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Polymer 44 (2003) 5885–5891
polymer
www.elsevier.com/locate/polymer

Synergistic gelation of solutions of isotactic polypropylene and bis-(3,4-dimethyl benzylidene) sorbitol and its use in gel-processing

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Received 28 February 2003; accepted 9 May 2003

Dedicated to Prof. Ian M. Ward on the occasion of his 75th birthday

Abstract

We report the synergistic, rapid gelation of solutions of isotactic polypropylene (*i*-PP) and the nucleating agent 1,3:2,4-bis-(3,4-dimethyl benzylidene) sorbitol (DMDBS) in decalin. Cooling to room temperature of a solution comprising, for instance, 3.0 wt% of a moderately high molecular weight *i*-PP ($M_v = 1.3 \times 10^6$ g/mol) and as little as 0.0075 wt% DMDBS (0.25 wt% based on the polymer) resulted in the fast formation of highly ductile gels. In reference experiments without DMDBS, often 'mud-cracked', brittle polymer films were obtained, and decaline solutions of DMDBS alone at the above concentration did not form macroscopically coherent gels. In the present work we employed this useful occurrence for gel-processing/drawing of *i*-PP, yielding material with Young's moduli of 35 GPa, tensile strengths of approximately 1 GPa and melting temperatures measured for constrained samples as high as 228 °C.

Keywords: Isotactic polypropylene; Sorbitol derivatives; Nucleating agent

1. Introduction

The production of high-modulus polyethylene through tensile drawing of melt-processed fibers and films was pioneered by Ian Ward and his co-workers, in the high-performance-polymers community collectively often referred to as 'the Leeds Group' [1–3]. Although considerable research was being carried out in the 1960s, among many others, by Peterlin and co-workers [4,5], on the mechanisms involved in deformation of polyethylenes, it was not until Ward and Capaccio reported their breakthrough in 1973 [1] that the field of generating high-performance materials from flexible chain polymers seriously progressed. In the following period a variety of different techniques were employed by a number of research groups to produce highly oriented polyethylene structures with mechanical properties that eventually would approach their theoretical limits. Among them are solid-state extrusion [6,7], flow-induced crystallization and a related technique referred to as surface growth [8,9] and solution-spinning/drawing of ultra-high molecular weight (UHMW) polyethylene [10,11]. Owing to the very long length of the latter polymer chains, extravagantly high draw ratios (well in excess of 100) and concomitant exceptional degrees of uniaxial orientation and outstanding mechanical properties can be obtained with this material, provided that the macromolecules are sufficiently freed from entanglements prior to deformation, for instance through crystallization from (semi-dilute) solution. Fibers spun from such solutions are cooled down to form gel-filaments in which the low entanglement density present in the solution is consolidated and remains also after removal of the solvent. The (erroneously) so-called 'gel-spun' fibers are subsequently drawn at elevated temperatures to draw ratios of 50 and more, yielding high-performance polyethylene fibers, which are commercially produced at speeds of hundreds of m/min with a Young's modulus of around 120 GPa and tensile strength of about 4 GPa [12].

It has long been recognized that another polymer of potential interest for application in high-performance fibers is isotactic polypropylene (*i*-PP). Although the theoretical, ultimate stiffness and strength of this polymer, due to a helical conformation in its crystalline form, are

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0032-3861/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00538-X

