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Phase behavior, nucleation and optical properties of the binary system isotactic polypropylene/*N*,*N*′,*N*″-tris-isopentyl-1,3,5-benzene-tricarboxamide

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Abstract

The phase behavior of the binary system consisting of isotactic polypropylene (*i*-PP) and *N*,*N*′,*N*″-tris-isopentyl-1,3,5-benzene-tricarboxamide (**1**)—a selected member of a class of novel, versatile 'designer' nucleating/clarifying agents—was investigated over the entire additive concentration range by means of differential scanning calorimetry (DSC) and optical microscopy. Experimental phase diagrams were constructed from data obtained in melting and crystallization studies, and a simple monotectic is advanced, very similar to the previously studied binary system *i*-PP/1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS). In contrast to the latter, the crystallization temperature in the present system *i*-PP/**1** was found to increase to ~120 °C already at the lowest additive concentration employed and remained constant at further increasing additive concentration. Liquid–liquid phase separation was observed at elevated temperatures for *i*-PP/**1** mixtures comprising more than ~2 wt% of **1**. A study on the optical properties of the *i*-PP/**1** system revealed that the values for haze and clarity of injection-molded plaques progressively decreased and increased, respectively, in the concentration range up to 0.15 wt%. An intermediate region of fairly concentration-independent optical properties was found between 0.15 and 1 wt%, followed by a rapid increase in haze at concentrations exceeding 2 wt%.

Keywords: Isotactic polypropylene; Clarifying agent; Phase behavior

1. Introduction

It is well known that relatively small quantities ($\phi \sim 0.20$ wt%) of certain sorbitol-based species may dramatically enhance nucleation of isotactic polypropylene (*i*-PP) and improve its optical characteristics, i.e. highly reduce haze and increase clarity (hence the often employed denotation 'clarifiers') [1,2]. Consequently, these additives have found widespread industrial use, most notably for packaging applications, and also have received considerable scientific interest. In addition to investigations of their ability to nucleate the common α-polymorph of *i*-PP [3–5], rheological studies on the formation of nanofibrillar networks by these compounds both in polymer melts [6] and organic solvents [7] and their visualization by means of transmission electron microscopy [8] have been carried out. Also, processing-related phenomena occurring in these systems have been investigated by various authors [9,10]. In a previous paper [11], we advanced a monotectic phase behavior for the *i*-PP/1,3:2,4-bis-(3,4-dimethyl benzylidene) sorbitol (DMDBS) binary system, with which the pronounced concentration dependence of the nucleating and clarifying effects of this class of additives could be rationalized and readily understood.

Aiming at a similar combination of structural features and properties as the above referred sorbitols, but attempting to avoid their drawbacks such as limited applicability and relatively poor thermal stability [12], a library of trisamides was synthesized and their potential use as nucleating/clarifying agents was investigated [13,14]. A significant number of these species were found to be remarkably

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efficient nucleators for *i*-PP, both of the common α- and the mechanically tough β-polymorph, and capable of dramatically reducing haze of the polymer—as a matter of fact, some at substantially lower concentrations than in the case of sorbitol-based clarifiers. In this paper, in analogy to our previous work on DMDBS [11], the phase behavior is presented of *i*-PP with one selected compound, i.e. *N*,*N*′,*N*″-tris-isopentyl-1,3,5-benzene-tricarboxamide, **1** (Fig. 1). Although certainly not the most efficient α-nucleator/clarifier [14], this species was chosen as a model compound, because, unlike most other members of the benzene trisamide family, its thermal properties (for instance a melting temperature of 263 °C) permitted exploration of the entire temperature/composition space, without concerns about significant degradation of the polymer.

2. Experimental

2.1. Materials

The *i*-PP grade used was Pro-fax PH350 (Montell), which contained a stabilizing additive package of 0.10 wt% Irgafos 168, 0.05 wt% Irganox 1010 and 0.10 wt% calcium stearate (N.B. the presence of these additives renders the present system pseudo-binary). The synthesis of nucleating agent **1** is described elsewhere [13].

