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From Heptazines to Triazines – On the Formation of Poly(triazine imide)

Fabian K. Kessler^[a] and Wolfgang Schnick^{*[a]}

Abstract. Poly(triazine imide), a 2D extended carbon nitride network compound that is obtained from ionothermal synthesis in LiCl/KCl or LiBr/KBr salt melt has been known for over a decade. We now have investigated the formation process of this material starting from various triazine- and heptazine-based precursors as well as the differences between ionothermal and conventional synthesis via thermal condensation. Independent of chosen starting material, melem (triamino-*s*-heptazine) is initially formed from the starting material as the imminent precursor to poly(triazine imide). We elucidate the impact of various different carbon nitride precursor compounds on the formation process, propose a mechanism for the back reaction of heptazines to triazines, and rationalize the occurring processes.

Introduction

Recent research in carbon nitride chemistry concerns itself almost exclusively with a single compound, namely polymeric carbon nitride (PCN), often also denoted as Liebig's melon or misleadingly as graphitic C₃N₄ (g-C₃N₄).^[1-3] This material with an approximate composition close to C₆N₉H₃ that, however, shows some variability, exhibits electronic properties that make it a promising candidate as a photocatalyst for various applications, such as pollutant degradation for wastewater purification, bacterial disinfection, CO2 reduction for photochemical fuel generation and most prominently H₂ generation via photocatalytic water splitting.^[4,5] The means to optimize PCN for these purposes include nanostructuring, metal and nonmetal doping and formation of heterojunctions and composite materials of various kinds.^[6-9] While the number of different approaches is large, the basic material almost always stays the same. Other carbon nitride materials, that exhibit very similar properties, are often overlooked due to a more complex synthesis process or simply because they are less known.

One such compound that especially deserves attention is poly(triazine imide) (PTI), an intercalation compound obtained from lithium halide salt melts.^[10,11] PTI is a 2D layered material based on sheets of imide-connected triazine rings. This is in stark contrast to PCN, which is generally assumed to be based on heptazine units interconnected by imide groups.^[12,13] The structure of poly(triazine imide) contains hexagonal channels along the crystallographic *c* axis in which Li⁺ and X^- (X = F, Cl, Br) ions are incorporated.^[11,14] Consequently, these compounds are often also denoted as PTI/Li⁺X⁻. For the carbon nitride network a sum formula of C₆N₉H₃ is obtained, which is identical to the formula of heptazine-based melon, an

* Prof. Dr. W. Schnick
E-Mail: wolfgang.schnick@uni-muenchen.de
[a] Department of Chemistry
Chair in Inorganic Solid-State Chemistry
University of Munich (LMU)
Butenandtstraße 5–13
81377 Munich, Germany

idealized variant of PCN.^[15,16] Furthermore, PTI/Li⁺Cl⁻, the most well characterized compound in this family, is known to possess H/Li disorder, thereby incorporating additional Li⁺ ions that substitute imide bound protons, resulting in a formula of $[(C_3N_3)_2(NH_xLi_{1-x})_3\cdot LiCl]$.^[17]

PTI, just as PCN, exhibits an extended conjugated π -system and therefore likewise is a semiconductor, with a bandgap of 2.8 eV.^[18] This is very close to PCN, for which a bandgap of 2.7 eV has been reported.^[19] However, for PTI it has been shown that the bandgap directly depends on the degree of LiCl loading and drops from 2.8 eV in the absence of LiCl to 2.2 eV for fully loaded PTI/Li+Cl-. This should give PTI a significant advantage over PCN concerning photocatalytic applications, since tunability of the bandgap is crucial in the optimization of light harvesting. Photocatalysis experiments showed that crystalline PTI exhibits a 20% increased hydrogen evolution rate compared to raw melon, as well as an increased oxygen evolution rate in the complementary half-reaction of water splitting.^[20,21] This can be rationalized not only by more suitable electronic properties, but also a much higher surface area for PTI.^[21] Doping of PTI with more carbon-rich heterocycles such as 4-amino-2,6-dihydroxypyrimidine or 2,4,6-triaminopyrimidine further increases the photocatalytic activity to up to 6 times the activity measured for melon-based materials.^[20,22] Nanostructuring of PTI via exfoliation is reported to yield PTI nanosheets whose photocatalytic activity is 8 times that of PCN and 17 times the activity of raw melon.^[23]