considerably lower than the corresponding values for polyethylene [13], the significantly higher melting temperature of the material—especially when constrained [14]—would provide distinct advantages over polyethylene. Taking advantage of the latter property, oriented polypropylene fibers have been shown to be highly useful in desirable all-*i*-PP, fully recyclable composites [15]. These 'self-reinforced' materials now comprise melt-spun/drawn fibers of relatively low molecular weight and are of associated modest mechanical characteristics [15]. Naturally, it would appear beneficial to produce fibers of UHMW *i*-PP, for instance through the above-referred 'gel-spinning' process. Remarkably few efforts have been directed towards this goal [16–19]. Careful reading of the published literature appears to indicate that the process of gelation/crystallization of *i*-PP under common conditions is impractically slow, which prevents fiber production on an industrial scale. For instance, Peguy and Manley [16] describe the formation of gel-films by quenching hot solutions of *i*-PP in decalin to −25 °C and leaving the material for several hours. Ohta et al. [18] advanced the method of pressing 'gel-like spherulites', which were prepared at a cooling rate as low as 1.5 °C/min. Finally, Kavesh and Prevorsek report to have produced gel-fibers of *i*-PP by extruding 8 wt% solutions of the polymer in paraffin oil and extracting the latter with trichlorotrifluoroethane at the low speed of about 6 m/min [19].

In order to address the above problem of slow gelation/crystallization of *i*-PP, we explored the potential advantage of adding the nucleating agent 1,3:2,4-bis(3,4-dimethyl-dibenzylidene) sorbitol (DMDBS, Millad 3988) to the polymer solutions. Sorbitol derivatives like DMDBS are known not only to efficiently nucleate the common α-crystalline form of this polymer [20–22], but also to gel a variety of organic liquids, including, among others, tetrahydrofuran, benzene, chlorinated solvents, cyclohexane, *o*-nitrophenyloctyl ether and propylene carbonate, as well as silicone fluids ([22–25] and references therein). Here we report the results of that study, in which we found a highly useful synergistic gelation behavior of the polymer/additive pair in solutions in decalin.

2. Experimental

2.1. Materials

A modestly high molecular weight *i*-PP was employed in this work. The viscosity-average molecular weight, measured in tetralin at 135 °C, of the polymer was $M_v = 1.3 \times 10^6$ g/mol and its limiting viscosity number 6.1 dl/g. The nucleating agent 1,3:2,4-bis-(3,4-dimethyl benzylidene) sorbitol (DMDBS, Millad 3988, Milliken Chemical, Belgium), the antioxidant tetra-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate] (Irganox 1010, Ciba Specialty Chemicals, Switzerland) and the solvent decalin (decahydronaphthalene, *cis*/*trans* isomeric mixture, Fluka) were used as received.

2.2. Sample preparation

2.2.1. DMDBS/decalin

Various amounts of DMDBS ranging from 0.01 to 1 wt% (with respect to the solvent) were dissolved in 20 ml of decalin at a temperature between 150 and 185 °C. For concentrations exceeding 0.4 wt% the dissolution temperature needed to be increased to values near the boiling point of the solvent to achieve complete dissolution. Subsequently, the homogeneous solutions obtained were allowed to cool down to room temperature.

2.2.2. i-PP/(DMDBS)/decalin

Solutions with concentrations of 0.3–5.0 wt% *i*-PP alone and with additional DMDBS contents ranging from 0 to 0.1 wt% were prepared in decalin. To prevent degradation of the polymer, the solutions were stabilized with 0.5 wt% antioxidant, based on the polymer. Mixtures comprising the solvent, polymer and additives were flushed several times with nitrogen and degassed for 30–45 min under vacuum. Subsequently, the suspensions were heated to 160–175 °C under nitrogen and held for 30 min under stirring until the polymer and additives were completely dissolved. The clear, homogeneous solutions obtained were maintained for another 10 min at the same temperature, then poured into aluminium trays at room temperature and the solvent was evaporated under ambient conditions, yielding films of a typical thickness of about 0.2 mm. In separate experiments, filaments were directly drawn from the polymer solution.

2.2.3. Tensile deformation

Drawing was performed using rectangular specimens (20 mm long and 2 mm wide), where possible (see below) cut from dried gel-cast films with an Instron tensile-tester (model 4464) equipped with a hot-air oven at temperatures ranging from 90 to 160 °C, at a rate of elongation of 100 mm/min. The draw ratios (λ = final/initial length) were determined from the separation of ink marks placed 2 mm apart on the sample prior to drawing.

