“Designer” Nucleating Agents for Polypropylene

Markus Blomenhofer, Sandra Ganzleben, Doris Hanft, and Hans-Werner Schmidt*

Macromolecular Chemistry I, Bayreuther Institut für Makromolekülforschung and Bayreuther Zentrum für Grenzflächen und Kolloide, Universität Bayreuth, D-95440 Bayreuth, Germany

Magnus Kristiansen and Paul Smith*

Department of Materials, Eidgenössische Technische Hochschule Zürich,
ETH Hönggerberg,
CH-8093 Zürich, Switzerland

Klaus Stoll, Dietmar Mäder, and Kurt Hoffmann

Ciba Specialty Chemicals, CH-4002, Basel, Switzerland

Received December 23, 2004; Revised Manuscript Received January 28, 2005

ABSTRACT: We report the discovery of a family of organic compounds, substituted 1,3,5-benzenetrisamides, that—depending on subtle details of their chemical structure—are capable of selectively and extremely efficiently nucleating the growth of the common α-crystal modification of the major industrial polymer isotactic polypropylene (*i*-PP), rendering this normally turbid material highly transparent (“clarified”) at exceedingly low concentrations (as low as a weight fraction of 0.0002), inducing the mechanically distinct, tough *i*-PP β-polymorph, or promoting growth of hybrids of both crystallographic modifications with heretofore unknown combinations of the above desirable optical-mechanical properties. In addition, these trisamide-based compounds exhibit excellent thermal stability and do not feature absorption of visible light, adding to a most favorable set of characteristics that provides marked benefits over the presently employed nucleating/clarifying agents.

1. Introduction

The phenomenon of nucleation invariably is involved in the transformation of matter from one physical state to another and manifests itself in different physical processes such as condensation, precipitation, and crystallization from solutions and solidification of metals, ceramics, and polymers.[1,2] In particular, in crystallization of the latter class of materials, nucleation often is hampered by the covalently bonded, long-chain nature of the crystallizing species, and it has become common place to employ suitable additives to (heterogeneously) promote this process. Such “nucleating agents” stand out not only because they may significantly enhance the rate of production of polymer artifacts but also because they may dramatically alter the solid-state structure of macromolecules and, therewith, broaden the spectrum of its material characteristics, for instance, stiffness, ductility, and clarity and transparency.[3]

Illustrative, and among industrial applications most relevant, is the use of nucleating agents in processing of the slowly nucleating and crystallizing bulk polymer isotactic polypropylene (*i*-PP). Addition of about 0.1−0.3 wt % of frequently employed nucleating agents that induce the common α-crystal modification of this polymer, i.e., particular sorbitol derivatives,[4,5] raises the peak crystallization temperature (when measured at a cooling rate of 10 °C/min) from ~110 °C for the neat polymer to about 125−130 °C for the mixtures, which drastically reduces the production cycle of objects made from this material by melt-processing. In contrast to commonly employed heterogeneous nucleating agents, which are insoluble in *i*-PP,[6] the sorbitol-based nucleating agents and clarifiers are depending on the concentration soluble during processing. As consequence and in the optimal concentration range the value of haze, commonly defined as that portion of visible light that is scattered at wider angles ($2.5° < \theta < 90°$)[7] and is a measure for the turbidity of a sample, may be reduced from approximately 65% for the neat polymer to < 20% for *i*-PP comprising about 0.3 wt % of 1,3:2,4-bis(3,4-dimethylbenzylidene)sorbitol (DMDBS), when determined on injection-molded plaques of a thickness of ~1 mm. Simultaneously, the clarity, which usually refers to the visible light scattering contribution at small angles ($\theta < 2.5°$)[7] and is related to the sharpness of an object when viewed through the sample, is improved from about 80% to > 99% for such specimen. Most unfortunately, however, the above sorbitol family is not broadly applicable and, owing to their sugar-based chemical structure, appear to suffer from one or more of the following problems: sublimation, blooming, and/or thermal decomposition during processing, which may lead to unwanted odorous products and discoloration;[8,9] until now, more efficient clarifiers are not known.

There also exist nucleating agents—to our knowledge not of the sorbitol family—that are capable of inducing the β-polymorph of *i*-PP[10,11], which displays highly useful, increased toughness. The latter beneficial property finds its origin in a stress-induced phase transition into (the more stable) α-modification.[10,12] Such “phase-transformation toughening” is known also for other materials, notably for zirconia-based ceramics,[13,14] which upon deformation undergo a martensitic phase transition, accompanied by an increase in the specific volume. Thereby, compressive forcefields are generated around

---

* Corresponding authors. (H.-W.S.) Telephone: 0049/921 55 3200. Fax: 0049/921 55 3206. E-mail: hans-werner.schmidt@uni-bayreuth.de. (P.S.) Telephone: 0041/16322637. Fax: 0041/16321178. E-mail: psmith@mat.ethz.ch.

