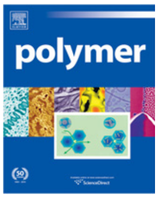
Polymer 51 (2010) 913–921

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



1,3,5-Benzenetrisamide based nucleating agents for poly(vinylidene fluoride)

Frank Abraham, Hans-Werner Schmidt*

Makromolekulare Chemie I, Bayreuther Institut für Makromolekülforschung (BIMF) and Bayreuther Zentrum für Grenzflächen und Kolloide (BZKG), Universität Bayreuth, 95440 Bayreuth, Germany

ARTICLE INFO

Article history:
Received 20 March 2009
Received in revised form
3 December 2009
Accepted 9 December 2009
Available online 16 December 2009

Keywords:
PVDF
Nucleating agents
1,3,5-Benzenetrisamides

ABSTRACT

This paper presents 1,3,5-benzenetrisamides as colorless α–nucleating agents for poly(vinylidene fluoride). In order to screen a large variety of 1,3,5-benzenetrisamide derivatives with respect to their nucleating potential an efficient and reliable test based on polarized light microscopy was established. For selected promising compounds the concentration dependence of the PVDF crystallization temperature, the dissolution behavior of the additive in the polymer melt, and the crystallization of the additive from the polymer melt was investigated in a concentration range between 1 wt% (10,000 ppm) and 70 ppm. It was found, that only two of the investigated compounds were able to raise the crystallization temperature about 8 °C at a concentration of 140 ppm and 580 ppm, respectively. These trisamides have the advantage being soluble in the polymer melt, not featuring absorption of visible light and therefore allowing the preparation of uniform and colorless PVDF products.

1. Introduction

Nucleating agents are wildly used in commercial semi-crystalline polymers to improve the materials properties and to reduce the cycle times in injection molding [1]. Polyvinylidene fluoride (PVDF; $-(CH_2-CF_2)_n-$) is a valuable thermoplastic resin due to its good mechanical strength, rigidity and toughness as well as its wide range of service temperatures and high chemical and temperature resistance [2,3]. This property profile opens applications for PVDF for example in pipes, fittings, pumps, and plenum wires [2,4].

The most common three crystalline polymorphs of PVDF are the α-phase (pseudo orthorhombic with the polymer chain conformation TGTG′), the β-phase (orthorhombic; TTTT) and the γ-Phase (monoclinic; $T_3G\,T_3G$) [5,6]. The α-phase is the most common polymorph and normally obtained by cooling of the melt or from solution for example with a mixture of monochlorobenzene/*N*,*N*-dimethylformamide [6–8]. Organic pigments based on indanthrone, perlyene, quinophthalone and phthalocyanine as well as mineral fillers such as talc, mica and carbon black act as nucleating agents and influence the crystallization kinetics of PVDF [9]. *Lotz* and *Wittmann* determined an efficiency scale by self-seeding experiments and described two nucleating agents for the α-phase of PVDF, notably the polymer PTFE and the yellow pigment flavanthrone [10]. In the β-modification the alternating two hydrogen atoms and two fluorine atoms in the polymer chain $-(CH_2-CF_2)_n-$ are leading to a dipole orientation in the polymer solid state, which therefore shows remarkable piezoelectric [11] and pyroelectric [12] properties. The β-phase is generally obtained by drawing films of the α-phase at relatively low temperatures (50 °C). Mechanical deformation at higher temperatures (150 °C) yields an increased percentage of the α-phase again [13]. Epitaxial growth between β-PVDF and KBr was found by *Lovinger* [14]. Organic sulfates and sulfites, in particular tetrabutylammonium hydrogen sulfate (TBAHS) [15], induce the β-phase from PVDF melt [15]. Solution derived PVDF films comprising magnesium nitrate hexahydrate on silicon substrates were reported to form the β-phase [16]. Also PVDF solutions in dimethyl sulfoxide with high concentrations of crystal violet form the β-polymorph while low concentrations yield the α- and γ-phases [17,18]. *Lovinger* also investigated the unit cell of γ-phase crystals epitaxially grown on Mica and NaCl [19]. Routinely the γ-polymorph is obtained by high temperature annealing (~165 °C) [20] or additivation with KBr powder [21].

Recently 1,3,5-benzenetrisamide based derivatives were introduced as a new class of nucleating agents and clarifiers for isotactic polypropylene (*i*-PP) [22,23]. Certain derivatives are efficient nucleating agents to nucleate the α-phase of *i*-PP at very low concentrations smaller than 200 ppm. A few derivatives are additionally capable to substantially improve the optical properties (clarity and haze) of *i*-PP resulting in a highly transparent *i*-PP for packaging applications. Other derivatives promote the mechanically tough β-phase and hybrids of both crystallographic forms with new combinations of optical and mechanical properties. A major advantage of this class of additives are the organoleptic excellence,

---

* Corresponding author. Tel.: +49 921 55 3200; fax: +49 921 55 3206.
E-mail address: hans-werner.schmidt@uni-bayreuth.de (H.-W. Schmidt).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.12.011

chemical and temperature stability preserving also performance in regrinds. This is particularly important in view of the properties of the currently applied sugar based (i.e. sorbitol or nonitol) clarifiers and nucleating agents, which have drawbacks such as blooming of the additive, thermal decomposition yielding bubble formation, increasing the yellowness index and forming odorous byproducts including migration of the additive itself [24–26].

This paper reports on the potential of 1,3,5-benzenetrisamides to nucleate PVDF in order to find colorless and soluble and therefore easy dispersible nucleating agents. In view of a large number of possible 1,3,5-benzetrisamide structures we established a reliable screening method using polarized light microscopy. Since the nucleation efficiency is strongly dependent on the additive concentration, promising derivatives were selected and investigated in concentrations ranging from 1 wt% (10,000 ppm) to 70 ppm. A comparison of the additive dissolution temperature in the polymer melt, the crystallization of the additive from the polymer melt and the crystallization temperature of PVDF for eight different 1,3,5-benzenetrisamides will be presented. These data are also compared to the commonly used reference compound flavanthrone.