2.3. Characterization

2.3.1. Gel dissolution temperatures

Gel dissolution temperatures were determined with a 'ball-drop' test in which a small steel ball (2 mm diameter, 30 mg weight) was placed on top of a gel in an open glass test tube that was subsequently heated in an oil bath until the steel ball dropped through the dissolved gel to the bottom of the tube. The temperature at which the latter event occurred hereafter is referred to as the gel dissolution temperature.

2.3.2. Mechanical properties

Stress–strain curves were recorded at room temperature

using Instron tensile testers (models 4464 and 4411) on samples drawn to different draw ratios. The initial sample length was 100 mm and the cross-head speed 100 mm/min.

2.3.3. Thermal analysis

Differential scanning calorimetry (DSC, Perkin Elmer DSC-7 Instrument) was used to determine the melting temperatures of drawn samples both under unconstrained and constrained conditions. For determination of melting temperatures of material under constrained conditions specimens (100 mm length) were wound around a thin copper wire and this assembly was placed into a DSC sample pan. Melting temperatures reported for unconstrained material were determined on samples cut to a length of about 2–3 mm. The values quoted in this paper invariably refer to the peak melting temperatures in the DSC-thermograms, which were recorded at a rate of 10 °C/min and under nitrogen.

2.3.4. X-ray diffraction

Wide-angle X-ray diffraction (WAXD) patterns were recorded with a flat-film camera, using Ni-filtered Cu K_α radiation produced by a Seifert X-ray generator operating at 35 kV and 30 mA.

3. Results and discussion

3.1. Gelation

3.1.1. i-PP/decalin

Solutions of *i*-PP at concentrations of 0.3–5.0 wt%, but no DMDBS, were prepared as described in Section 2. Cooling of these solutions resulted in the formation of elastic gels in periods in excess of 1 h. Removal of the solvent from gels formed from solutions containing 3 wt% or less resulted in 'mud-cracked', brittle films that could not be directly drawn. Only gels produced with solutions containing 5 wt% of *i*-PP consistently yielded coherent, ductile films. The fact that no coherent gel films were formed from the more dilute polymer solutions is in contrast to observations reported by Peguy and Manley [16], which we attribute to the relatively modest molecular weight of the polymer used in this work (see below, It should be noted that when the mud-cracked films obtained from the more dilute gels were compacted at 130 °C at a pressure of approximately 100 MPa, also these materials could form coherent objects, similar to those previously obtained for certain virgin UHMW PE powders [26]).

3.1.2. DMDBS/decalin

Various amounts of DMDBS were dissolved in decalin in glass tubes at temperatures ranging from 150 °C to close to the boiling point of this solvent (189 °C). Subsequently, the homogeneous solutions were allowed to cool down to room temperature. Expectedly [22–25], rapid gel formation was observed upon cooling solutions containing DMDBS at concentrations of 0.1 wt% and more, hereafter referred to as 'concentrated DMDBS systems'. Upon re-heating, all these gels formed again a homogeneous solution at the 'gel-dissolution temperatures' presented in Fig. 1. Naturally, the gel dissolution temperature was observed to increase with increasing DMDBS concentration. At DMDBS concentrations below 0.075 wt% ('dilute DMDBS systems') no macroscopic gels were formed upon cooling the solutions down to room temperature. We attribute this observation to the insufficient quantity of the nucleating agent in the mixture to generate a macroscopically coherent network. The latter statement is substantiated by the fact that relatively small gel particles were found in such dilute DMDBS systems after cooling to room temperature.

3.1.3. i-PP/DMDBS/decalin

Unlike in the above case of solutions containing 0.3–5.0 wt% *i*-PP, but no DMDBS, rapid gelation was observed upon cooling polymer solutions that additionally contained 0.1 wt% DMDBS. This finding is not unexpected, since the latter compound alone was found to be capable to cause decalin to gel at that concentration (concentrated DMDBS systems). It should be noted that 0.1 wt% of the (relatively expensive) nucleating agent may amount to a significant fraction in the final polymer if the solvent is removed through evaporation as in one commercial process [12]. Such quantities of added matter not only may be economically unattractive but also adversely affect the mechanical properties of the final fibers.