2.2. Sample preparation

Various dry-blended mixtures of *i*-PP and **1** with contents ranging from 0.1 to 5 wt% of the additive were compounded in a laboratory, co-rotating mini-twin-screw extruder (Technical University Eindhoven, The Netherlands) at 240 °C under a nitrogen blanket during 5 min, after which the mixtures were discharged. Films for optical microscopy studies were prepared by compression molding a granule of mixed material between two glass slides at 240 °C and subsequent quenching to room temperature. Samples of higher additive concentrations ($\phi > 10$ wt%) were prepared by compression molding powdered mixtures between two glass slides and heating at 280 °C for 3 min.

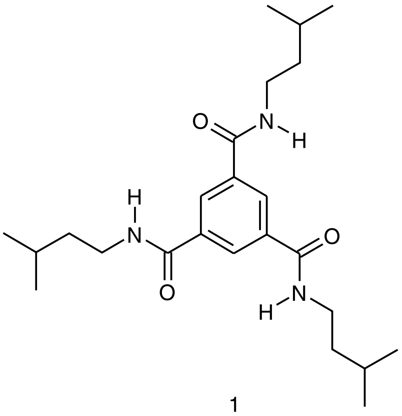

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Fig. 1. Chemical structure of the *i*-PP nucleating/clarifying agent *N*,*N*′,*N*″-tris-isopentyl-1,3,5-benzene-tricarboxamide, **1**.

2.3. Injection molding

Samples for optical characterization were prepared by melting previously compounded mixtures for 5 min at 260 °C under a nitrogen blanket and subsequent injection molding (mold at room temperature) using a micro-injector (DACA Instruments, CA, USA), yielding circular plaques of 1.1 mm thickness and 25 mm diameter.

2.4. Optical properties

The optical characteristics haze and clarity were determined according to ASTM standard D1003 [15] with a Haze-Gard Plus instrument (BYK Gardner GmbH, Germany).

2.5. Thermal analysis

Thermal analysis was conducted with a Netzsch differential scanning calorimeter (DSC, Model 200) with samples of 5–10 mg at a standard heating or cooling rate of 10 °C/min under nitrogen. Prior to recording cooling thermograms, the samples were held at 280 °C for 3 min to ensure complete melting of **1**. Crystallization and melting temperatures reported herein refer to peak temperatures in the corresponding DSC thermograms.

2.6. Optical microscopy

Optical microscopic studies were carried out with a Leica DMRX instrument equipped with a hot-stage (Mettler, model FP82TM). Cooling and heating rates used in dynamic experiments were 5 °C/min.

3. Results and discussion

Temperature/composition diagrams of the (pseudo-) binary system *i*-PP/*N*,*N*′,*N*″-tris-isopentyl-1,3,5-benzene-tricarboxamide, **1**, were constructed from data obtained by thermal analysis and optical microscopy. The resulting non-equilibrium phase diagrams are presented in Fig. 2 for both cooling and heating. Similar to the system *i*-PP/DMDBS [11], owing to the partial polar nature of the benzene trisamides, a broad regime of liquid–liquid phase separation was observed, ranging from about $\phi = 2$ wt% up to virtually the axis of **1**. For the sample containing 2.09 wt% **1** a clearing point, above which the liquid–liquid phase-separated mixture formed a homogeneous fluid, was detected at $T_{\text{clear}} = 284$ °C.

At compositions comprising less than 2 wt% of the additive, a pronounced concentration dependence of the