Apart from water splitting, several other potential applications for PTI have been proposed in recent years. In dye-sensitized solar cells PTI-based counter electrodes could replace conventional Pt electrodes, thereby dramatically reducing the prize while maintaining a comparable power conversion efficiency.^[24] Due to its porosity, PTI has also been proposed as a N₂-selective membrane for flue gas purification.^[25] Furthermore, it deserves mention that an even higher condensed carbon nitride phase of composition C_3N_4 has reportedly been found as a side phase in PTI/Li⁺Br⁻ syntheses. This triazinebased graphitic carbon nitride (TGCN) is noteworthy in that it

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represents the only known carbon nitride phase that is completely free of hydrogen.^[26]

Thus, PTI appears to be a material of great significance. However, apart from the necessity of salt melts in the synthetic process very little is known about its formation. For PCN (or melon) the formation process is well known (Scheme 1). Starting from the molecular precursor melamine (triamino-*s*-triazine) a cascade of thermally induced condensation reactions is started, leading initially to the formation of the dimeric triazine compound melam [bis(diamino-*s*-triaziny1)amine], which under further deammonation forms melem (triamino-tri-*s*-triazine). At further elevated temperatures melem condenses into heptazine-based polymers that make up PCN.^[12,15,27,28]



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Scheme 1. Carbon nitride compounds and condensation reaction pathways. Dashed arrows indicate reaction pathways of thermal condensation, bold arrows indicate reaction pathways in salt melt.

It should be noted that above temperatures of 380 °C all of the compounds appearing in this reaction cascade are heptazine-based.^[28] The formation of triazine-based PTI at 550 °C exemplifies the fundamental influence of salt melts as a reaction medium. This contrast to classic solid-state syntheses makes the investigation of the occurring mechanisms all the more important. In this work, we have examined the formation mechanism of PTI/Li⁺Cl⁻ and PTI/Li⁺Br⁻ in order to gain further insights into these promising materials as well as the fundamental mechanisms in the formation of carbon nitride compounds in general.

Results and Discussion

In order to elucidate the formation pathway of PTI, several series of synthesis experiments were conducted. PTI/Li⁺Cl⁻ and PTI/Li⁺Br⁻ were synthesized in LiCl/KCl and LiBr/KBr salt melts, respectively, according to literature.^[10,14] Mixtures of the respective salt melt and varying carbon nitride precursors – namely dicyandiamide, melamine, melam, melem, and melon – in a weight ratio of 5:1 were sealed in silica glass ampoules, quickly heated to reaction temperature and then rapidly quenched after a defined amount of time by submerging the hot ampoules in ice water. Both salt melts were applied in copious excess. The obtained products were identified by IR spectroscopy and powder X-ray diffractometry. Results of syntheses in LiCl/KCl melt are listed in Table 1 and for LiBr/KBr melt in Table 2.

Products obtained after each time step can be seen as intermediate steps in the condensation process of PTI. In the case of the chloride salt melt as well as the bromide salt melt the reactions appear to proceed with only moderate speed so that defined intermediate products, themselves thermodynamically stable compounds, could be isolated. Starting materials with a low degree of condensation yielded especially valuable insights, as they allowed us to map the complete pathway of PTI condensation. In LiCl/KCl, dicyandiamide yielded melam after 5 min and it took up to 20 min to completely convert it to heptazine-based melem. This is, in itself, noteworthy since the condensation pathway from melamine to melem and the role of melam in it has not been unambiguously elucidated, as well. There are indications for a direct conversion of melamine to melem as well as for a route that contains melam as an intermediate in the form of adduct compounds of melamine and melem on the one and melam and melem on the other hand.^[29,30] At least for syntheses in salt melts our results seem to favor the latter route.

Comparing reactions in LiCl/KCl to those in LiBr/KBr melt, it appears that in bromide melt at least the initial steps proceed swifter than in chloride melt, in which products of low degrees of condensation (melamine, melam) could still be observed after longer periods of heating. However, it cannot unambiguously be determined whether this is due to a facilitated reaction process in the bromide melt or simply due to concentration effects, considering that under the chosen conditions experiments in bromide melts applied a higher carbon nitride precursor concentration than those in chloride melts.