In a study of cooling decalin solutions containing 0.3–4.0 wt% of *i*-PP and only 0.00725–0.04% of DMDBS, i.e. at concentrations, where solutions of the latter compound did not display gelation, we observed rapid, synergistic formation of gels. Gelation times, here taken as the time at

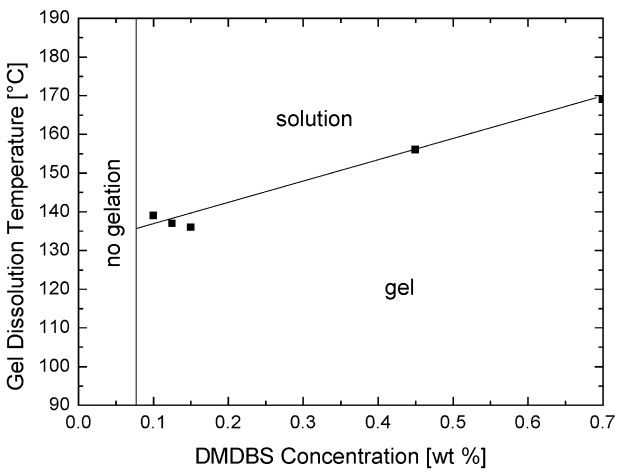

Fig. 1. Low-concentration-section of the phase diagram of decahydronaphthalene (decalin) and the nucleating agent 1,3:2,4-bis-(3,4-dimethyl benzylidene) sorbitol (DMDBS). At DMDBS concentrations >0.1 wt% macroscopic coherent gels were formed upon cooling homogeneous solutions to room temperature, but not below that concentration.

which the solutions formed somewhat a turbid, elastic and coherent mass, were found to be dominated by the process of heat removal and to a lesser extent by the composition of the solutions. For the present compositions and the experimental casting procedure employed, which yielded gels of a thickness of about 5 mm, gelation times were between 30 and 90 s, as opposed to the previously reported several hours [16,27]. For gelling masses of reduced thickness, such as thin filaments, the gelation time concomitantly decreased. As a matter of fact, fibers of a diameter of approximately 0.5 mm drawn from the polymer solution gelled virtually instantaneously (Fig. 2).

Owing to the minor amounts of DMDBS present, the dissolution temperatures of the above gels were found to depend principally on the concentration of the polymer. Typical values of these temperatures were between about 100 and 110 °C for *i*-PP concentrations between 2.5 and 4.0 wt%, virtually independent of the DMDBS content.

3.2. Tensile drawing

Various dried, gel-cast films were drawn at elevated temperatures (120–160 °C). Starting with the compacted films obtained from *i*-PP solutions of a concentration of 0.3 wt% and no DMDBS, these displayed stress–strain curves characterized by strain softening, which lead to unstable deformation and early failure; the latter behavior was comparable to that of dried gel films of UHMW PE obtained from dilute solutions (i.e. around or below the coil overlap concentration) [11]. Remarkably, gel films produced from 0.3 wt% polymer solutions additionally comprising 0.01 wt% DMDBS, exhibited strain hardening, but displayed premature fracture. Compacted 'mud-cracked' films obtained from *i*-PP solutions comprising up to 3 wt% of polymer and no DMDBS also displayed strain hardening and low maximum draw ratios.

By contrast, all films that contained 1 wt% of *i*-PP or more and 0.00725 wt% or more of DMDBS could readily be drawn to relatively high draw ratios. By one-stage drawing draw ratios up to 30 were achieved. Ultimate draw ratios of about 60 were obtained by two-stage drawing. Generally these specimens were first drawn at 120 °C to a draw ratio between 10 and 20, and in a second step drawn at higher temperatures to the desired draw ratio. As expected [11], lower initial polymer concentrations generally were associated with improved drawability.