10.1021/ma0473317 CCC: $30.25

a crack tip, that prevent further propagation of the crack, leading to distinct toughening of the material. Among the relatively few nucleating agents that induce the β-polymorph of *i*-PP, the calcium salt of suberic acid, which induces the formation of β-*i*-PP in pure form is most effective.[15] γ-Quinacridone is most remarkable in that it causes this crystal modification to form already at additive concentrations as low as 0.00005 wt %.[16] One principal drawback of this highly efficient additive is its extreme absorbance of light in the 470 and 540 nm range,[17] which renders even such low-additive-content blends pink and apparently limits widespread use. Another β-nucleating agent is *N,N′*-dicyclohexyl-2,6-naphthalenecarboxamide (DCHN,[18]), which was shown to be effective at concentrations exceeding 0.03 wt %.[19] Although the latter three β-nucleating agents are thermally stable and display excellent performance at low concentrations, they do not dissolve in the polymer melt, which impedes homogeneous dispersion of the additive during processing of the polymer and limits their use.

In attempts to rationally design and create a wider range of nucleating/clarifying agents that would not display the above drawbacks, we discovered a new family of remarkably efficient and highly versatile additives that we found to be capable of inducing different crystal structures of *i*-PP and imparting drastically improved optical properties at exceedingly low concentrations, in combination with excellent thermal stability and absence of intrinsic color. Here, we present a brief account of that study.

2. Experimental Section

Materials. Two *i*-PP homopolymer grades with rather similar molecular weight distributions (M_n ~6×10^4 g/mol; M_w ~4×10^5 g/mol) were used throughout this study: Appryl (Elf Atochem) and Profax PH 350 (Montell). Both polymer grades contained about 0.05 wt % of the antioxidant Irganox 1010, 0.10 wt % Irgafos 168 and about 0.1 wt % Ca−stearate. Prior to use, the polymer pellets were pulverized in a freezer mill (Retsch ZM100, Schieritz & Hauenstein AG, Switzerland). In addition to the selection of 1,3,5-benzenetrisamides presented in Table 1, the nucleating agent 1,3:2,4-bis(3,4-dimethyl benzylidene)sorbitol (DMDBS, Millad 3988, Milliken Chemical Co.) and *N,N′*-dicyclohexyl-2,6-naphthalenedicarboxamide (DCHN)) were employed as references and used as received.

Compounding. Dry-blended powdrous mixtures of *i*-PP and the respective additives 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. Neat *i*-PP was similarly treated to produce blank control samples. Series of mixtures of different concentrations were produced by dilution of initial batches, typically containing 0.25 wt % of the additive, by addition of defined quantities of the neat polymer.

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

Optical Properties. The standard optical characteristics "haze" and "clarity" were measured for the injection-molded disks with a "Haze-Gard Plus" instrument (BYK Gardner GmbH, Germany), which conforms to ASTM D-1003.[20]

Thermal Analysis. Differential scanning calorimetry (DSC) was conducted with Netzsch (DSC, model 200) and Perkin-Elmer (DSC-7) instruments with samples of 5−10 mg at standard heating or cooling rates of 10 °C/min, under nitrogen. Prior to recording of cooling and heating thermograms the samples were held at 230 °C for 5 min to erase thermal history and prevent self-seeding of *i*-PP. Thermal transition temperatures hereafter reported refer to peak temperatures in the DSC thermograms. Thermogravimetric analysis (TGA) was conducted with a Netzsch STA 409 instrument under nitrogen at a heating rate of 10 °C/min.

Optical Microscopy. Optical micrographs were taken with an optical microscope (Leica DMRX) equipped with a hot-stage (Mettler, model FP82TM).

***β*-Content**. Wide-angle X-ray scattering (WAXS) patterns were recorded in transmission with a Bruker D8 Advance X-ray diffractometer. The wavelength used was Cu K_α ($\lambda = 1.54$ Å) and spectra were recorded in the 2θ range of 8−30° (step size 0.025°). The content of the β-crystal modification in injection-molded *i*-PP plaques comprising a standard amount of 0.15 wt % of the various additives, was deduced from these X-ray data according to standard procedures described in the literature,[12] employing the relation:

$$k = \frac{H_{\beta(300)}}{H_{\beta(300)} + H_{\alpha(110)} + H_{\alpha(040)} + H_{\alpha(130)}} \quad (1)$$

where $H_{\Omega(hkl)}$ represents the height of the (hkl) peak belonging to the phase Ω (α or β; always with respect to the amorphous halo).

Refractive Index Determination. The refractive indices were determined by a modified immersion method developed and described by Nussbaumer.[21] In this method, a small amount of the respective additive powders was deposited onto plasma-cleaned glass slides. These assemblies were then immersed into liquids of different refractive indices and the UV/vis transmission at 570 nm was determined with an uncovered glass slide as a reference. The refractive index of the respective additive material was obtained by fitting a Lorentz function to the transmission vs the refractive indices of the liquids used.

3. Results and Discussion

An extensive library of 1,3,5-trisamides of the generic structure **A**−(**X**-**R**)$_3$ was synthesized according to methods described elsewhere.[22−24] The species were designed to comprise three functional moieties: (i) a (generally symmetrically substituted) central core, **A**, here benzene; (ii) moieties capable of forming hydrogen bonds, **X**, here amides, which promoted predominantly one-dimensional crystal growth of the compounds and, therewith, provided a high surface/volume ratio; (iii) a peripheral group, **R**, here apolar substituents, the selection of which permits subtle manipulation of the crystallographic order of the species to advantageously induce the formation of one or more crystal modifications of *i*-PP, and simultaneously serve to enable dissolution of the (semipolar) compounds in the molten, hydrophobic polymer. The chemical structures of a limited selection of compounds produced are presented in Table 1.