Independent of the chosen precursor and so observed for both investigated salt melt systems, melem takes a central position in the reaction pathway. Not only is it observed in every series of experiments and the dominating product over a long period of time, it also appears to be the imminent step in the pathway before the formation of the final product PTI. In this, eine Chemie

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Table 1.	Products	obtained a	from s	vntheses ir	1 LiCl/KCl	melt	after	defined	amounts	of	time.
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Starting material	Product after 5 min	Product after 10 min	Product after 20 min	Product after 30 min	Product after 120 min	Product after 720 min
Dicyandiamid Melamine	Melam Melamine + melam Melam	Melem + melam Melem + melam	Melem Melem+ melam	Melem Melem	PTI/Li ⁺ Cl ⁻ PTI/Li ⁺ Cl ⁻ PTI/Li ⁺ Cl ⁻	PTI/Li ⁺ Cl ⁻ PTI/Li ⁺ Cl ⁻ PTI/Li ⁺ Cl ⁻
Melem Melon	Melem Melon	Melem Melon	Melem Melon	Melem Melon	PTI/Li ⁺ Cl ⁻ Melon	PTI/Li+Cl- PTI/Li+Cl-

Table 2. Products obtained from syntheses in LiBr/KBr melt after defined amounts of time.

Starting material	Product after 5 min	Product after 10 min	Product after 20 min	Product after 30 min	Product after 120 min	Product after 720 min
Dicyandiamid	Melem	Melem	Melem	Melem	PTI/Li+Br-	PTI/Li+Br- + melem
Melamine	Melem	Melem	Melem	Melem	PTI/Li+Br-	PTI/Li+Br- + melem
Melam	Melem	Melem	Melem	Melem	PTI/Li+Br- + melem	PTI/Li+Br-
Melem	Melem	Melem	Melem	Melem	PTI/Li+Br- + melem	PTI/Li+Br-
Melon	Melon	Melon + melem	Melem	Melem	Melem	PTI/Li+Br-

we want to point out the experiment utilizing melon as starting material in LiBr/KBr melt, where depolymerization of melon towards monomeric melem was observed. This is the back reaction of the condensation of melem, which was considered irreversible. The mechanism of this back reaction is yet unclear. However, since melon is derived from melem via condensation and release of ammonia, a source of NH₃ would be required. As the only potential source is melon itself, it has to be assumed that under the chosen reaction conditions a certain degree of decomposition takes place. This would have to yield an additional carbon-rich decomposition product such as graphite or an even higher condensed carbon nitride compound. However, no such byproduct could be detected. It therefore has to be assumed that any further decomposition products are either gaseous or soluble in water and thus removed together with the salt melt during workup. As the thermodynamic driving force of this back reaction, we propose solvation effects. The suitability of eutectic LiCl/KCl melts as a solvent for nitrides, cyanates, thiocyanates, and cyanides has been shown by Sundermeyer as early as 1961.^[31-35] Melon is known to exhibit very poor solubility in any solvent due to its polymeric nature and tight hydrogen bridge network. It is highly probable that monomeric melem would possess a better solubility and thus be dissolved in the salt melt, making the depolymerization energetically favorable.

Since all the conducted experiments indicate melem as the precursor compound of PTI – even in case of triazine-based starting materials such as melamine or melam – another aspect requires thorough discussion: the formation of a triazine-based material from a compound exclusively comprised of heptazine nuclei. The formation of heptazine nuclei from triazines is a well known process and although the mechanism of this conversion has not been unambiguously elucidated, several feasible propositions have been discussed in literature.^[13] A mechanism based on the addition of cyanamide, generated through decomposition of melamine, to an undecomposed melamine molecule has been proposed by *May*.^[36] This is followed by ring closure reactions accompanied by the elimi-



Scheme 2. Proposed reaction mechanisms for the transformation of triazine-based melamine to heptazine-based melem, (a) as proposed by *May*, (b) in analogy to *Shahbaz et al.*^[36,37]

nation of ammonia (Scheme 2a). Another postulated mechanism comprises the addition of two molecules of dicyandiamide to melamine, followed by elimination of cyanamide, in