Selected WAXD patterns of dried films cast from 3 wt% *i*-PP/0.015 wt% DMDBS solutions that were subsequently drawn to different draw ratios are shown in Fig. 3. Already at moderate draw ratios ($\lambda = 10$) the concentric diffraction pattern characteristic of the undrawn, isotropic films transformed into a pattern with distinct arc-shaped reflections indicating significant orientation of the samples. As it is well documented [16–18], further increasing the draw ratio led to patterns composed of sharp diffraction spots of the (130), (040), (110) and (111) planes of the α crystal modification of *i*-PP, indicating a high degree of orientation of the *c*-axis in the stretching direction.

3.3. Mechanical properties

Values of the Young's modulus, tensile strength and elongation at break of various dried gel-films drawn to

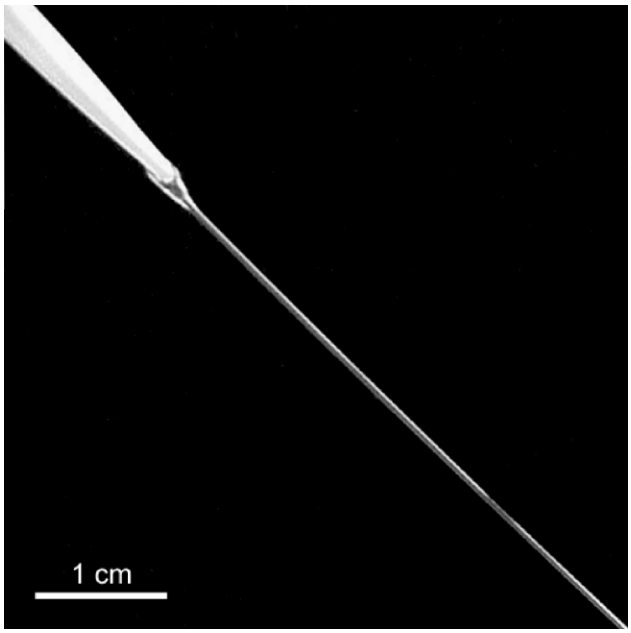

Fig. 2. Photograph of a gel fiber drawn directly out of a decalin solution containing 3 wt% *i*-PP and 0.015 wt% DMDBS.

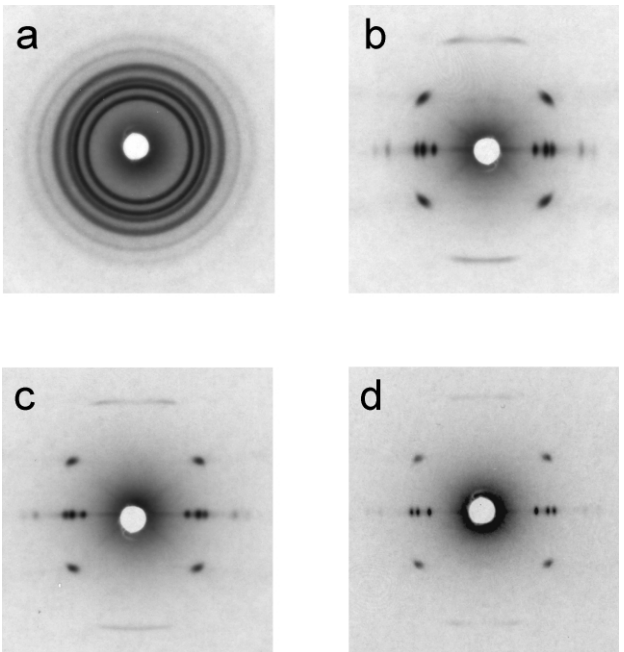

Fig. 3. Wide-angle X-ray diffraction patterns of films cast from 3 wt% *i*-PP/0.015 wt% DMDBS solutions that were subsequently dried and drawn to different draw ratios (λ) : $\lambda = 1$ (a), $\lambda = 10$ (b), $\lambda = 20$ (c), $\lambda = 40$ (d). Draw direction vertical.

