

Relation between Liquid–Liquid Phase Separation and Crystallization in Isotactic and Syndiotactic Polypropylene Solutions

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ABSTRACT: The effects of the stereospecificity of a polymer chain and of the interaction in polypropylene (PP) solutions on the relation between liquid–liquid phase separation and crystallization were investigated by using an isotactic PP (i-PP) and a syndiotactic PP (s-PP) of high stereoregularity and of similar molar mass. Dialkyl phthalate was used as a solvent. A series of dialkyl phthalates with a different number of carbon atoms in the alkyl chain was employed to control the interaction between polymer and solvent. Phase transition temperatures were measured by optical microscopy with a hot stage. Liquid–liquid phase separation temperature (T_{L-L}) in the system of i-PP and dihexyl phthalate was located below its melting temperature (T_m). However, T_{L-L} for the s-PP system in the same solvent was elevated much above its T_m due to a decreased T_m and increased T_{L-L} . The reduced solubility of s-PP is primarily attributed to enhanced hydrophobicity arising from alternate positioning of the methyl groups along the polymer chain. As the length of the alkyl chain in the phthalate increases, T_{L-L} decreases significantly and T_m decreases slightly, resulting in the value of T_{L-L} shifting below that of T_m for the solution of s-PP and dinonyl phthalate. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 159–163, 1998

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INTRODUCTION

Liquid–liquid (L–L) phase separation in crystallizable polymer solutions is important in the structure formation of polymeric materials and can be utilized to produce microporous membranes^{1–3} and low-density forms.⁴ To control the multiphase structures, one has to understand the equilibrium phase behavior and the kinetics of

nonequilibrium competition between L–L phase separation and crystallization of the polymer. While the degree of undercooling necessary to induce rapid liquid demixing is very small for polymer solutions,⁵ the temperature to obtain a reasonable rate of crystallization is much lower than the equilibrium melting point due to the high nucleation barrier to polymer crystallization. Consequently, liquid demixing can precede crystallization and influence the resulting morphology significantly where the L–L phase separation temperature curve is located below the melting point depression curve in a temperature–concentration diagram.⁶ The relation between liquid de-

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mixing and crystallization can be changed systematically by controlling the thermodynamic condition through selection of a proper solvent under the same thermal condition because the binodal curve is remarkably influenced by the polymer–solvent interaction, but the crystalline–liquid phase boundary remains more or less constant.⁶

In this work we are concerned with the relation between L–L phase separation and crystallization in isotactic and syndiotactic polypropylene (i-PP and s-PP) solutions. Because the tacticity of PP influences crystallographic packing⁷ and θ temperature,⁸ the phase behavior of a PP solution in a given solvent is expected to be dependent on the stereospecificity of the polymer. The structure formation under a given thermal condition should be governed by the extents of liquid demixing and crystallization.

In this article we report the effects of different stereospecificities of a polymer chain and of the interaction in PP solutions on the coupled phase transitions. An i-PP and s-PP of high stereoregularity and of similar molar mass were used with dialkyl phthalate as the solvent. The variation of the number of carbon atoms in the alkyl substituent of phthalate was employed to systematically control the interaction between the polymer and solvent.

EXPERIMENTAL

Materials

The i-PP used was highly crystalline (M_w of 1.2×10^5 and M_w/M_n of 2.5) and was supplied by Himont R&D Center (Wilmington, DE). The s-PP (M_w of 1.5×10^5 and M_w/M_n of 2.3) was kindly supplied from Mitsui Toatsu Chemical Ltd. (Osaka, Japan). The syndiotacticity was evaluated to be greater than 92% racemic pentad configuration by ¹³C-NMR.

The solvents used were a series of 1,2-dialkyl phthalates with different numbers of carbon atoms in the alkyl chains, designated as C6 (hexyl), C7 (heptyl), C8 (2-ethylhexyl), C9 (nonyl), and C10 (decyl). C6 and C10 were purchased from Pfaltz & Bauer (Waterbury, CT), and C7–C9 were from Aldrich Chemical Co. (Milwaukee, WI). All the solvents were used as received without further purification.