2. Experimental

2.1. Materials

The polyvinylidenfluoride resin (Solef 1008/1001) used in this study, is a high purity, low viscosity, injection molding, powdered grade, purchased from Solvay Solexis [27]. The head-to-head inversion ratio is reported with $\sim$3,5–4% of the vinylidenfluoride homopolymer. Its molecular weight average distributions are given with $M_n \sim 39 \times 10^3$ g/mol, $M_w \sim 110 \times 10^3$ g/mol and $M_z \sim 240 \times 10^3$ g/mol for the corresponding mean. The 1,3,5-benzenetrisamides used, shown in Table 1, were synthesized according to standard procedures [23]. Flavanthrone (purity 98% min.) was purchased from ABCR and used as received.

2.2. Compounding

Powders of PVDF comprising 1.0 wt% of the powdered additives were mixed in a 100 ml tumble mixer for 24 h and afterwards compounded in a laboratory scale co-rotating twin-screw mixer (Technical University Eindhoven, The Netherlands) at 240 °C under nitrogen for 4 min. To produce a concentration series via dilution the mixer was filled with 11.8 g of the additivated PVDF. About 6.0 g of the compounded mixture were discharged. To the remaining 5.8 g additive comprising polymer an amount of 6.0 g of neat PVDF was added resulting in a mixture with 0.49 wt% additive. Again 6.0 g of the mixture were discharged and an addition of 6.0 g neat PVDF results in a mixture of 0.24 wt% These two steps and further dilution runs yielded the additive concentration series: 1.0 wt%, 0.49 wt%, 0.24 wt%, 0.118 wt%, 0.058 wt%, 0.028 wt%, 0.014 wt% and 0.007 wt%. Neat PVDF was treated analogously to obtain control extrudate.

2.3. Thermal analysis

Thermogravimetric analysis (TGA) of the additives was conducted with a Netzsch STA 409 instrument under nitrogen at a heating rate of 10 K/min. Temperatures are reported here at a weight loss of 10%. Melting temperatures of the compounds were simultaneously detected with DTA (differential thermal analysis) and reported as the peak maximum of the endothermic transition. DSC (differential scanning calorimetry) investigations were performed under nitrogen with a Perkin Elmer DSC (Diamond) with sample weights of 7–14 mg at standard heating and cooling rates of 10 K/min. Two heating and cooling scans between 50 °C to 250 °C and 250 °C to 50 °C were performed. Before each cooling scan a temperature of 250 °C was held for 5 min to erase thermal history. Temperatures for the polymer crystallization ($T_{c\,p}$) were determined at the exothermic minimum of the first cooling scan and confirmed by a second cooling scan. Melting temperatures are reported at the maximum of the endothermic peak of the second heating scan.

We used self-seeding experiments as established by *Lotz* et al. [28,29] for polypropylene and adapted for PVDF [10] were performed to determine the efficiency of 1,3,5-benzenetrisamides as nucleating agents. The nucleation efficiency is calculated by:

$$\text{Efficiency}(\%) = 100(\Delta T_c/\Delta T_{cmax}) = 100(T_{cnucl} - T_{c1})/(T_{c2} - T_{c1})$$

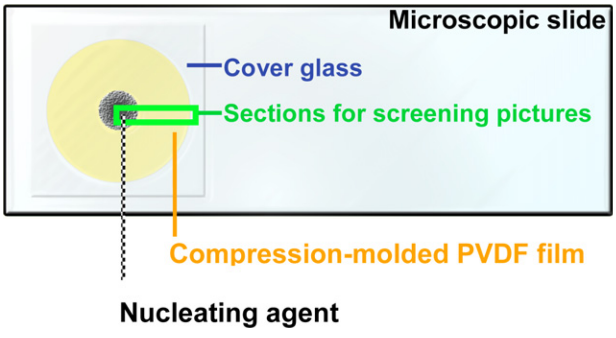
T_{c1} is determined upon cooling with 10 K/min from the melt well above the equilibrium melting temperature where the prior thermal history is erased. By incomplete melting at a selected temperature T_s, which is located in between the maximum of the melting peak and its high temperature end, the optimum concentration of crystalline fragments remain and act as nuclei for the crystallizing polymer upon subsequent cooling. This provides the upper limit of the crystallization temperature T_{c2} and is the case for an ideal self-nucleation. The temperature $T_{c\,nucl}$ reflects the increased crystallization temperature by the addition of a nucleating agent which is measured under the same conditions as T_{c1}. All temperature scans were performed at a cooling rate of 10 K/min and prior to all cooling runs the samples were maintained for 5 min.

2.4. Optical microscopy

Light microscopy was performed between crossed polarizers with an optical microscope (Nikon, DIAPHOT 300) equipped with a hot stage (Mettler, FP82HT). Light optical micrographs were recorded by Nikon ACT-1 software using a digital camera (Nikon, DMX1200) attached to the microscope. Heating and cooling rates were 5 K/min. The dissolution ($T_{d\,a}$) and crystallization temperatures ($T_{c\,a}$) of the additives were determined at disappearance or reappearance of birefringent additive structures at 10 times magnification.

2.5. Screening method

Samples were prepared on a microscopic slide by carefully positioning a small amount of additive in the middle of a thin ($\sim$100 μm) compression-molded PVDF film. The samples were covered and placed, except when otherwise noted, at 280 °C for 10 min on a precision hot plate. Thereafter samples were directly positioned in a hot stage under a microscope equipped with perpendicular positioned polarizers and rapidly cooled to 138 °C. The crystallization processes of the additive and the PVDF were recorded from the live image of ACT-1 software through screen recording with 12 pictures/s and a resolution of 640 × 480 pixels. The sample setup and section where the micrographs were taken is shown below.



2.6. Injection molding

The PVDF and the PVDF additive mixtures were injection molded with a microinjector (DACA Instruments, California) under the following conditions: Barrel temperature of 240 °C, mold temperature of 20 °C and nitrogen blanket. PVDF specimens of 25 mm diameter and 1.1 mm thickness were injection molded.

2.7. WAXD

The above described specimens were used to determine the crystal morphology. Wide-angle X-ray scattering measurements were performed in transmission in the range of $8–30^\circ = 2\theta$ with 0.025° step size at a step time of 10 s with a Bruker D8 Advance X-ray diffractometer using Cu K_α ($\lambda = 0.154$ nm). The d-spacings of the diffraction peaks were calculated by Bragg's formula $2d\sin\theta = n\lambda$ where n is an integer determined by the order given, λ is the X-ray wavelength and θ is the scattering angle giving the diffraction peak [30].