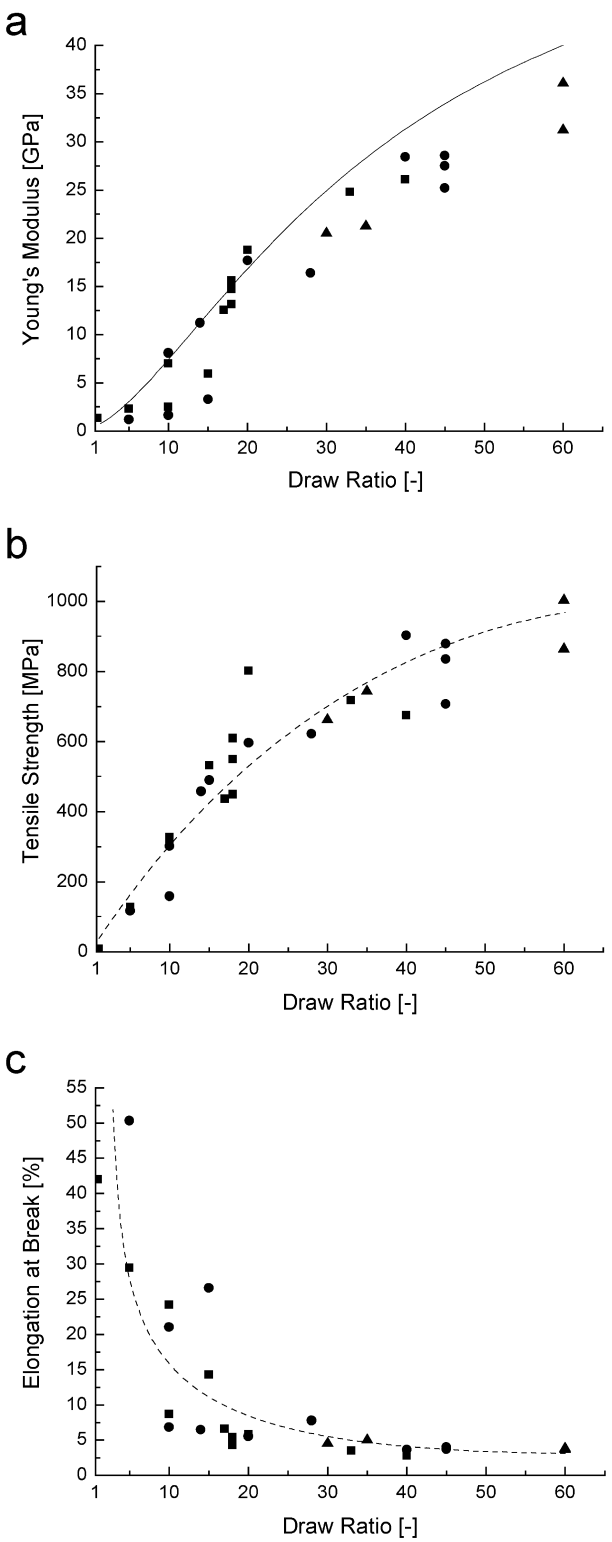

Fig. 4. Young's modulus (a), tensile strength (b) and elongation at break (c) as a function of draw ratio for *i*-PP ($M_m = 1.3–10^6$ g/mol) samples prepared by DMDBS-assisted gel-processing/drawing. In the diagrams the symbols refer to experimental data obtained for dried gels produced from solutions of the following concentrations: (▲) 2.5 wt% *i*-PP/0.0125 wt% DMDBS, (■) 3.0 wt% *i*-PP/0.015 wt% DMDBS, (●) 4.0 wt% *i*-PP/0.02 wt% DMDBS. Also plotted in (a) is the development with draw ratio of the Young's modulus calculated with Eq. (1) according to Ref. [28] (solid line).