The following initial screening methods were employed to qualitatively investigate the potential nucleating and clarifying capabilities of the various trisamides (Figure 1).

Crystals of the different compounds were grown by dissolving ca. 0.01 wt % of the material at 300 °C in the high boiling hydrocarbon squalane under a nitrogen blanket, followed by cooling the solution to room temperature. Subsequently, a few of the crystals, which often were obtained in the form of whiskers, were placed onto a glass slide, and a thin (~100 μm) compression molded film of the polymer and a coverslip were positioned on top. The assembly was then heated in a hot stage in the optical microscope to a temperature

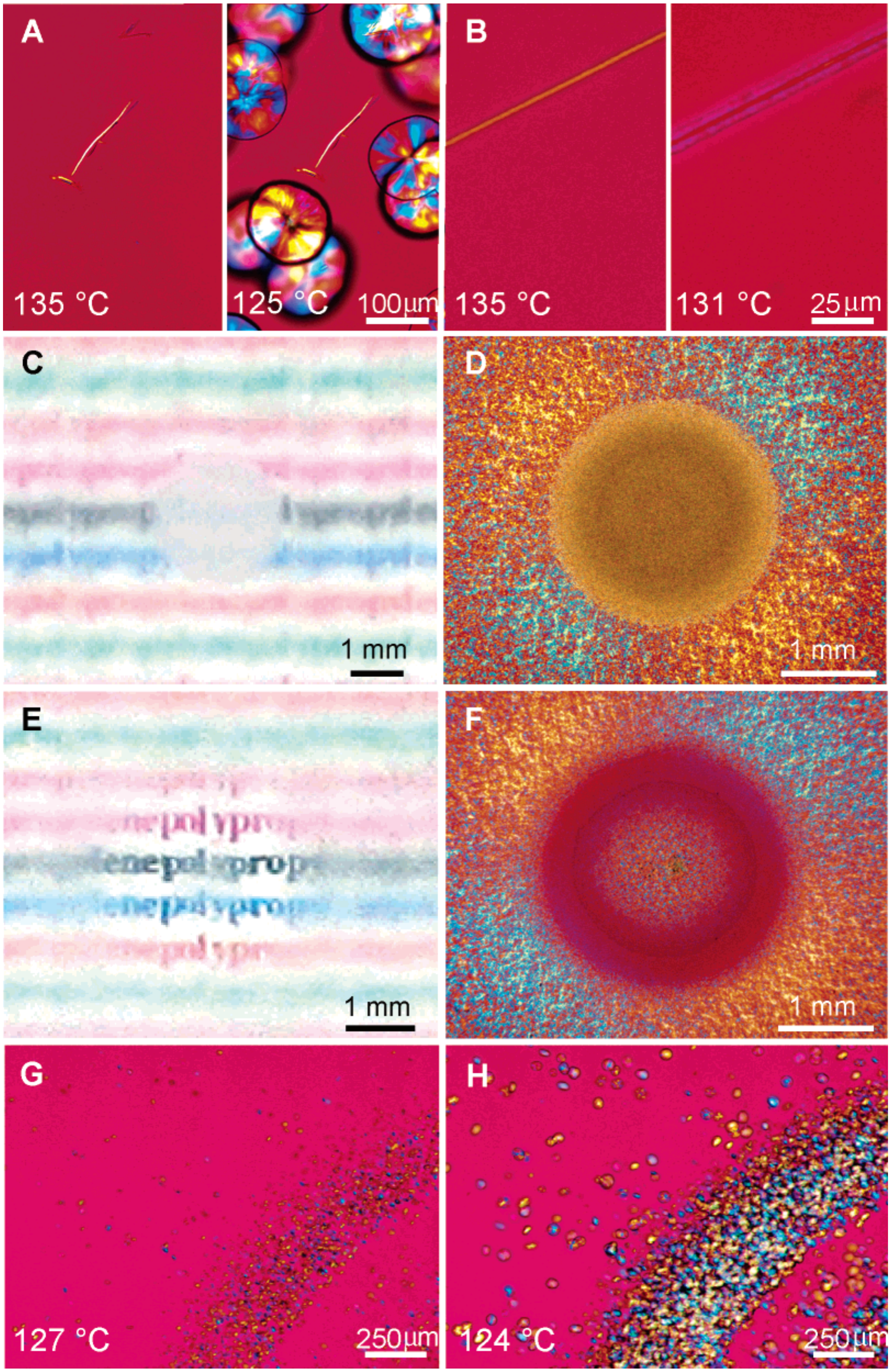


Figure 1. Representative results of qualitative screening tests for nucleation and clarification abilities of the trisamide additives. (**A**) Polarized optical micrographs of crystals of compound **1**, surrounded by a supercooled melt of *i*-PP, which failed to induce crystal growth of the polymer; photographs taken with $\lambda/4$ plate at the temperatures indicated. (**B**) Corresponding photographs of a whisker of compound **3**, which nucleated crystal growth of *i*-PP (appearing in purple) on its surface at 131 °C. Note the absence of any *i*-PP crystals in the surrounding supercooled liquid. (**C**−**F**) Optical micrographs of typical samples produced in “diffusion screening” experiments. (**C**, **D**) A strong light-scattering circular area developed for the β-nucleating agent **15**. (**E**, **F**) A clear transparent ring was observed for the α-nucleator **18**, indicative of the clarifying effect of this particular additive in *i*-PP. Pictures **C** and **E** were taken with reflective, unpolarized light, illustrating the high haze/low clarity obtained with compound **15**, and low haze and excellent clarity with **18**. **D** and **F** were taken in transmittance with crossed polarizers and a $\lambda/4$ plate. (**G**, **H**) Set of polarized optical micrographs (crossed polarizers, $\lambda/4$ plate) taken at the temperatures indicated during cooling of an *i*-PP film in which additive **3** was previously allowed to diffuse at 260 °C, demonstrating enhanced nucleation of *i*-PP in a distinct band, i.e., a limited concentration range.