Sample Preparation

Each of the dried thin films (20–40 μm) of i-PP and s-PP was prepared according to the following procedure: the polymer powder was dissolved in hot decalin containing 2,6-di-*tert*-butyl-4-methylphenol (0.5 wt % on the polymer) under nitrogen to form about 0.5 wt % solution. The temperature was close to the boiling point of decalin; the solution was held under reflux for 30 min after dissolution. The hot solution was quenched by pouring it into an aluminum tray in an ice-water bath. The bulk of the solvent was allowed to evaporate in a current of air under ambient conditions, and a transparent film was obtained. The residual solvent was removed by extraction with methanol, and the films were dried in a vacuum. Mixtures of polymer film and dialkyl phthalate were carefully weighed to obtain a known concentration on concavity microslides. A cover glass was placed over the sample.

Phase Transition Temperature Determination

Phase transition temperatures were measured by optical microscopy (American Optical 120) with a Mettler hot stage (FP82) and controller (FP80) under a nitrogen purge. The samples were slowly heated to 10°C above the higher value of either the melting point (T_m) or the L–L phase separation temperature (T_{L-L}). The heating was continued for 5–10 min to ensure a homogeneous state. The value of T_{L-L} obtained by phase-contrast microscopy was assigned to the temperature at which fine droplet structures started to appear during cooling at a rate of 10°C/min. The crystallization temperature (T_{cry}) observed by polarized light microscopy was considered as being the point at which a birefringent entity started to appear on cooling at the same rate. The value of T_m by polarized light microscopy was the temperature at which the last traces of crystallinity disappeared between crossed polarizers on the reheating cycle at a rate of 10°C/min. Evaporation of solvents was checked by weighing the samples after running and was found to be negligible in the experimental conditions.

RESULTS AND DISCUSSION

Figure 1 contains the experimental phase diagrams for i-PP and s-PP solutions in the same solvent of C6 phthalate showing L–L phase sepa-

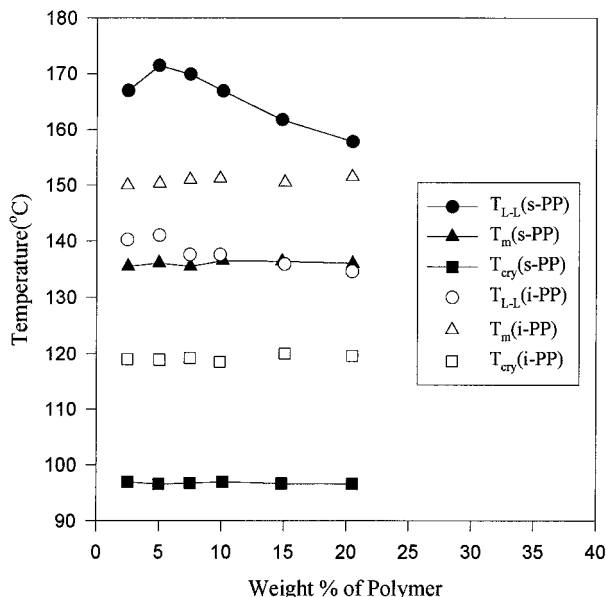


Figure 1 L-L phase separation, melting, and crystallization temperatures as a function of polymer concentration for i-PP and s-PP solutions in C6 phthalate.

ration, melting, and crystallization as a function of polymer concentration. The observed transitions are by no means the equilibrium transitions because nonequilibrium phenomena may be involved under the thermal conditions applied. The effects of cooling and heating rates on the coupled phase transitions in the system of i-PP and dialkyl phthalate were reported in the previous study.⁶ Melting and crystallization temperatures of s-PP solutions are lower than those of i-PP solutions in Figure 1, which is expected from the melting temperature of the pure i-PP and s-PP.⁹ On the other hand L-L phase separation temperatures of s-PP solutions are interestingly higher than those of their isotactic counterparts, even higher than 161°C, the literature value of the equilibrium melting temperature for highly s-PP,¹⁰ when the polymer concentration is lower than 15 wt %. Consequently, liquid demixing of s-PP solution occurs above its melting temperature but that of the i-PP solution occurs below its melting temperature. The results should be attributed to the difference in polymer-solvent interaction related to the stereospecificity of the polymer chain because both polymers used are in a similar range of molecular mass and polydispersity. To take this point into account, the effect of the stereospecificity of the polymer on the solubility relevant to this work is briefly reviewed.

