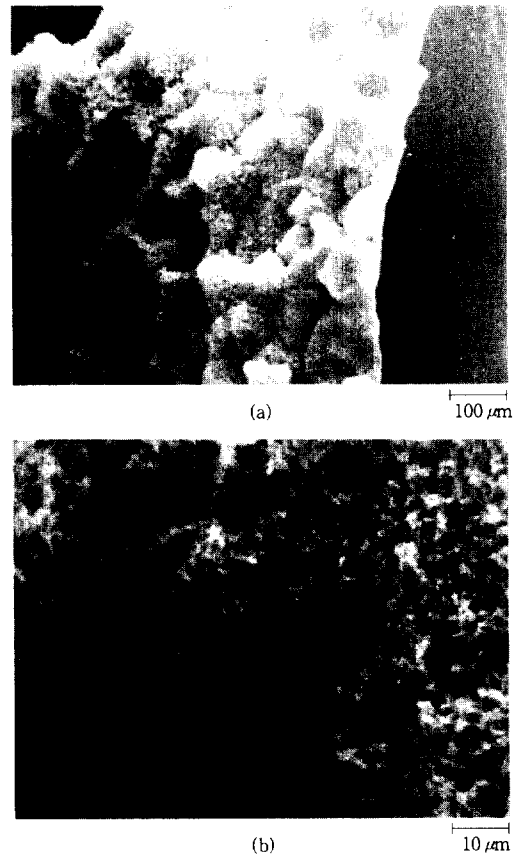

(a)　　　　100 μm

(b)　　　　10 μm

Figure 8. Scanning electron micrographs for 2.5 wt% i-PP solution in C8 phthalate cooled to 0 ℃ at 200 ℃/min and held for 5 min at a low magnification (a) and at a high magnification (b).

in Fig. 8 (a) are observed indicating that spinodal decomposition occurred during cooling. It is clearly seen in the high magnification of Fig. 8 (b) 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 temperature-jump experiment in Fig. 6, suggesting that the spherulites were formed before the temperature reached 0 ℃ during DSC run.

The morphology of the C8 system cooled to 70 ℃ for 10 wt% i-PP concentration is repre

(a)

(b)

(c)

(d)

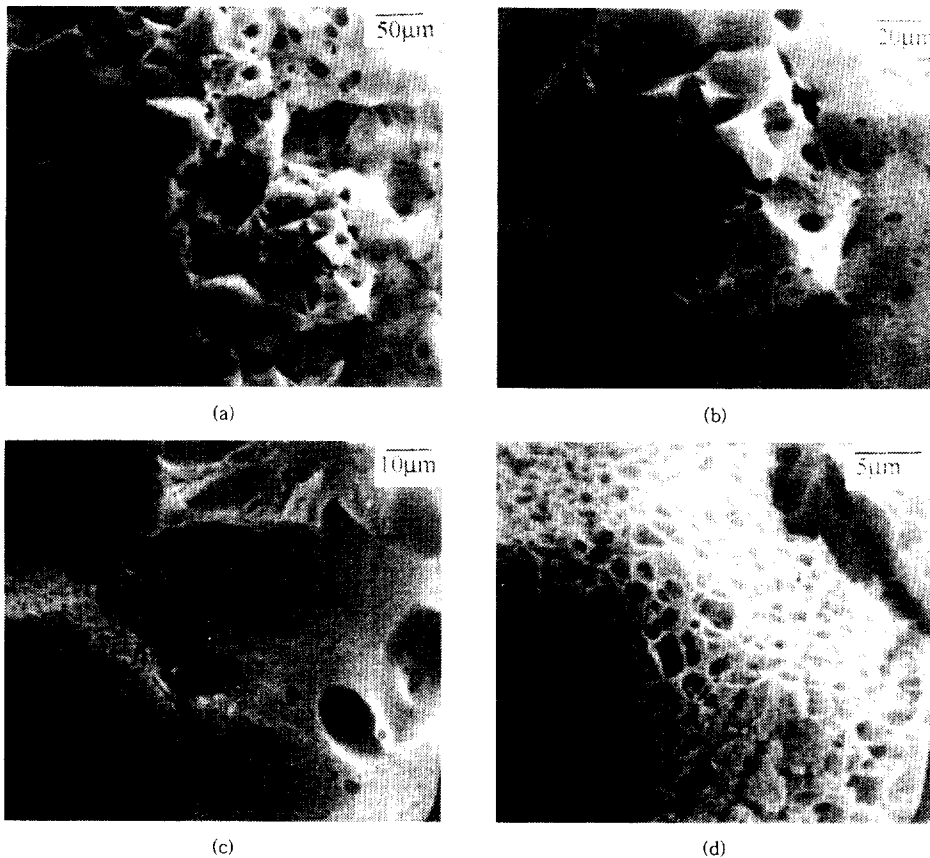Figure 9. Scanning electron micrographs for 10 wt% i-PP solution in C8 phthalate cooled to 70 ℃ at 200 ℃/min and held for 5 min. Magnification is increased in the sequence of (a), (b), (c), and (d).

sented in Fig. 9. The magnification of scanning electron micrographs was gradually increased in the sequence of (a), (b), (c), and (d) in Fig. 9 in order to show the overall feature of the structure formed. The peculiar perforated spherulitic 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 Fig. 9 (d) indicates that L-L phase separation occurred according to NG regime since the concentration of the specimen was in the off-critical region.

CONCLUSIONS

The structure formation by L-L phase separation coupled with crystallization in i-PP solutions was investigated by 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. An a-PP was used to probe L-L phase separation of a strongly in-

teracting system excluding interference by crystallization. When the interaction between poly-mer and solvent becomes more favorable, T_m decreases negligibly but $T_{L\text{-}L}$ does significantly. 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.

REFERENCES

1. R. E. Kesting, "Synthetic Polymeric Membranes: A Structural Perspective", 2nd ed., Wiley-Interscience, New York, 1985.
2. W. R. Burghardt, *Macromolecules*, **22**, 2482 (1989).
3. H. K. Lee, A. S. Myerson, and K. Levon, *Macromolecules*, **25**, 4002 (1992).
4. N. Inaba, K. Sato, S. Suzuki, and T. Hashimoto, *Macromolecules*, **19**, 1690 (1986).
5. N. Inaba, T. Yamada, S. Suzuki, and T. Hashimoto, *Macromolecules*, **21**, 407 (1988).
6. P. Schaaf, B. Lotz, and J. C. Wittman, *Polymer*, **28**, 193 (1987).
7. J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.*, **31**, 688 (1959).
8. J. W. Cahn and J. E. Hilliard, *J. Appl. Phys.*, **29**, 258 (1958).
9. Van Aarsten, *Eur. Polym. J.*, **6**, 919 (1970).
10. H. D. Keith and F. J. Jr. Padden, *J. Appl. Phys.*, **35**, 1270 (1964).
11. H. D. Keith and F. J. Jr. Padden, *J. Appl. Phys.*, **34**, 2409 (1963).
12. H. Tanaka and T. Nishi, *Phys. Rev. Lett.*, **55**(10), 1102 (1985).
13. H. Tanaka and T. Nishi, *Phys. Rev. A*, **39**(2), 783 (1989).
14. H. K. Lee, Ph. D. Dissertation, Polytechnic University, 1992.