Table 1. Chemical Structures of Substituted 1,3,5-Benzenetrisamides and Their Properties as Additives in Isotactic Polypropylene[c]

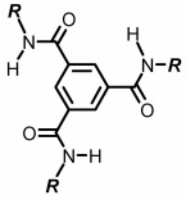
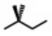
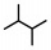
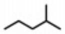
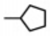
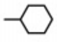
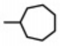
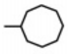
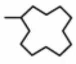
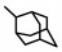
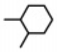
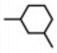
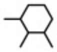
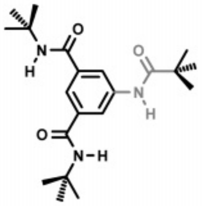
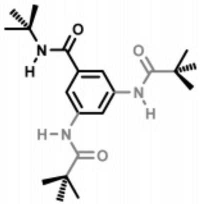
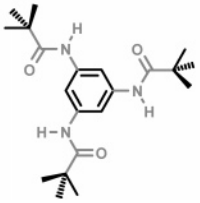
No.	Additive/Substituent	R	$T_{m,a}$ [°C]	$T_{c,p}$ [°C]	$T_{d,a}$ [°C]	$T_{c,a}$ [°C]	*k* [-]	*Haze* [%]	*Clarity* [%]
I	*i*-PP, no additive	n.a.	~ 165	110.0	n.a.	n.a.	<0.10	64.0	79.0
II	DMDBS	n.a.	275	125.0	170	138	<0.10	37.3	98.4
III	DCHN	n.a.	300	123.7	>300	n.a.	0.70	100.0	49.9
1-15a)									
1	*n*-Propyl		289	114.8	287	200	<0.10	72.7	85.3
2	*tert.*-Butyl		subl.	128.7	>300	n.a.	<0.10	36.2	97.9
3	1,1-Dimethylpropyl		subl.	126.7	289	254	<0.10	36.2	97.7
4	1,2-Dimethylpropyl		subl.	124.7	280	248	<0.10	30.0	98.2
5	3-Methylbutyl		263	121.3	215	201	<0.10	27.4	98.7
6	1,1,3,3-Tetramethylbutyl		315 e	124.3	250	178	0.40	35.8	98.9
7	Cyclopentyl		375 e	121.0	>300	n.a.	<0.10	28.8	97.8
8	Cyclohexyl		376 e	124.8	268	229	0.10	34.5	97.6
9	Cycloheptyl		394 e	123.3	>300	n.a.	0.29	71.7	91.2
10	Cyclooctyl		dec.	124.3	>300	n.a.	0.64	97.6	83.3
11	Cyclododecyl		392 e	122.1	>300	n.a.	0.38	87.0	91.7
12	2-Adamantyl		subl.	130.9	>300	n.a.	0.15	62.5	92.3
13	2-Methylcyclohexyl		subl.	125.0	>300	n.a.	<0.10	37.2	97.6
14	3-Methylcyclohexyl		381 e	120.5	>300	n.a.	0.37	96.1	84.0
15	2,3-Dimethylcyclohexyl		418 e	121.6	>300	n.a.	0.74	98.2	72.3
16b)			subl.	124.7	280	245	<0.10	26.0	94.1
17b)			subl.	123.1	265	240	<0.10	23.7	94.8

Table 1 (Continued)

No.	Additive/Substituent	$T_{m,a}$ [°C]	$T_{c,p}$ [°C]	$T_{d,a}$ [°C]	$T_{c,a}$ [°C]	k [-]	*Haze* [%]	*Clarity* [%]
18[b)]		subl.	124.8	280	265	<0.10	16.6	98.3