3. Results and discussion

As revealed for *i*-PP the nucleation efficiency and the impact on the physical properties of the polymer solid state depends strongly on the chemical structure of the additives on a molecular level and consecutively on the supramolecular nanoaggregate which acts as nucleus. Subtle changes of the chemical structures can have dramatic effects [22]. The class of 1,3,5-benzenetrisamides contains three structural parts allowing to control the dissolution behavior in the polymer melt, to vary the self-assembly processes on several hierarchical levels and to influence the order of the surface of the nuclei. The benzene core with its 1,3,5-substitution assigns the C_3-symmetry of the molecule and planar structure. The three amide groups are responsible for the well defined formation of intermolecular hydrogen bonds resulting in a pronounced one dimensional self-assembly and crystallization. The peripheral substituents allow fine tuning of the dissolution in the polymer melt, crystallization behaviour of the additive from the polymer melt and more importantly define the order of the surface, responsible for the epitactic nucleation of the polymer. Based on the experience with *i*-PP we investigated several 1,3,5-benzenetrisamide derivatives, with respect to their capability to nucleate polyvinylidene fluoride.

3.1. Chemical structure and properties of the additives

The chemical structures of the different 1,3,5-benzenetrisamides investigated in this study are shown in Table 1. Ten compounds (**1**–**10**) are based on 1,3,5-benzenetricarboxylic acid. The peripheral substituents ranged from short linear aliphatic substituents **1**–**3**, to long branched aliphatic substituents **4**–**8**. In addition cyclohexyl **9**, and the phenyl derivative **10** were investigated. In addition the direction of the amide linkage was inverted. Compounds **11** and **12** are based on 5-aminoisophthalic acid (one amide linkage inverted), **13** and **14** on 3,5-diaminobenzoic acid (two amide linkages inverted) and **15** and **16** on 1,3,5-triaminobenzene (all three amide linkages inverted). In all three pairs the substituents are $R =$ *tert*-butyl and $R =$ cyclohexyl, respectively.

The class of 1,3,5-benzenetrisamides exhibit high melting temperatures or sublime directly at temperatures far above 300 °C. This is due to the formation of strong intermolecular hydrogen bonds during crystallization. Table 1 presents the melting temperatures of the 1,3,5-trisamide derivatives and the temperature at 10% weight loss. From compound **1** with methyl substitution to compound **2** with ethyl substitution both the melting temperature and weight loss temperature is decreased. Increasing the chain length to propyl **3** the melting point is increased again indicating the beginning of an odd even effect which is commonly found in discotic liquid crystalline compounds [31]. Bulky and branched substituents, *tert*-butyl substituent of compound **4** and both pentyl isomers **5** and **6**, resulted in materials which do not melt instead sublime at temperatures about 360 °C and above. It should be noted that these compounds show a 100% weight loss indicating in addition the very high thermal stability. The lowest melting temperature was found with 263 °C for the relatively flexible isopentyl derivative **7**. Increasing the bulkiness by substitution with *tert*-octyl in compound **8** the melting temperature is increased again and occurs at 315 °C. Comparing compound **9** with cyclohexyl substituent to compound **10** with phenyl substituent it is interesting to note that the cyclohexyl derivative has a melting temperature about 60 °C higher than the phenyl derivative. This indicates better packing due to flexibility of the cyclohexane substituent in comparison to the planar and rigid benzene substituent. It is also noticeable that all *tert*-butyl substituted derivatives **4**, **11**, **13** and **15** sublime independently of inversion of the amide bonds. In contrast all the cyclohexyl substituted derivatives **9**, **12**, **14** and **16** show distinct melting transitions, the highest for **9** with 371 °C while the melting temperatures of the other three compounds are in the similar range around 290 °C. For all above 1,3,5-benzenetrisamide based compounds the temperature at a weight loss of 10% is in all examples above 340 °C, indicating that the additives display excellent temperature stability and are suitable for processing temperatures usually applied for PVDF.

As reference, the literature known PVDF nucleating agent, flavanthrone **17**, was also investigated [10,32]. Flavanthrone is a yellow pigment which is highly temperature stable and sublimes above 500 °C.

3.2. Additive screening method

The nucleation properties depend strongly on subtle changes of the chemical structure of the nucleating agent. As consequence many compounds have to be experimentally investigated to find suitable candidates. Therefore a rapid screening process is of great advantage. We utilized polarized light microscopy to efficiently and reliably screen nucleating agents. In view of the PVDF nucleation we investigated more than fifty 1,3,5-benzenetrisamide derivatives in this work.

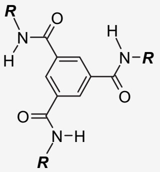
The screening test was conducted in the following way. A compression-molded PVDF film was placed on a microscopic slide and a small amount of additive was carefully positioned in the centre on top of the film. After covering the sample with a cover glass the complete setup was placed on a precision hot plate and kept at 280 °C for 10 min. At this temperature a certain amount of the additive dissolves and diffuses into the PVDF melt. Subsequently the setup was placed in a hot stage at a temperature of 138 °C and observed. A temperature of 138 °C was chosen just below the peak crystallization temperature of neat PVDF (139.3 °C). This allows a slow crystallization rate and does not promote the growth of the γ-phase at high temperature annealing. The crystallization processes were monitored by the optical microscope between crossed polarizers, and recorded with a digital camera. In the supporting information of this paper movies of two 1,3,5-benzenetrisamide derivatives **4** and **6** which nucleate PVDF, one 1,3,5-benzenetrisamide **2** which does not nucleate PVDF and the reference compound flavanthrone **17** can be viewed.

Fig. 1 compares for compounds **4**, **6**, **2** and **17** a sequence of five micrographs at different stages of the crystallization experiment. Micrograph **A** of compound **4** with *tert*-butyl substituents shows in the left area the birefringent non-dissolved whiskers of the additive in the PVDF melt. In micrograph **B** (26 s) the crystallization of the

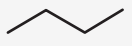
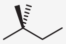
Table 1

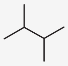
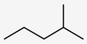
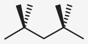
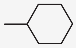
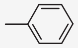
Chemical structures of the substituted 1,3,5-benzenetrisamides **1**–**16**, the melting temperature, temperature at 10% weight loss and results of the screening test obtained by polarized optical light microscopy, as reference the data for flavanthrone **17** are given. The substituents R, are drawn with its bond to amide linkage to the left.