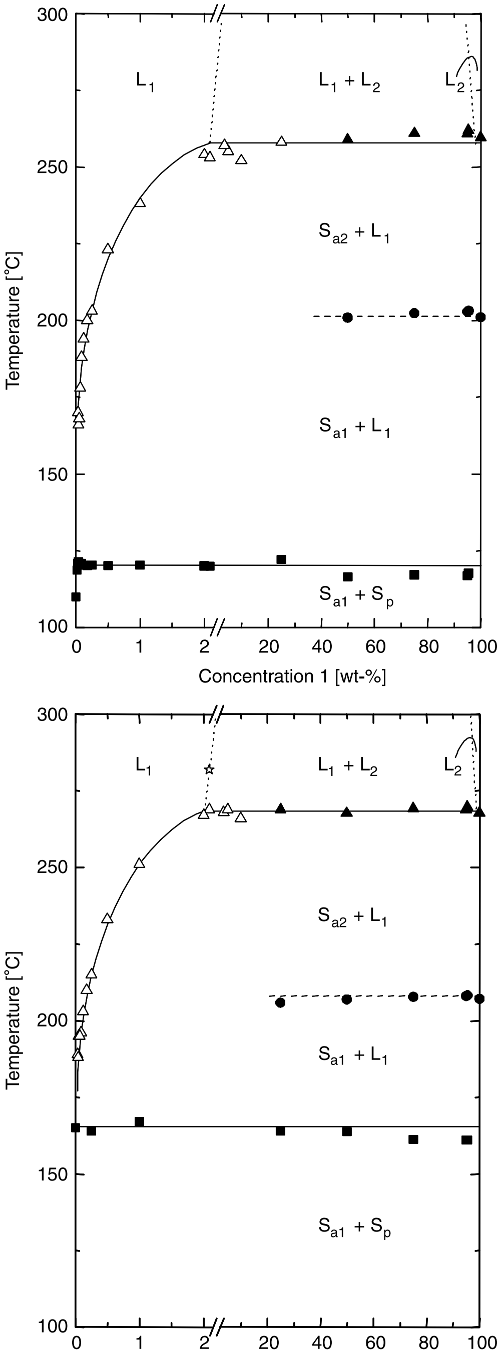

Fig. 2. Temperature/composition diagrams for the (pseudo-)binary system *i*-PP/**1** obtained in cooling (top) and heating (bottom) experiments. Symbols refer to data for different transitions: crystallization and dissolution/melting (△, ▲) and solid-state transition of **1** (●), crystallization or melting of the polymer and eutectic (■) and clearing point (☆), respectively. Open symbols denote experimental data obtained from optical microscopy and solid symbols refer data obtained by thermal analysis. The denotation L refers to liquid and S to solid; subscripts 'a1' and 'a2' refer to the two solid-state structures of additive **1**, and 'p' to *i*-PP.

dissolution and crystallization temperatures of **1** was found. The crystallization temperature of *i*-PP sharply increased to 119 °C, already for mixtures of the lowest additive concentration prepared ($\phi=0.02$ wt%), and remained constant at an average level of ~120 °C for $\phi \geq 0.04$ wt%. The lower liquidus and solidus in the present monotectic phase diagram were observed to terminate close to the *i*-PP axis. Concomitantly, and in contrast to the monotectic *i*-PP/DMDBS system, no composition region of reduced nucleation efficiency was found down to concentrations as low as 0.02 wt% of **1**, whereas DMDBS ceases to function as a nucleating/clarifying agent below approximately 0.1 wt% [11,16], and was claimed to be maximally effective at 0.25 wt% and more [17].

Values of haze, a measure of the turbidity of a sample, and clarity, reflecting the sharpness of an object placed behind it [18], of injection-molded *i*-PP/**1** mixtures were investigated in the most relevant additive concentration range between 0 and 5 wt%, and are presented as a function of additive content in Fig. 3. Already at very low concentrations of **1** ($\phi \leq 0.20$ wt%), haze was found to sharply decrease, accompanied by a dramatic increase in clarity. An intermediate region of fairly concentration-independent optical properties (haze ~27%, clarity 98%) was found between 0.15 and 1 wt%, followed by a rapid increase in haze and a reduction of the clarity at concentrations exceeding about 2 wt%, indeed where liquid–liquid phase separation was observed in the molten state. For comparison, in our hands, in the additive composition range from 0.25–1 wt%, injection-molded *i*-PP/DMDBS plaques displayed values of haze of about