[a] Compounds **1**–**15** are based on 1,3,5-benzenetricarboxylic acid; the structure of the substituent **R** is drawn with its bond to nitrogen to the left. [b] Compounds **16**, **17**, and **18** all feature **R** = *tert*-butyl, but the direction of the amide bond connecting this moiety to the benzene core was reversed, respectively 1, 2, and 3 times in comparison with compound **2**. [c] The different properties should be compared to neat *i*-PP (for $T_{c,p}$), *i*-PP containing 0.15 wt % DMDBS (for *haze*), and *i*-PP containing 0.15 wt % DCHN (for *k*), respectively. $T_{m,a}$ = melting temperatures, where applicable. $T_{c,p}$ = crystallization peak temperatures of *i*-PP.[26] $T_{d,a}$ and $T_{c,a}$ = additive dissolution and crystallization temperature in mixtures comprising 0.15 wt % of the various additives. k = β-content (eq 1,[12]). Here *haze* and *clarity*[20] additive are of injection molded 1.1 mm thick plaques of that same composition. n.a. = not applicable. dec. = decomposition. e = evaporation. subl. = sublimation, typically at temperatures in excess of 300 °C.

above the melting temperature of the polymer (~165 °C), but below the end-dissolution temperature of the species in the molten polymer. Finally, the thus produced samples were cooled at a rate of 5 °C/min, and the nucleation and crystallization behavior of the polymer was recorded. Parts A and B of Figure 1 show illustrative optical micrographs of whiskers of the compounds **1** and **3** surrounded by a supercooled melt of *i*-PP at the temperatures indicated. Clearly, crystals of compound **1** failed to induce or promote growth of *i*-PP (Figure 1A, right). In contrast, **3** effectively nucleated crystal growth of the polymer, as evidenced by the transcrystalline overgrowth of the α-form of *i*-PP (appearing purple) onto the whisker and the absence of any polymer crystals in the surrounding melt (Figure 1B, right).

A small amount (~0.1 mg) of powder of a compound was positioned in the center of a previously compression molded ~100 μm thick film of *i*-PP, and a coverslip was put on top. Subsequently, the assembly was placed onto a hot stage, typically at a temperature of 260 °C, but always below the melting temperature of the additive and above that of *i*-PP, and left for a few minutes, after which the sample was cooled to room temperature. During the heating phase of this process, the compound was allowed to radially diffuse into the polymer melt, resulting in a "radial composition diagram". Figures 1 C–F show optical micrographs of the structures obtained in these "diffusion screening" experiments. The film containing **15** is characterized by the presence of an opaque circular area (Figure 1C,D), typically associated with the presence of the generally strong light-scattering β-polymorph. The sample comprising compound **18**, on the other hand, displayed a readily detected optically clear ring at some distance from the position where the additive was initially placed (Figure 1E,F), indicating the clarifying potential of the respective additive at certain concentrations. The set of optical micrographs in Figure 1G,H, taken during cooling after the diffusion experiment with nucleator/clarifier **3**, illustrate the drastically enhanced number of nucleation sites for growth of *i*-PP within a relatively narrow (concentration) band leading to a macroscopic clear ring, as in Figure 1E. The "morphology pattern" in Figure 1E–H is consistent with and, in fact, indicative of monotectic phase behavior of the systems at hand, analogous to that of *i*-PP/DMDBS shown previously.[25] More detailed studies concerning the foregoing will be published elsewhere.

More quantitative data, obtained for mixtures of *i*-PP comprising a standard amount of 0.15 wt % of the different additives, as well as the corresponding reference values of the neat polymer (**I**) and *i*-PP containing 0.15 wt % DMDBS (**II**) and 0.15 wt % DCHN (**III**), are summarized in Table 1. These results demonstrate that the present family of substituted 1,3,5-benzenetrisamides provides a truly exceptionally broad spectrum of properties in combination with *i*-PP, indeed ranging from nucleating essentially the α- to predominantly the β-polymorph (k from <0.10 to up to 0.74, Figure 2 see also particularly illustrative series **7**-**10**), from highly efficient nucleation ($T_{c,p}$ = 130.9 °C; compound **12**) to virtually no increase of the polymer crystallization temperature (**1**), and from a reduction of haze that, at the additive concentration of 0.15 wt % employed, surpasses that obtained with DMDBS to essentially "whiteners" (haze ~100%). In addition, certain compounds were found to reproducibly induce mixtures of the two polymorphs. Compound **6** deserves special notice and is most unusual indeed, because it induces a relatively high β-phase content (k = 0.40) combined with a relatively low haze (35.8%), a unique combination of desirable properties.

As noted above, the data in Table 1 were produced for mixtures of a fixed additive content of 0.15 wt %.

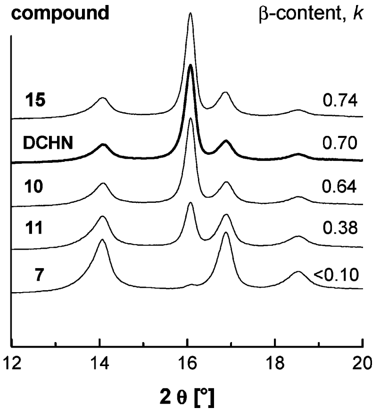


Figure 2. Wide-angle X-ray diffractograms of injection-molded samples of *i*-PP comprising 0.15 wt % of different additives (compounds indicated left; see Table 1), displaying various contents of the β-crystal modification (k, eq 1, marked right).