different draw ratios are shown in Fig. 4a–c. As seen in these figures, for the present *i*-PP sample, Young's moduli (E) of 35 GPa and tensile strengths (σ) of up to about 1 GPa were obtained. Maximum mechanical properties were obtained for samples processed from 2.5 wt% *i*-PP/0.0125 wt% DMDBS solutions, which were subsequently drawn to a draw ratio of 60. The above data are in line with those previously reported [16–19] for gel-processed UHMW PP, taking into account the relatively modest molecular weight of the present polymer of M_v of 1.3×10^6 g/mol: Ref. [16]: $E = 36$ GPa, $\sigma = 1.03$ GPa, $M_w = 3.4 \times 10^6$ g/mol; Ref. [17]: $E = 40.4$ GPa, $\sigma = 1.56$ GPa, $M_w = 4.4 \times 10^6$ g/mol; Ref. [18]: $E = 26.7$ GPa, $\sigma = 1.1$ GPa, $M_w = 1.84 \times 10^6$ g/mol; and Ref. [19]: $E = 164$ g/den (13.1 GPa), $\sigma = 9.6$ g/den (= 0.77 GPa), $M_w = 2.1 \times 10^6$ g/mol.

Also shown in the graph in Fig. 4a is the development of the Young's modulus with draw ratio (λ) calculated according to Refs. [28,29] with Eq. (1)

$$E = [E_h^{-1} + (E_u^{-1} - E_h^{-1}(3\pi/4)\lambda^{-3/2}]^{-1} \quad (1)$$

where E_h and E_u refer to, respectively, the theoretical axial stiffness (60 GPa) and the stiffness of isotropic *i*-PP (0.6 GPa) [29]. Generally, the experimental values for the Young's modulus of the present gel-processed material are in reasonably good agreement with the theoretical predictions. As noted previously, deviation from the calculated values occurred at draw ratios that were close to its maximum value [29].

3.4. Thermal properties

A brief study was devoted to the thermal properties of the present gel-processed *i*-PP. Since it is well known that the melting behavior of highly oriented forms of this polymer is strongly dependent on the experimental conditions [14], DSC was carried out on both unconstrained and constrained samples. DSC-thermograms recorded for gel-processed films that were drawn to a draw ratio of 20, 40 and 60, respectively, are presented in Fig. 5. Under constrained conditions, the present highly drawn *i*-PP displayed a peak melting temperature as high as 228 °C, which compares with values previously reported [14]. The latter finding once more illustrates the most interesting and useful thermal characteristics of constrained, oriented isotactic polypropylene. The same three materials when tested under unconstrained conditions displayed a rather similar melting behavior (shown for a sample of $\lambda = 20$).

4. Discussion

A number of the above-described results warrant some discussion. Among them are the absence of the consistent formation of ductile (i.e. drawable) films of the present neat

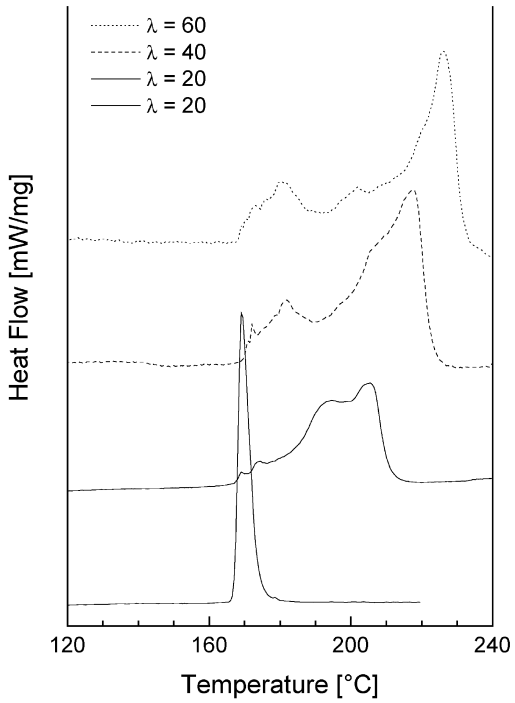

Fig. 5. DSC melting thermograms of gel-processed/drawn *i*-PP ($\lambda = 20, 40, 60$) under constrained (black lines) and unconstrained ($\lambda = 20$, gray line) conditions (see text).