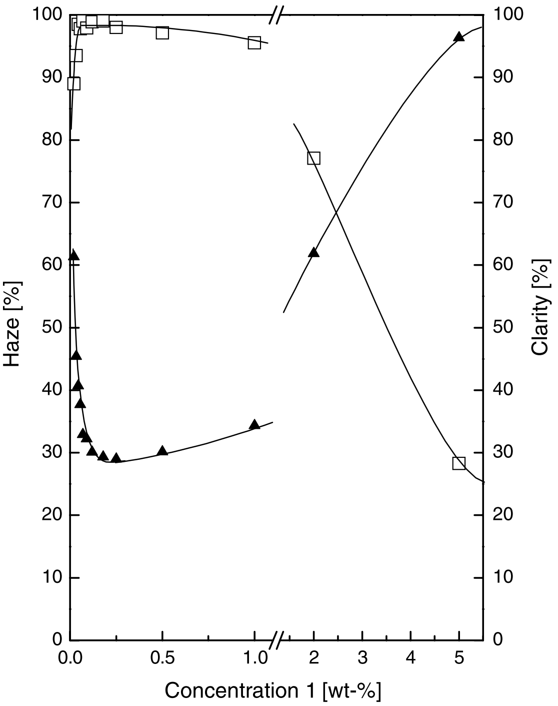

Fig. 3. Dependence of haze (▲) and clarity (□) on additive concentration for injection-molded *i*-PP/**1** plaques of 1.1 mm thickness.

35–17%, while below 0.20 wt%, values in excess of 40% were recorded [11].

The liquid–liquid miscibility gap observed in the present system is illustrated in Fig. 4 (top) for a mixture containing 25 wt% of **1**. Upon cooling, such concentrated mixtures formed distinct composite morphologies. An example is shown in Fig. 4 (bottom) for a mixture containing 50 wt% of **1**. Crystallization of **1** commenced in the additive-rich domains, ultimately resulting in coarsened fibrous structures (upper left) surrounded by the *i*-PP-rich phase (lower right). The latter morphological characteristics expectedly, and similar to those found for the system *i*-PP/DMDBS [11], significantly compromised the optical properties.

In Fig. 5, finally, are presented optical micrographs of an *i*-PP/**1** sample produced with the 'diffusion-screening' method presented elsewhere [14]. About 0.1 mg of the additive powder was positioned in the center of a compression-molded *i*-PP film (thickness ∼100 μm), and a glass cover slip was placed on top. Subsequently, the assembly was placed onto a hot stage at a temperature of 220 °C, and left for a few minutes, after which the samples was removed and left to cool to room temperature. In the heating phase, **1** radially diffused into the molten polymer, yielding a 'radial' composition diagram, which—after cooling—featured a distinct clear ring at some distance from the position where the additive was originally placed. The relatively large width of the clear ring is, of course, consistent with the large concentration range in which the present clarifying agent was found to be effective. For illustrative purposes, a schematic of the monotectic phase

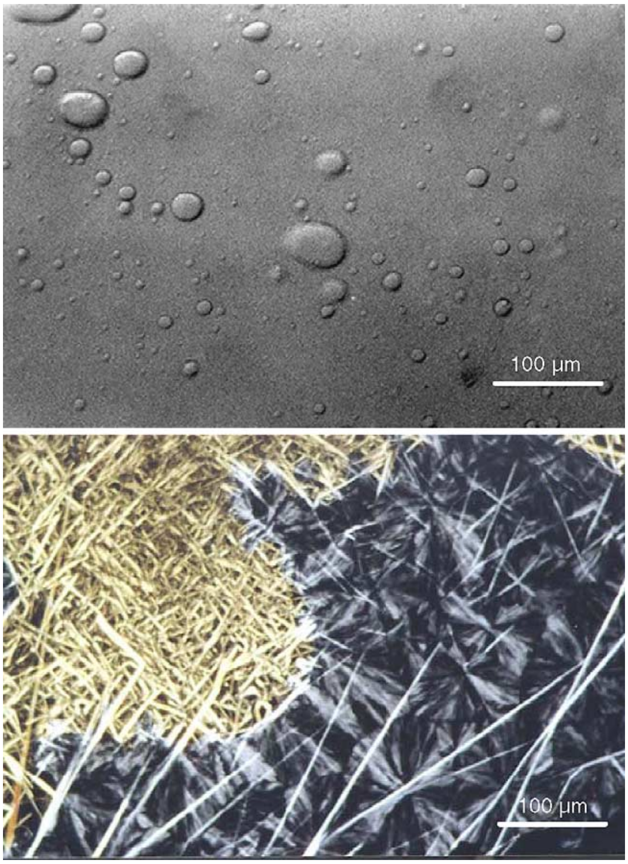

Fig. 4. Top: optical micrograph displaying liquid–liquid phase separation at 270 °C in a mixture containing 25 wt% of **1** in *i*-PP. Bottom: photomicrograph, taken between crossed polarizers at 80 °C, of the solid-phase structure of a 50/50 *i*-PP/**1** wt%-mixture. The structures in the upper left corner crystallized from a droplet rich in **1**.