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analogy to the synthesis of unsubstituted tri-s-triazine by Shahbaz et al. (Scheme 2b).^[13,37]

As mentioned above for the depolymerization of melon, the formation of PTI from melem indicates the reversibility of the formation of the heptazine nucleus. Depending on the mechanism of this reaction, either ammonolysis or nucleophilic addition of cyanamide would be required as a first step in the back reaction, thus a certain amount of ammonia or cyanamide has to be formed in advance to initiate this process. The back reaction step appears to occur for any chosen carbon nitride precursor and thus independent of the autogenic ammonia pressure inside the reaction vessel, which would be created by prior condensation reactions (such as of melamine or melam to melem). A certain degree of decomposition has thus to be assumed, at least for reactions starting from melem or melon. However, since this would potentially lead to a variety of further gaseous compounds, including cyanamide, within the ampoule, no clear preference for any of the above presented mechanisms can be derived. No intermediates of either of the two proposed routes could be isolated - supposedly because they are rather short-lived - thus neither could any indication be obtained in this way. We do tend, however, towards the mechanism depicted in Scheme 2a, as it is easily imaginable for the intermediate to form the carbon nitride network of PTI.

We propose a mechanism, in which a ring opening is induced ammonolytically in melem. The 2D network of triazine rings is then formed through condensation of two such intermeditates under deammonation (Scheme 3). In this a guanyl C atom is attacked nucleophilically by an amino group and ammonia eliminated from the guanyl group. In a second step, the ring is closed and a second amino group of the guanyl group is eliminated as ammonia. The salt melt would propagate this reaction by stabilizing the intermediate, which should exhibit a greater solubility than melem. As product, 1D zigzag strands of melon-analogous poly(aminoimino)triazine would be ob-



Scheme 3. Reaction mechanism proposed for the formation of poly(triazine imide) from an intermediate of the melamine-to-melem reaction. tained. In a final step, these strands could condense along their backbones to form 2D extended sheets of poly(triazine imide).

This mechanism allows to draw analogies to poly(heptazine imide) (PHI), another 2D extended carbon nitride compound. PHI can also be obtained from LiCl/KCl salt melt, however, using substituted triazoles or tetrazoles as starting materials,^[38,39] thus requiring a formation mechanism that fundamentally diverges from all herein described mechanisms for C/N/H compound formation. However, the material has also been obtained as a side phase of melon syntheses in closed ampoules under rather harsh conditions and thus a second reaction pathway appears to be viable.^[40] Although this process has neither been elucidated, a mechanism is immediately evident when assuming melon as the precursor and the formation of PHI as a further condensation step. This would require just the same type of polycondensation along the strand backbones that we propose for PTI. Considering the obvious structural relationship between PHI and PTI, it seems only sensible to expect a melon-like precursor for the latter.

Conclusions

We have investigated the formation mechanism of poly(triazine imide) (PTI) in LiCl/KCl and LiBr/KBr salt melt. For this, reactions starting from various different carbon nitride precursor materials were carried out for short durations of time between 5 and 720 min and then quenched and the obtained products analyzed by IR spectroscopy and powder X-ray diffraction.

It could be observed that independent of the chosen precursor melem was formed prior to the formation of PTI. This is remarkable since it necessitates reversing the heptazine formation reaction to obtain triazine-based PTI. To elucidate this curious behavior we thoroughly discussed the formation mechanism of the heptazine core from triazine-based precursors and, based on this, proposed a mechanism for the melemto-PTI transformation. In this, the melem heptazine nucleus undergoes ring opening via ammonolysis, followed by condensation reactions, in which 1D strands of poly(aminoimino)triazine are formed, which form 2D PTI sheets via polycondensation. The latter part of this is compared to a proposed formation mechanism for poly(heptazine imide) from melon.

The importance of solvation effects in the salt melt is discussed as an explanation for the diverging reaction behavior compared to conventional thermal condensation of carbon nitride compounds, which lead to melon instead. Furthermore, it could be shown that in salt melts melon experiences depolymerization to monomeric melem, which then reacts on towards PTI.