Core: 1,3,5-benzenetricarboxylic acid

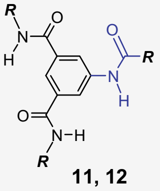


1-10

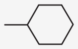
No.	1	2	3	4	5
R					
T_m [°C]	333	282	subl.	289	subl.
$T_{-10\ wt\%}$ [°C]	380	368	380	362	358
Screening	−	−	+	+	+

No.	6	7	8	9	10
R					
T_m [°C]	subl.	263	371	315	312
$T_{-10\ wt\%}$ [°C]	362	374	380	342	412
Screening	+	+	+	+	−

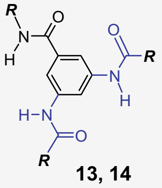
Core: 5-aminoisophthalic acid



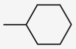
11, 12

No.	11	12
R		
T_m [°C]	subl.	291
$T_{-10\ wt\%}$ [°C]	354	388
Screening	+	−

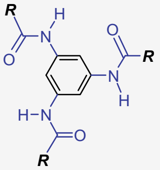
Core: 3,5-diaminobenzoic acid



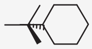
13, 14

No.	13	14
R		
T_m [°C]	subl.	290
$T_{-10\ wt\%}$ [°C]	360	396
Screening	+	−

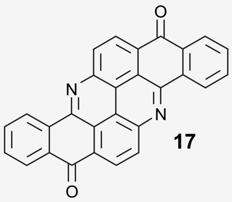
Core: 1,3,5-triaminobenzene



15, 16

No.	15	16
R		
T_m [°C]	subl.	286
$T_{-10\ wt\%}$ [°C]	374	402
Screening	+	−

Reference compound: flavanthrone



No.	17
T_m [°C]	subl.
$T_{-10\ wt\%}$ [°C]	512
Screening	+

T_m: melting temperature; $T_{-10\ wt\%}$: 10% weight loss (heating rate 10 K/min, nitrogen atmosphere); *subl.*: sublimation; *Screening*: (+) nucleation of PVDF; (−) no nucleation.

additive in the proximity of the whiskers occurs. This is visible by the haziness around the whiskers. It should be pointed out that the additive diffused further to the right, but this is not visible in optical light microscopy. However a proof for this is the nucleation of PVDF induced by the additive, which is revealed in micrograph **C** (29 s). The border of the additive containing nucleated area (birefringent) and the area of non-nucleated PVDF (black) is clearly visible at this stage. In micrograph **D** (33 s) the first crystallites of PVDF are formed in the right area without additive. Micrograph **E** (75 s) shows the completely crystallized sample. The three areas (nucleating agent/nucleated PVDF/neat PVDF) are still distinguishable. As expected the spherulite size in the nucleated area is much smaller than in the non-nucleated area.

In comparison compound **6** is better soluble based on the longer and more flexible 1,2-dimethylpropyl-substituent. This is revealed in the sequence of micrographs. Micrograph **A** shows the whiskers of the additive, **B** the crystallization of the additive in the PVDF melt and **C** the induced nucleation of PVDF by the additive. The better solubility and diffusion of the additive in PVDF is noticeable by the fact that the crystallization of the additive and the crystallization of PVDF on the additive surface is shifted further to the right even at shorter times. Micrograph **D** (31 s) shows the crystallization of the neat PVDF (right area), and micrograph **E** the completely crystallized sample. Fig. 2 illustrates the dependence of the spherulite size of crystallized PVDF without and with additive. The samples were prepared under the same conditions by compression molding and cooling from 280 °C to room temperature at a cooling rate of 10 K/min. Micrograph **A** shows the typical spherulite texture of PVDF with diameters up to 30 μm. In Micrograph **B** crystallized PVDF comprising 0.014 wt% of compound **6** is shown. The additive strongly reduces the spherulite size.

With the 1,3,5-benzenetrisamide derivative **2** a compound was selected which does not nucleate PVDF. The additive is very soluble in the PVDF melt. Therefore the diffusion temperature was at 250 °C (5 min). The additive crystallizes uniformly from the PVDF melt (compare micrograph **A** to **C**) and no nucleation occurs induced by the additive. In micrograph **D** the crystallite formation of the neat PVDF starts in the area where no additive is present, and in **E** the sample is completely crystallized. The screening experiments with flavanthrone **17**, the literature know nucleating agent for PVDF, are also shown for comparison. Flavanthrone has, if at all, a very lo6w solubility in the PVDF melt (micrograph **A** and **B**). The