There are several reports on the solubility dif-

ference between atactic and isotactic configurations of poly(α -olefins). i-PP has a ca. 4–8°C lower θ temperature than atactic polypropylene (a-PP) in a given solvent.^{11,12} However, when the size of R in the chain of $-(CH_2-CHR)_n-$ is increased, such as in the cases of poly(1-butene),¹³ poly(1-pentene),¹⁴ and polystyrene,^{15,16} the atactic configuration has better solubility than the isotactic counterpart. The different results with the size of the substituent may be interpreted as that, with the bulky side group, the isotactic polymer molecule has a bigger hydrodynamic volume in a given solvent at the same temperature compared to atactic polymer. In the case of PP, the isotactic configuration favors the helical conformation of tg in solutions¹⁷ and in the amorphous state,¹⁸ resulting in a slightly contracted form compared to that of a-PP.⁸ Here t denotes the trans form and g the gauche form. Upon increasing the molecular volume of the substituent R, the isotactic configuration would tend to bring the chain to a more extended form due to steric hindrances. The effects of the syndiotactic stereoregularity on L-L phase separation were studied for a few systems. The θ temperature of PP in isoamyl acetate was found to increase proportionately with its syndiotacticity, showing 34°C for an a-PP and ca. 70°C for a highly s-PP.⁸ The syndiotacticity of polystyrene in *trans*-decalin seems to play a role in elevating the L-L phase transition temperature because precipitate formation in syndiotactic polystyrene solutions occurs 40–50°C above the binodal temperature of atactic polystyrene solutions, although the origin of gel formation is debatable.¹⁹ In syndiotactic polystyrene and *trans*-decalin L-L phase transition may be difficult to observe properly due to competing rapid crystallization.

The elevation of the θ temperature of s-PP in isoamyl acetate with increasing syndiotacticity may explain clearly why L-L phase separation temperatures in s-PP solutions are higher than those in i-PP solutions. The results can be partly related to the molecular conformation in solution, but this effect should be negligible. The s-PP chains are stabilized with the ttgg conformation in solutions²⁰ and in the amorphous state,¹⁸ leading to dimensions greater than i-PP chains but smaller than a-PP chains.⁸ The primary contribution to the reduced solubility of s-PP in phthalate may be due to the difference in polar interactions arising from alternate positioning of methyl groups. While PP is considered to be slightly polar compared to polyethylene, alternate positioning

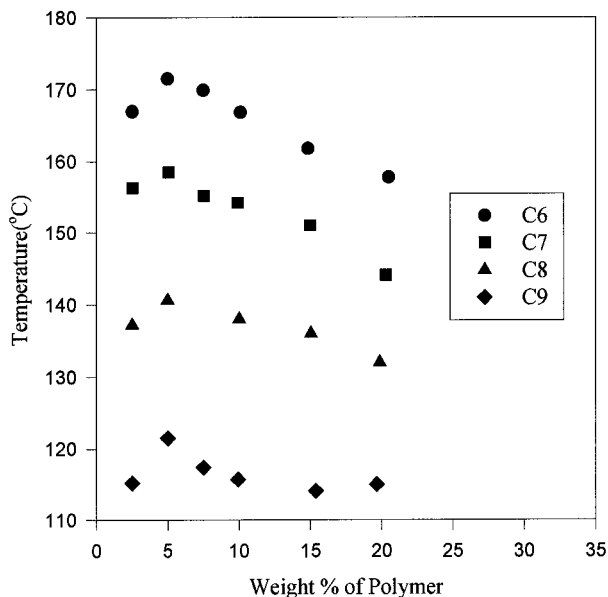


Figure 2 L–L phase separation temperatures as a function of polymer concentration for s-PP solutions in a series of dialkyl phthalates (C6, C7, C8, and C9).

of methyl groups in s-PP would give rise to more evenly distributed electron density donated from methyl groups along the skeletal C–C bonds than in i-PP.