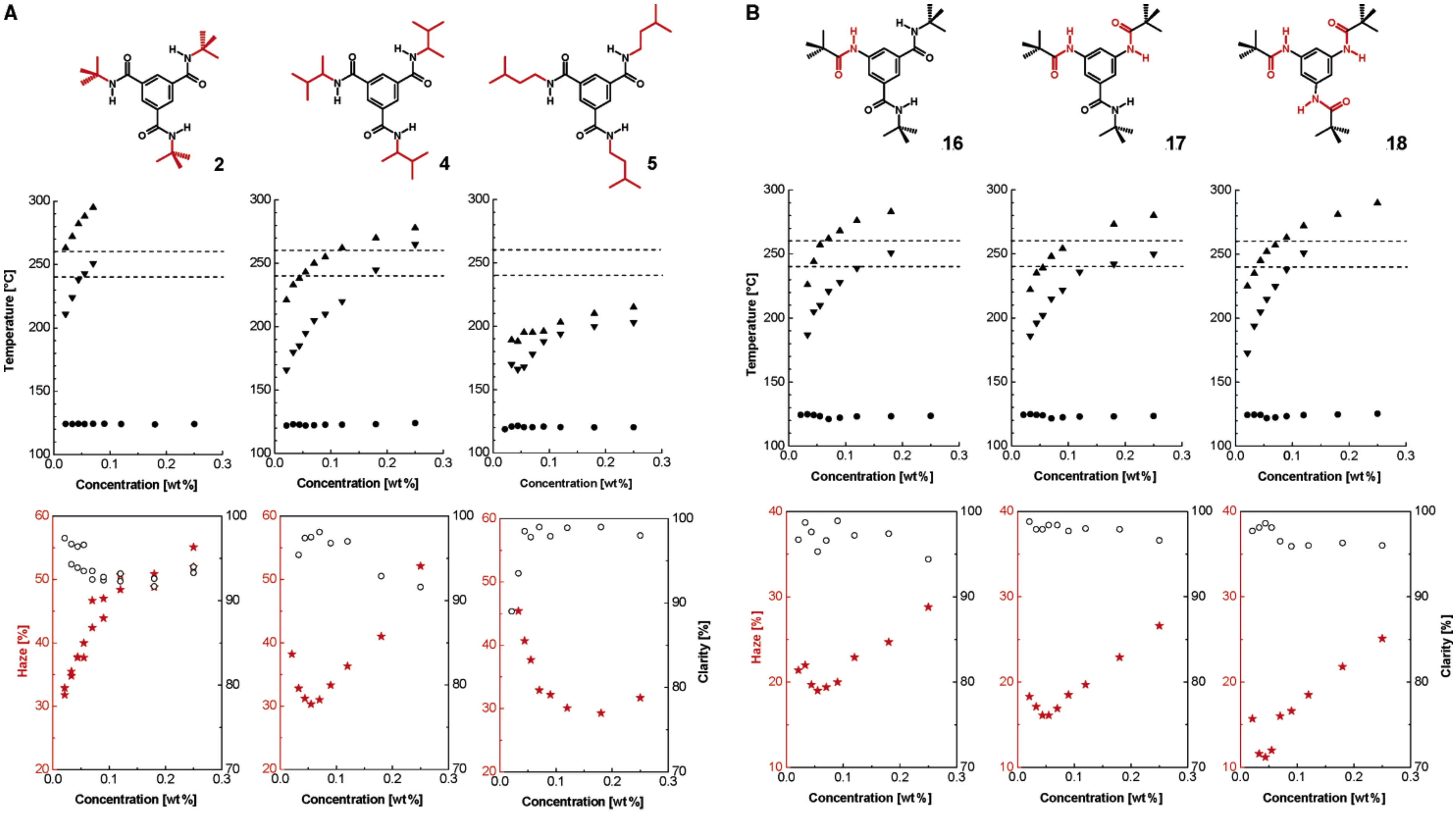


Figure 3. Partial temperature-composition diagrams (top graphs) and corresponding haze/clarity-composition diagrams (bottom graphs) for *i*-PP comprising, respectively, the compounds **2**, **4** and **5** (**A**), and **16**, **17** and **18** (**B**). The various symbols refer to the end-dissolution ($T_{d,a}$, ▲) and onset crystallization temperatures ($T_{c,a}$, ▼) of the different additives, the crystallization temperatures of *i*-PP ($T_{c,p}$, ●; see also ref 26), as determined by DSC and optical microscopy, and haze (★) and clarity (○) of 1.1 mm thick injection-molded plaques. Dashed lines in the top graphs indicate the processing temperature window employed in this work.

These "single-point" measurements were sufficient to establish the nucleation characteristics of the additives (i.e., values of the crystallization temperature, $T_{c,p}$, and β content, k), as the latter, above a relatively low minimum content, vary only modestly with the amount of additive. By contrast, and as we demonstrated earlier for the system *i*-PP/DMDBS,[25] the optical characteristics haze and clarity, as well as the dissolution and crystallization temperatures of the additives, critically depend on the composition of the mixture. Hence, the concentration dependence of haze and clarity and partial phase diagrams were determined for *i*-PP comprising additives based on 1,3,5-benzene tricarboxylic acid with selected branched alkyl substituents **R** of increasing flexibility, **2**, **4**, and **5** (Figure 3A). In a second set, the effects associated with "inversion" of amide bonds—to reduce their conjugation with the phenyl core—were investigated (compounds **16**−**18**, Figure 3B); the latter are to be compared with results obtained with compound **2**.