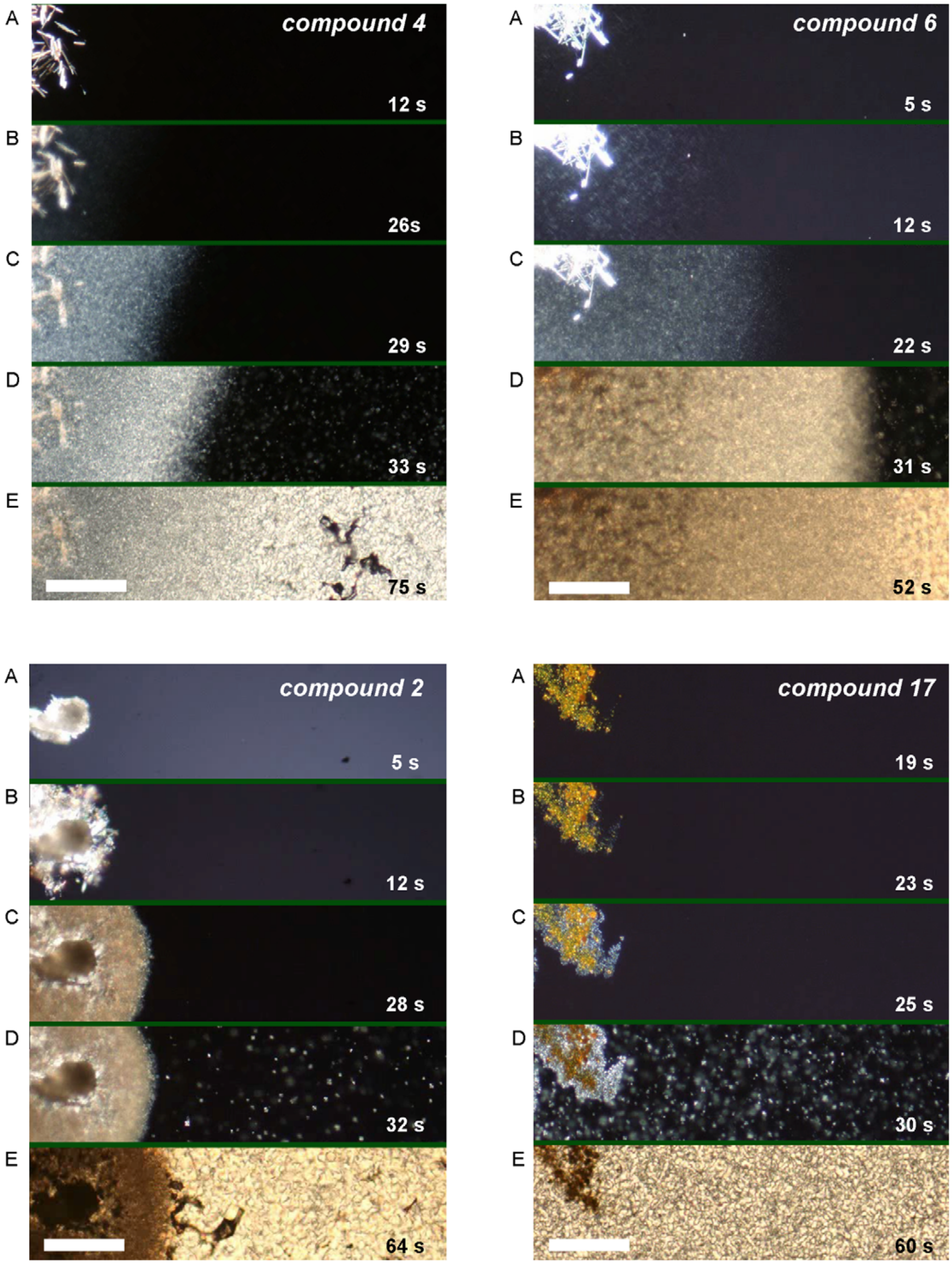


Fig. 1. Optical micrographs of the screening test by polarized light microscopy of the 1,3,5-benzenetrisamides **4** ,**6**, **2** and flavanthrone **17**. The samples were heated, kept at 280 °C for 10 min, rapidly cooled to 138 °C and observed at this temperature. The additive which is placed in the PVDF is on the left area. If soluble, the additive diffuses to the right and induces in case of **4** and **6** nucleation of PVDF. Compound **2** is a negative example were the additive dissolves in the melt and does not induce nucleation of PVDF. Flavanthrone **17** is not dissolved under these conditions and nucleation occurs only on the additive surface. All scale bars are 200 μm.

nucleation of PVDF on the flavanthrone crystals occurs only in close proximity (**C**). Micrograph **D** shows the crystallization of PVDF from the melt in the area were no additive is present. In **E** the sample is completely crystallized and only two regions are visible, confirming the non-solubility of flavanthrone in PVDF.

The above experiments with polarized optical light microscopy demonstrate that the screening test is suitable to reliably and efficiently screen potential polymer nucleating agents. The screening results for the other 1,3,5-benzenetrisamides are presented in Table 1. Distinct nucleation of PVDF is indicated with (+) and no nucleation of PVDF with (−). With exception of compounds with the peripheral substituents methyl (**1**), ethyl (**2**) and phenyl (**10**) all other presented trisamides based on 1,3,5-benzenetricarboxylic acid are capable to nucleate PVDF. An interesting structure–property relation was found by comparing the derivatives **11** and **12**, based on 5-aminoisophthalic acid, **13** and **14** based

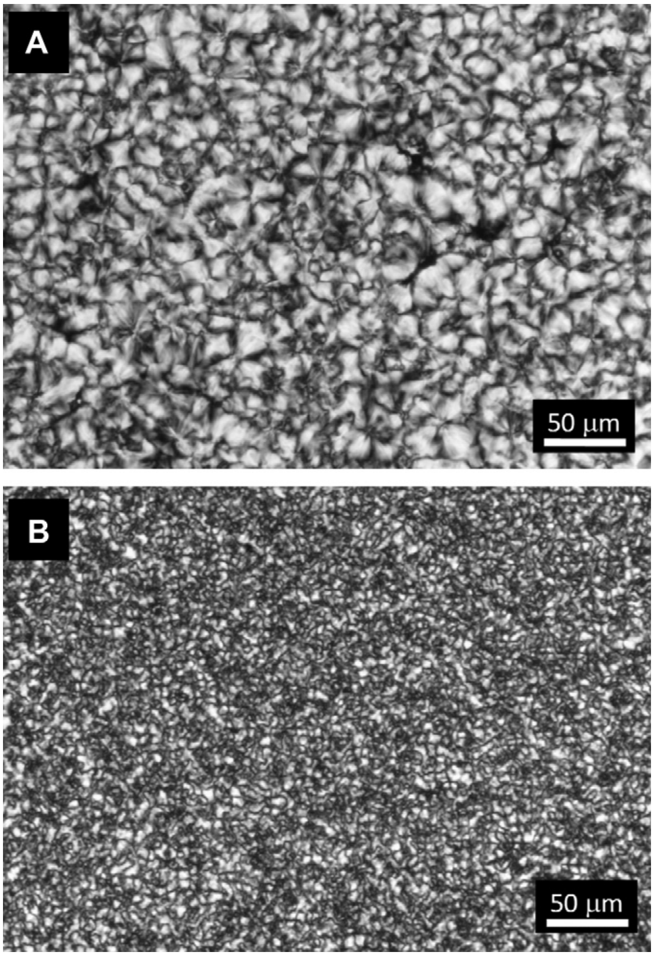


Fig. 2. Optical light micrographs between crossed polarizers of compression-molded PVDF films: (A) PVDF with no additive and (B) PVDF comprising 0.014 wt% of compound **6**. Samples were cooled from 280 °C to room temperature at a cooling rate of 10 K/min. Both micrographs were taken at room temperature.

on 3,5-diaminobenzoic acid amide and **15** and **16** based on 1,3,5-triaminobenzene with the substituents $R = tert$-butyl and $R =$ cyclohexyl. Only the compounds with *tert*-butyl substituent showed a positive nucleating effect for PVDF.

In addition to the compounds presented in Table 1, more 1,3,5-benzenetrisamide derivatives have been screened with respect to the potential to nucleate PVDF. The data are presented in the supporting information to this publication. Most of them showed no nucleation effect. Also several compounds with partially fluorinated, perfluorinated aliphatic and aromatic substituents were investigated. Surprisingly none of them were capable to nucleate PVDF.