As the interaction between polymer and solvent becomes more favorable, L–L phase transition temperatures of s-PP solutions decrease systematically as shown in Figure 2. As expected, melting and crystallization temperatures decreased slightly with increasing solvent power. When the alkyl group in the phthalate is changed from hexyl to nonyl, the melting temperature of the s-PP solution for 5 wt % polymer concentration dropped from 136 to 130°C (Fig. 3) and the crystallization temperature dropped from 97 to 92°C. The liquid demixing temperature of the s-PP/C9 system above 10 wt % polymer concentration is higher than expected, suggesting that interplay of crystallization and L–L phase separation occurred. When the temperature is below the melting point of the s-PP in solution on cooling, nuclei may be formed and induce local phase separation. This phenomenon should be discriminated from crystallization because the absence of birefringence under crossed polarizers confirmed that no crystallites were present in the demixed solution. Similar results were reported for i-PP solutions⁶ and polyethylene solutions.²¹ In the system of s-PP and C10 phthalate, L–L phase transition temperature could not be determined precisely be-

cause liquid demixing and crystallization occurred competitively on cooling at a rate of 10°C/min. In i-PP systems liquid demixing started to couple with crystallization in C7 phthalate.

The effects of the stereospecificity of PP and solvent quality for 5 wt % polymer concentration on the relation of melting points and L–L phase transition temperatures are summarized in Figure 3. In the solution of i-PP and C6 phthalate the L–L phase separation temperature is located 9°C below the melting point. When the stereospecificity of PP is changed to syndiotacticity in the same solvent system, the L–L phase separation temperature rises 35°C above its melting point due to a reduced melting point and elevated liquid demixing temperature. As the number of carbon atoms in the alkyl chain of phthalate increases, the L–L phase separation temperature decreases significantly but the melting temperature decreases slightly. When C9 phthalate is used as a solvent, the L–L phase separation temperature of the s-PP solution shifts again below the melting temperature due to the enhanced favorable interaction.

CONCLUSIONS

The relation between L–L phase separation and crystalline–liquid transition in i-PP and s-PP so-

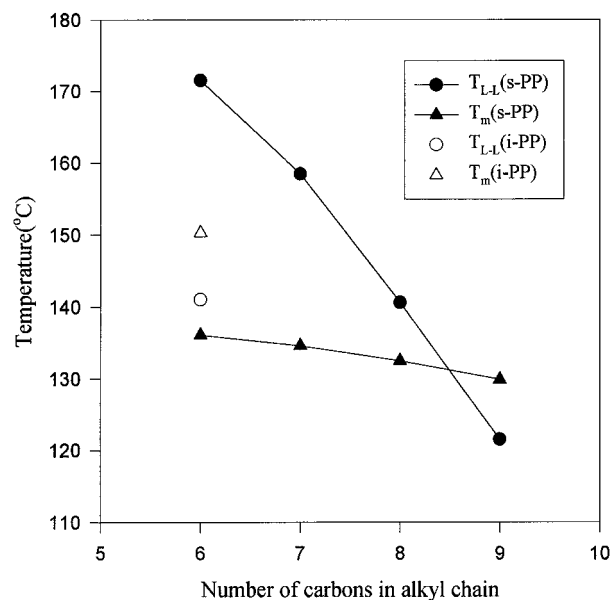


Figure 3 L–L phase separation and melting temperatures of i-PP and s-PP solutions for 5 wt % polymer concentration as a function of solvent quality (number of carbons in the alkyl chain of phthalate).

lutions was investigated with a series of dialkyl phthalates. The value of T_{L-L} in the system of i-PP and dihexyl phthalate was located below its T_m but the value in the s-PP system in the same solvent elevated much above its T_m due to a decreased T_m and increased T_{L-L} . The reduced solubility of s-PP was primarily attributed to enhanced hydrophobicity arising from alternate positioning of methyl groups along the polymer chain. As the length of the alkyl chain in phthalate increased, T_{L-L} decreased significantly and T_m decreased slightly, resulting in the value of T_{L-L} shifting below that of T_m for the solution of s-PP and dinonyl phthalate.

Dependence of the relation between L-L phase separation and melting transition on stereospecificity may provide an opportunity to control the morphology of polymer solutions when used in combination with the selection of solvent and application of various thermal conditions of quench depth and cooling rate.

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