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 membranes1–3 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-
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 tactility 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 \(\times 10^5\) 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 \(\times 10^5\) 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 \(^{13}\)C-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 \(\mu\)m) 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-\(\text{tert}\)-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 a birefringent entity started to appear on reheating cycle (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 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-
L±L PHASE SEPARATION AND CRYSTALLIZATION IN i-PP AND s-PP

The difference 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. However, when the size of R in the chain of —(CH₂—CHR)ₙ— is increased, such as in the cases of poly(1-butene), poly(1-pentene), and polystyrene, 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 solutions and in the amorphous state, resulting in a slightly contracted form compared to that of a-PP. 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. 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. 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 solutions and in the amorphous state, leading to dimensions greater than i-PP chains but smaller than a-PP chains. 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
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-
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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