3.3. *Additive concentration dependence*

In view that the nucleation properties depend strongly on the concentration, we investigated selected nucleating agents over a concentration range from 1 wt% (10,000 ppm) to 0.007 wt% (70 ppm). To rapidly provide the different concentrations PVDF comprising 1 wt% of additive was diluted with neat PVDF in a twin-screw mixer yielding the following additive concentration series: 1.0 wt%, 0.49 wt%; 0.24 wt%, 0.118 wt%; 0.058 wt%; 0.028 wt%; 0.014 wt% and 0.007 wt%. Crystallization temperatures of the PVDF samples were measured by DSC at a standard heating rate of 10 K/min. Each heating scan was followed by an annealing step for 5 min at 250 °C to erase the thermal history. Crystallization temperatures of PVDF samples comprising the additives are reported at the exothermic peak minimum of the first cooling curve. The second cooling confirmed these crystallization temperatures and showed that no degradation of the additive or the PVDF occurred. The measured crystallization temperature for the non-nucleated PVDF is at 139.3 °C. We also confirmed that no degradation occurred under the processing conditions of the dilution runs. For all runs the crystallization temperature was found at 139.3 ± 0.5 °C. The dissolution temperature and crystallization temperature of the additive in the PVDF melt was determined for each concentration by polarized optical light microscopy. The dissolution temperature was determined at the completed disappearance of birefringent additive in the optically isotropic PVDF melt. The crystallization temperature of the additive from the PVDF melt was determined by the first appearance of birefringent structures. In these experiments the heating and cooling rates were 5 K/min.

The concentration dependence of the nucleation properties, the dissolution temperatures of the additive and the crystallization temperatures of the additive in the PVDF melt are compared for selected compounds in Fig. 3. For each investigated compound the top graphs show the crystallization temperature of PVDF ($T_{c\ p}$, squares) versus the additive concentration and the bottom graphs the dissolution temperature ($T_{d\ a}$, triangles up) and crystallization temperature ($T_{c\ a}$, triangles down) of the additive. The dashed line in the top graphs represents the crystallization temperature of extruded neat PVDF $T_{c\ p} = 139.3$ °C and the dotted line in bottom graphs represents the maximum temperature (250 °C) applied during DSC measurements.

The crystallization temperatures of PVDF as function of the concentration of additive 1,2-dimethylpropyl substituted 1,3,5-benzenetrisamide **6** is presented top left. To ensure reproducibility of the overall procedure, we measured the crystallization temperatures of two different dilution series. With exception of one concentration (0.028 wt%) the crystallization temperatures of PVDF were found to be the same (compare filled and open squares). As already shown in the screening results compound **6** is a good nucleating agent for PVDF. Typically in these diagrams three concentration ranges I, II, III can be identified. In range I the additive concentration is too low and the crystallization of the additive $T_{c\ a}$ occurs not prior to crystallization of PVDF itself. Therefore PVDF is not nucleated by the additive. In range II the additive is completely soluble, upon cooling the additive crystallizes in fine fibrillar structures from the polymer melt providing a surface to induce nucleation. In range III the additive is only partially soluble and nucleation can occur both on the formed fibrillar structures and on the surface of the non-dissolved fraction of the additives. The maximum crystallization temperature of PVDF was found at 147.4 °C for a concentration of 0.058 wt%. It is interesting to note that the crystallization temperature increases in range III with decreasing amount of additive which may be attributed to the better dispersion at lower concentration.

In comparison PVDF comprising additive **4** exhibits in range III a small decrease in the crystallization temperature with decreasing concentration, 149.2 °C at 1 wt% and 147.4 °C at 0.058 wt%. In agreement with the observations from the screening test additive **4** is less soluble in the PVDF melt and the dissolution curve of additive **4** is shifted towards higher temperatures compared to additive **6**. The additive crystallization temperature curve for **4** is somewhat steeper compared to **6**. For this compound **4** range II is almost not present. At lower concentrations (range I) the additive is not crystallized prior to the crystallization of PVDF, consequently no nucleation can occur. Compound **5** is the most efficient 1,3,5-benzenetrisamide to nucleate PVDF. The crystallization temperatures of PVDF comprising additive **5** show a slight increase with