We hope that the insights gained from these investigations lead to greater understanding of the yet only poorly examined processes of carbon nitride condensation and could thus allow a more directed synthesis of carbon nitride materials.

Experimental Section

Chemicals: Dicyandiamide (99%) was purchased from Avocado, melamine (\geq 99%) was purchased from Fluka, melam, melem, and

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melon were prepared according to literature (see below). Lithium chloride (pure) was purchased from AppliChem, lithium bromide (98%) was purchased from Fluka, potassium chloride (99.5%) and potassium bromide were purchased from Merck Chemicals GmbH.

Preparation of Melam: Melam was prepared in a two-step synthesis via melamium chloride ammonium chloride.^[27,41] Melamine (365 mg, 2.90 mmol) and ammonium chloride (83 mg, 1.56 mmol) were ground together and sealed in a glass ampoule (length 120 mm, inner diameter 11 mm). The ampoule was heated to 723 K in a vertical tube furnace with a rate of 1 K·min⁻¹, held at this temperature for 12 h and cooled to room temperature with 6 K·min⁻¹. The melamium chloride ammonium chloride adduct sublimed at the upper end of the ampoule was stirred in aqueous ammonia solution (25%) for 2 h and washed with water. The thus obtained melam hydrate was dried in a muffle furnace at 473 K for 12 h to yield melam as a colorless powder. The product was identified by FTIR spectroscopy and powder X-ray diffractometry.

Preparation of Melem: Melamine (30.09 g, 239 mmol) in a porcelain crucible covered with a lid was placed in a muffle furnace pre-heated to 473 K and heated to 673 K with 10 K·min⁻¹. It was held at this temperature for 24 h and then cooled to room temperature at 10 K·min⁻¹. The product was ground with mortar and pistil and exposed to the identical temperature program again. Melem was obtained as a pale beige powder. The product was identified by FTIR spectroscopy and powder X-ray diffractometry.

Preparation of Melon: Melamine (37.82 g, 300 mmol) in a porcelain crucible covered with a lid was placed in a muffle furnace pre-heated to 473 K and heated to 773 K with 10 K·min⁻¹. It was held at this temperature for 24 h and then cooled to room temperature at 10 K min⁻¹. The product was ground with mortar and pistil and exposed to the identical temperature program again. Melon was obtained as a yellow powder. The product was identified by FT-IR spectroscopy and powder X-ray diffractometry.

Synthesis of PTI/Li⁺Cl⁻: Carbon nitride precursor material (100 mg) was ground together with 500 mg of a eutectic salt mixture, either LiCl (226 mg, 5.44 mmol) and KCl (274 mg, 3.67 mmol) or LiBr (239 mg, 2.75 mmol) and KBr (261 mg, 2.19 mmol), and sealed in silica glass ampoules (length 120 mm, inner diameter 11 mm). Amounts of salt were chosen well in excess as described in literature.^[10,14] Following these protocols, identical weights of chloride melt and bromide melt instead of identical amounts of substance were used for practical reasons, since no significant influence was expected. The ampoules were placed in a vertical tube furnace pre-heated to 773 K and kept there for either 5 min, 10 min, 20 min, 30 min, 120 min, or 720 min. Afterwards, the ampoule was removed from the hot oven and the reaction quenched by submerging in an ice-water mixture. The reaction product was isolated and identified by FT-IR spectroscopy and powder X-ray diffractometry.

General Techniques: FT-IR spectra were recorded with a Perkin–Elmer BX II FTIR spectrometer equipped with a DuraSampler Diamond ATR (attenuated total reflection) unit. Measurements were conducted at room temperature under exposure to air. Powder X-ray diffractograms were recorded with a Huber Imaging Plate Guinier Diffractometer G670 (guinier geometry, Cu- $K_{\alpha 1}$ radiation, $\lambda = 1.5406$ Å) equipped with a CCD camera and an oscillating flat specimen holder.

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Keywords: Carbon nitrides; Layered compounds; Ionothermal synthesis; Reaction mechanisms; Heterocycles

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F. K. Kessler, W. Schnick* 1-7

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