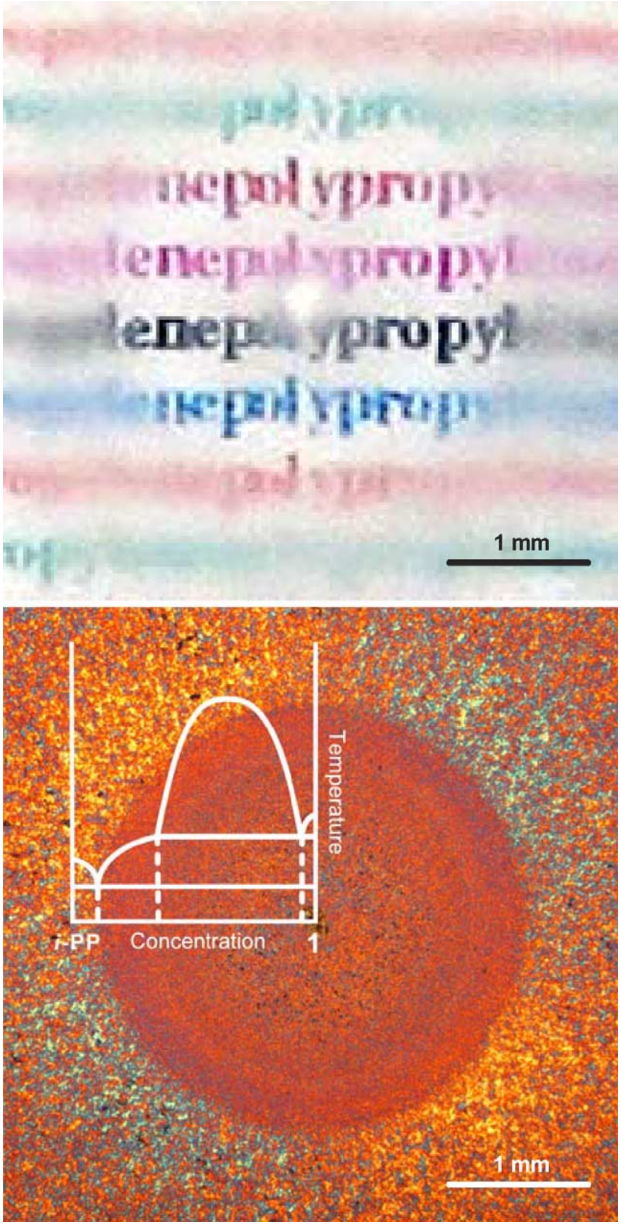

Fig. 5. Top: optical micrograph, taken in reflected light, of a sample produced with a 'diffusion–screening' method by placing powder of **1** in the center of a compression-molded film of *i*-PP and allowing the additive to radially diffuse at 220 °C, after which the sample was cooled down to room temperature. The clear ring is indicative of the clarifying ability of compound **1**. Bottom: corresponding optical micrograph taken in transmittance with crossed polarizers and a $\lambda/4$ plate. A schematic of the *i*-PP/**1** monotectic phase diagram is drawn onto the micrograph to approximate the different characteristic optical regimes and the corresponding composition ranges.

diagram is drawn onto the micrograph (taken in transmission (Fig. 5, bottom)), such as to indicate the different composition ranges and the associated optical features of the *i*-PP/**1** mixtures.

4. Conclusions

In conclusion, monotectic phase behavior was demonstrated for the novel nucleating and clarifying agent N,N',N''-tris-isopentyl-1,3,5-benzene-tricarboxamide with *i*-PP, similar to that previously reported for DMDBS [11]. Clearly, the liquid–liquid phase separation that typifies both pseudo-binaries is extremely beneficial, because it efficiently positions the eutectic composition close to the polymer axis, causing already at low concentrations the additive to first crystallize, and therewith provide the active solid surface suitable for nucleation of the polymer.

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