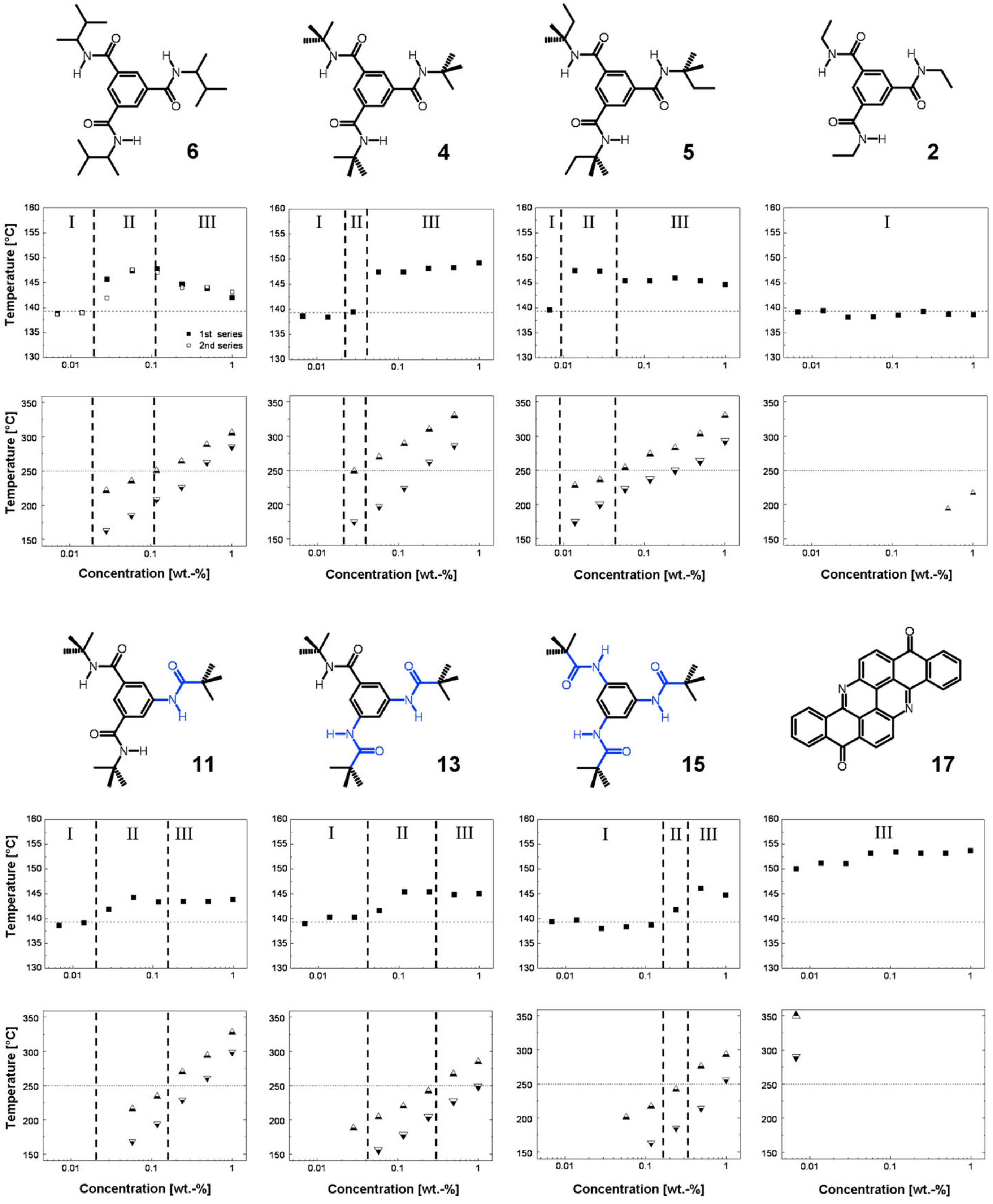


Fig. 3. Comparison of different nucleating agents as function of the concentration with respect to the crystallization temperature of PVDF (squares, top graphs) and the dissolution temperature of the additive in the PVDF melt (triangles up) and crystallization temperature of the additive from the PVDF melt (triangles down, bottom graphs). The dashed line in the top graphs represents the crystallization temperature of extruded neat PVDF $T_{c\ p} = 139.3$ °C. The dotted line in bottom graphs represents the maximum temperature (250 °C) during DSC measurements.

decreasing additive concentration in range III. The maximum crystallization temperature is found in range II at 147.4 °C at only 0.014 wt% (140 ppm). The mixture comprising 0.007 wt% (range I) of compound **5** shows the crystallization temperature of neat PVDF.

As expected from the screening test compound **2** does not promote any nucleation of PVDF. This is confirmed by the DSC measurements. Over the entire investigated concentration range additive **2** does not crystallize from the polymer melt prior to the crystallization of PVDF, due to the too good solubility. This was also seen in the screening test. Only in case of the highest concentrations of 1 wt% and 0.49 wt% the melting of PVDF occurs prior to the dissolution of compound **2**. For both concentrations dissolution temperatures $T_{d\ a}$ could be obtained.

In the following a comparison of four isomeric 1,3,5-benzenetrisamides, all substituted with *tert*-butyl substituents will be presented. All four compounds are capable to nucleate PVDF. Additive **4** is based on 1,3,5-benzenetricarboxylic acid. In the additives **11**, **13** and **15** the amide linkage is subsequently inverted. Additive **11** is based on 5-aminoisophthalic acid, **13** on 3,5-diaminobenzoic acid and **15** on 1,3,5-triaminobenzene. These very moderate structural changes yielded better solubility of the additive in the polymer melt. The lowest solubility exhibits additive **4**, the highest solubility was found for additive **15**. As consequence a higher additive content is required to achieve a maximum in the crystallization temperature of PVDF. The lowest concentration which yields a maximum crystallization temperature was found for additive **4** at 0.058 wt% with a T_c 147.4 °C. Additive **11** resulted in a lower T_c of 144.2 °C at the same concentration Additive **13** has at a two fold increased concentration of 0.118 wt% a T_c of 145.4 °C. Compared to compound **4**, additive **15** requires a more than eight fold increased concentration and exhibits at 0.49 wt% a T_c of 146.1 °C. All three compounds **11**, **13**, **15** show the already discussed three concentration rages I to III.

All the above additives induce the nucleation of the α-phase of PVDF. This was confirmed by the melting behavior obtained from DSC-heating curves as well as wide angle X-ray diffraction (WAXD). *Yang* and *Thomas* [33] reported the melting point of the α phase at around 174 °C and for the β phase at around 184 °C. *Priya* and *Jog* [34] published a melting temperature of the α phase for Solef 1008 at 172 °C and of the β phase at around 178–180 °C depending on nanoclay content used as nucleating agent. All PVDF samples comprising compounds from Fig. 3 have a maximum in the melting curve at around 173 °C (second heating scan). A higher melting peak indicating the β phase, was not observed. The WAXD investigations revealed the typical α peaks for $2\theta = 17.7°$, 18.4° and 19.9°, with the corresponding d-spacing of 0.500 nm, 0.482 nm and 0.446 nm which can be attributed to the diffractions in the (100), (020) and (021) planes, respectively. The β-peaks [4,34] for $2\theta = 20{,}8°$ and 20,7° with the corresponding d-spacing of 0.427 nm and 0.429 nm of the [(110) + (200)] planes were not observed in the control samples.

3.4. *Nucleation efficiency*

In order to compare the nucleation efficiency of 1,3,5-benzenetrisamides to the commonly known α-nucleating agent flavanthrone [10] we utilized a reported procedure. This procedure is based on self-seeding experiments established by the group of *Lotz* and *Wittmann* for polypropylene [28,29] and PVDF [10]. As a result of the higher melting temperature of the Solef 1008 PVDF ($T_m = 173.0$ °C) compared to grade Kynar 740 used in the literature the temperature T_s to induce self nucleation was in our case at 176.0 °C yielding a maximum crystallization temperature T_{c2} of 156.7 °C.