i-PP solutions at polymer concentrations of 4 wt% and less and the phenomenon of the synergistic gelation in the presence of minute quantities of DMDBS. Critical to these issues is the molecular weight of the particular *i*-PP sample used. As stated in Section 2.1, the polymer was of a viscosity-average molecular weight $M_v = 1.3 \times 10^6$ g/mol and a limiting viscosity number of $[\eta] = 6.1$ dl/g. Based on the latter characteristic, the coil overlap concentration c^* can readily be estimated using the well-known relation [30]

$$[\eta]c^* \approx 1 \quad (2)$$

Carrying out the operation yields a value of about 0.16 wt% for the concentration for the onset of overlap of the macromolecular coils in solution.

To address the observed gelation behavior of solutions of the present *i*-PP first, the polymer concentrations employed (0.3–4.0 wt%) significantly exceeded—up to a factor 25—the concentration for the onset of coil overlap (≈0.16 wt%) and, thus, one would expect the formation of macroscopic gels upon crystallization especially from the more concentrated solutions, provided, of course, that no substantial disentanglement takes place, i.e. that the loosely entangled macromolecular topology in solution is essentially 'frozen in'. Owing, however, to the extremely slow nucleation and crystallization of *i*-PP, when compared to for instance polyethylene, the polymer molecules may disengage from each other through the process of 'reeling in', which may lead to partial or complete loss of their initial connectivity. The latter process was previously shown to occur during deliberately slow gelation/crystallization of UHMW PE solutions carried out at elevated temperatures [31]. Under such kinetic conditions no formation of macroscopically coherent, ductile gels occurs, indeed as observed for the present *i*-PP solutions void of DMDBS. The process of disentangling during crystallization may be hampered by employing substantially higher polymer concentrations, which, however, has a negative impact on the maximum draw ratio that can be obtained for films and fibers produced from such more concentrated solutions [11]. Alternatively, using *i*-PP of considerably higher molecular weight would hinder the disentangling of polymer chains, which explains why other authors that employed UHMW PP (values of M_w of up to about 3.5 times that of the present material) were able to produce gels [16–19], albeit under unattractive experimental conditions. In our view, the addition of minute amounts of the nucleating agent DMDBS, in quantities that were insufficient to cause gelation of the solvent by the additive alone (<0.075 wt%), dramatically enhanced the rate of nucleation and crystallization of polypropylene, therewith preventing the above disengagement of the macromolecules, yielding coherent, ductile gels, unlike in the absence of DMDBS. Most illustrative in this respect are the observations made with films produced from the *i*-PP solutions comprising 0.3 wt% of the polymer, i.e. in the range of the coil overlap concentration. In the absence of DMDBS, compacted, dried gel films displayed strain softening, while in the presence of the nucleating agent films were obtained that showed strain hardening, indicative of the preservation of an increased amount of entanglements.

5. Conclusions

In this work we demonstrated that the rate of gelation of solutions of *i*-PP can be dramatically enhanced by the addition of surprisingly minute amounts of the nucleating/gelling agent DMDBS. This synergistic effect allowed us to gel-process *i*-PP under industrially feasible conditions, yielding material with Young's moduli up to 35 GPa, tensile strengths of about 1 GPa and melting temperatures determined for constrained samples of up to 228 °C.

Acknowledgements

The authors thank Professor T. Ohta for the polymer sample, M. Colussi (ETH Zürich) for providing its characterization, Michael Werner (ETH Zürich) for his valuable assistance in the gelation experiments and Professor Hans-Werner Schmidt (Universität Bayreuth) for many fruitful discussions.

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