Inspection of the diagrams in Figure 3 reveals that for most of these binary systems the solubility limit at the processing temperature range (here 240−260 °C) coincided with the additive concentration at which a minimum in the value of haze was observed (Figure 3A,B). At lower additive concentrations, the optical properties were found to rapidly deteriorate due to the reduction of available nucleation sites. On the other hand, at concentrations exceeding the solubility limit, a fairly linear increase in haze was encountered, which we attribute to the presence of increasing quantities of undissolved additive particles, causing additional scattering of visible light. It is noteworthy that certain of the present species were found to become effective α-nucleators and clarifiers already at concentrations as low as 0.02 wt % (e.g., **2**, **18**, Figure 3). This finding is in sharp contrast with the behavior of DMDBS, which commercially is employed at concentrations of about 0.20 wt % and more, i.e., a 10-fold amount, and was previously shown to be ineffective at concentrations below about 0.1 wt %[25,27] and stated to be maximally effective at 0.3 wt % or greater.[28]

The data presented in Figure 3A show that the dissolution and crystallization temperatures of the additive in *i*-PP decreased with already a modest increase in the flexibility of the substituent **R**. This resulted in an increased concentration range in which the additive is fully dissolved during processing, which, in turn, yielded an increased additive-content-regime over which low haze was observed.

Considering a change of direction of one or more of the amide bonds that connect **R** to the central core (**16**−**18**; Figure 3B), the phase behavior of the *i*-PP/additive systems was found to be relatively little affected. On the other hand, the clarifying ability of the different species varied in a most remarkable and—to us—unexpected manner. The haze values of *i*-PP comprising the additives with 0, 1, 2, and 3 "reversed" amide bonds (**2**, **16**−**18**) displayed a systematic, very significant additional reduction in haze, the present minimum value being as low as 11% for *i*-PP mixtures comprising species **18** at a concentration of only 0.04 wt %. (For comparison, a standard—much thinner, ~0.1 mm vs 1.1 mm—overhead transparency sheet exhibits a value of haze of 6%). In view of the strong similarities in the phase behavior of these *i*-PP/additive mixtures, this pronounced effect is likely to originate in changes in the details of the crystal unit cell of the additive and its possibly enhanced epitaxial matching with that of the crystallizing polymer and/or a reduction of the differences in the refractive index, n, of the compounds and *i*-PP (1.519 (**2**), 1.513 (**16**), 1.511 (**17**), and 1.509 (**18**); n of semicrystalline *i*-PP = 1.503[29]), which—depending on the additive particle size—are expected to determine the minimum level of haze at the optimum concentration.

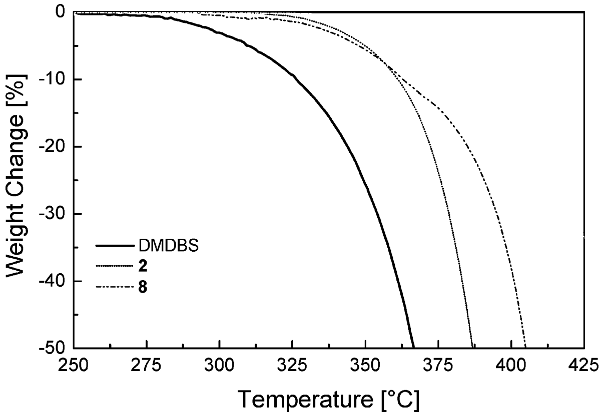


Figure 4. Thermogravimetric analysis (TGA) of compounds **2** and **8** as well as, for reference, 1,3:2,4-bis(3,4-dimethyldibenzylidene)sorbitol (DMDBS), illustrating the superior thermal stability of the new compounds.

Finally, in Figure 4 are presented dynamic thermogravimetric measurements for compounds **2** and **8**, representative of the present trisamide family, as well as of the reference nucleating agent DMDBS. The data indicate that rapid thermal decomposition of the latter species occurred at temperatures exceeding 260 °C, while **2** and **8** remained stable up to 300 °C, illustrating the excellent thermal stability of the present compounds, which significantly broadens the processing window that can be exploited with these additives.

4. Conclusions

We presented a new family of thermally stable substituted 1,3,5-benzenetrisamides, that—depending on subtle details of their chemical structure—are capable of selectively and extremely efficiently nucleating the α-crystal modification of isotactic polypropylene (*i*-PP); and obtain highly transparent and clarified polypropylene at weight fractions as low as 0.0002. In addition, selected derivatives form the mechanically distinct and tough *i*-PP β-polymorph. Of special interest is also the promotion of growth of hybrids of both crystallographic modifications with heretofore unknown combinations of the above desirable optical-mechanical properties. In addition, these trisamide-based compounds exhibit excellent thermal stability, and do not feature absorption of visible light, adding to a most favorable set of characteristics that provides marked benefits over presently employed nucleating/clarifying agents. It is anticipated that the present study advances the development of multifunctional additives for tailoring physicochemical properties also of other polymers.