For the best three additives we calculated the efficiencies and will compare them to the reference compound flavanthrone. The most efficient additives were found to be compound **4** ($E = 56.9\%$, $T_{c\ nucl} = 149.2$ °C at 1 wt%), compound **5** ($E = 46.6\%$, $T_{c\ nucl} = 147.4$ °C at 0.014 wt%; compared to flavanthrone $E = 68.4\%$, $T_{c\ nucl} = 151.2$ °C at 0.014 wt%), and compound **6** ($E = 46.6\%$, $T_{c\ nucl} = 147.4$ °C at 0.058 wt%). However the efficiency of flavanthrone **17** was not reached. As shown in Fig. 3 flavanthrone is a remarkably good nucleating agent for PVDF. Over the entire investigated concentrations the crystallization temperatures are in the range from 150.0 °C to 153.7 °C. This yields for example a nucleation efficiency of $E = 79.9\%$ ($T_{c\ nucl}$ 153.2 °C) for flavanthrone at a concentration of 0.49 wt%. In the literature a similar efficiency of $E = 83.3\%$ ($T_{c\ nucl}$ 143.5 °C) at a concentration of 0.5 wt% was reported for flavanthrone in the PVDF grade Kynar 740 [10].

4. Conclusion

Certain 1,3,5-benzenetrisamide derivatives are capable to efficiently nucleate PVDF. Namely the derivative *N*,*N*′,*N*″-tris(1,1-dimethylpropyl)-1,3,5-benzenetricarboxamide (**5**) increases the PVDF crystallization temperature to 147.4 °C at a very low concentration of 140 ppm. In contrast to the literature reported nucleating agent flavanthrone 1,3,5-benzenetrisamides are soluble under standard PVDF processing conditions allowing an easy dispersion of the additive in the PVDF melt. In addition 1,3,5-benzenetrisamides do not feature the absorption in the range of visible light yielding colorless PVDF products, whereas the pigment flavanthrone yields strongly yellow colored products even at additive concentrations as low as 70 ppm.

This comprehensive study demonstrates also that in a given family of compounds it is the individual chemical structure which determines the nucleation efficiency. Up to now this cannot be predicted and therefore detailed experimental investigations on structure–property relations have to be carried out. In this context the reported screening test is a reliable and useful tool. However detailed investigations with respect to the concentration dependence have to be carried out to fully evaluate the performance of a nucleating agent.

Acknowledgment

We gratefully acknowledge Sandra Ganzleben and Doris Hanft (Makromolekulare Chemie I, Universität Bayreuth) for the synthesis and characterization of most of the 1,3,5-benzenetrisamides.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the on-line version, at doi:10.1016/j.polymer.2009.12.011.

References

[1] Zweifel H, editor. Plastics additives handbook. 5th ed.; 2001.
[2] Domininghaus H, Eyerer P, Elsner P, Hirth T, editors. Plastics and their characteristics. 6th ed.; 2005.
[3] Lovinger AJ. Developments in Crystalline Polymers 1982;1:195.
[4] Salsmone JC, editor. Polymeric Materials Encyclopedia, Twelve Volume Set; 1996.
[5] Bachmann MA, Gordon WL, Koenig JL, Lando JB. Journal of Applied Physics 1979;50:6106.
[6] Hasegawa R, Kobayashi M, Tadokoro H. Polymer Journal 1972;3:591.
[7] Prest Jr WM, Luca DJ. Journal of Applied Physics 1975;46:4136.
[8] Lovinger AJ. Journal of Polymer Science: Polymer Physics Edition 1980;18:793.
[9] Pillin I, Pimbert S, Levesque G. Polymer Engineering and Science 2002;42:2193.
[10] Schneider S, Drujon X, Lotz B, Wittmann JC. Polymer 2001;42:8787.
[11] Kawai H. Japanese Journal of Applied Physics 1969;8:975.

[12] Bergman JG, McFee JH, Crane GR. Applied Physics Letters 1971;18:203.
[13] Lando JB, Olf HG, Peterlin A. Journal of Polymer Science Part A-1: Polymer Chemistry 1966;4:941.
[14] Lovinger AJ. Polymer 1981;22:412.
[15] Kitamura H, Teramoto Y, Matsunaga S. EP 942038.
[16] Chen S, Yao K, Tay FEH, Liow CL. Journal of Applied Physics 2007;102:104108/1.
[17] Schmolke R, Künstler BEW, Danz R, Geiss D. Acta Polymerica 1988;39:164.
[18] Danz R, Elling B, Kuenstler W, Hirsch G. DD 298188.
[19] Lovinger AJ. Macromolecules 1981;14:322.
[20] Lovinger AJ. Journal of Applied Physics 1981;52:5934.
[21] Miyazaki T, Takeda Y, Akasaka M, Sakai M, Hoshiko A. Macromolecules 2008;41:2749.
[22] Blomenhofer M, Ganzleben S, Hanft D, Schmidt H-W, Kristiansen M, Smith P, et al. Macromolecules 2005;38:3688.
[23] (a) Schmidt H-W, Smith P, Blomenhofer M. WO 2002046300;
(b) Maeder D, Hoffmann K, Schmidt H-W. WO 2003102069;
(c) Schmidt H-W, Blomenhofer M, Stoll K, Meier H-R. WO 2004072168.
[24] McDonald JG, Cummins CL, Barkley RM, Thompson BM, Lincoln HA. Analytical Chemistry 2008;80:5532.
[25] Mannion MJ. US 5198484.
[26] Phan H-D, Killough L, Santamaria E. Proceedings of the 5th European Conference on "Additives & Colors". Mondorf-les-Bains, Luxembourg; Mar. 14-15 2007. 69.
[27] (a) Deberraly JM. Ultrapure Water 1987;4:36;
(b) SOLEF 1008 PVDF product Datasheet SOLVEY.
(c) Solef Pvdf brochure - "Physical properties" SOLVAY - Br 1527d-B-1–0302.
[28] Fillon B, Lotz B, Thierry A, Wittmann JC. Journal of Polymer Science Polymer Physics 1993;31:1395.
[29] Fillon B, Wittmann JC, Lotz B, Thierry A. Journal of Polymer Science, Part B: Polymer Physics 1993;31:1383.
[30] Polanyl M. Zeitschrift Für Physik A Hadrons and Nuclei 1921;7:149.
[31] (a) Demus D, Goodby JW, Gray GW, Spiess HW, Vill V, editors. Handbook of liquid crystals, vol. 4. Weinheim, Germany: Wiley-VCH; 1998;
(b) Matsunaga Y, Miyajima N, Nakayasu Y, Sakai S, Yonenaga M. Bulletin of the Chemical Society of Japan 1988;61:207.
[32] Masahiro S, Yukichika K. US 3701749.
[33] Yang DC, Thomas EL. Journal of Materials Science Letters 1984;3:929.
[34] Priya L, Jog JP. Journal of Applied Polymer Science 2003;89:2036.