Acknowledgment. The authors are grateful to Prof. L. J. Gauckler for enlightening discussion about phase-transformation toughening, Drs. Kirill Feldman, Theo Tervoort, and Reiner Giesa for experimental assistance, to Dr. Natalie Stingelin-Stutzmann for valuable suggestions regarding the manuscript.

References and Notes

(1) Price, F. P. In *Nucleation*; Zettlemoyer, A. C., Eds.; Marcel Dekker: New York, 1969; p 405.
(2) Walton, A. G. *Science* **1965**, *148*, 601.
(3) Kurja, J.; Mehl, N. A. In *Plastics Additives Handbook*, 5th ed.; Zweifel, H., Ed.; Hanser: Munich, Germany, 2001; p 949.
(4) E.g. 1,3:2,4-dibenzylidenesorbitol (DBS, Millad 3905, Milliken Chemical Company and Irgaclear D, Ciba Speciality Chemicals), 1,3:2,4-bis-(*p*-methylbenzylidene)sorbitol (MDBS, Millad 3940, Milliken Chemical Company and Irgaclear DM, Ciba Speciality Chemicals), 1,3:2,4-bis-(*p*-ethylbenzylidene)sorbitol (EDBS, NC-4, Mitsui Chemical) and 1,3:2,4-bis-(3,4-dimethylbenzylidene)sorbitol (DMDBS, Millad 3988, Milliken Chemical Co.).
(5) Hamada, K.; Uchiyama, H. US Patent 4,016,118. Mahaffey, R. L. US Patent 4,371,645. Machell, G. US Patent 4,562,-265. Rekers, J. W. US Patent 5,049,605.
(6) Binsbergen, F. L. *J. Polym. Sci., Polym. Phys.* **1973**, *11*, 117.
(7) Willmouth, F. M. In *Optical Properties of Polymers*; Meeten, G. H., Ed.; Elsevier Applied Science Publisher: Essex, England, 1986; p 265.
(8) Fujiyama, M.; Wakino, T. *J. Appl. Polym. Sci.* **1991**, *42*, 2749.
(9) Rekers, J. W. US Patent 5,049,605, col. 1, l. 13.
(10) Varga, J. *J. Macromol. Sci.* **2002**, *41*, 1121.
(11) Stocker, W.; Schumacher, M.; Graff, S.; Thierry, A.; Wittmann, J.-C.; Lotz, B. *Macromolecules* **1998**, *31*, 807.
(12) Turner-Jones, A.; Aizlewood, J. M.; Beckett, D. R. *Makromol. Chem.* **1964**, *75*, 134.
(13) Garvier, R. C.; Hannink, R. H.; Pascoe, R. T. *Nature (London)* **1975**, *258*, 703.
(14) Hannink, R. H. J.; Kelly, P. M.; Muddle, B. C. *J. Am. Ceram. Soc.* **2000**, *83*, 461.
(15) Varga, J.; Mudra, I.; Ehrenstein, G. W. *J. Appl. Polym. Sci.* **1999**, *74*, 2357.
(16) Sterzynski, T.; Calo, P.; Lambla, M.; Thomas, M. *Polym. Eng. Sci.* **1997**, *37*, 1917.
(17) Zollinger, H. In *Color Chemistry*, 2nd rev. ed.; VCH: Weinheim: Germany; 1991; p 241.
(18) Ikeda, N.; Kobayashi, T.; Killough, L. In *Polypropylene '96*; World Congress: Zürich, Switzerland, 1996.
(19) Kotek, J.; Raab, M.; Baldrian, J.; Grellmann, W. *J. Appl. Polym. Sci.* **2002**, *85*, 1174.
(20) ASTM Standard D 1003 *Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics* 1961.
(21) Nussbaumer, R. J. Synthese und Charakterisierung von Rutilnanopartikeln und deren Einbau in transparente Polymer-Nanoverbundwerkstoffe. Ph.D. Thesis No. 15516, ETH Zürich, 2004.
(22) Schmidt, H.-W.; Smith, P.; Blomenhofer, M. WO 02/46300 A2.
(23) Mäder, D.; Hoffmann, K.; Schmidt, H.-W. WO 03102069 A1.
(24) Schmidt, H.-W.; et al. WO 2004072168 A2.
(25) Kristiansen, M.; Werner, M.; Tervoort, T.; Smith, P.; Blomenhofer, M.; Schmidt, H.-W. *Macromolecules* **2003**, *36*, 5150.
(26) Strictly speaking, for these binaries, this temperature actually refers to the crystallization temperature of the eutectic composition (cf. ref. 25), but in view of the minute amounts of the additives in that composition, this is considered to be a semantic issue and, for the sake of simplicity, is ignored here.
(27) Hoffmann, K.; Huber, G.; Mäder, D. *Macromol. Symp.* **2001**, *176*, 83.
(28) Marco, C.; Ellis, G.; Gomez, M. A.; Arribas, J. M. *J. Appl. Polym. Sci.* **2003**, *88*, 2261.
(29) Seferis, J. C. In *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds. Wiley: New York, 1999; p VI/581.

MA0473317