(Supercritical) Ammonia for Recycling of Thermoset Polymers

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Summary: Chemical recycling of thermosetting bisphenol-A-polycyanurate, triphenylisocyanurate and of N-phenylmaleimide (pPMI) as well as 4,4′-methylenbis-(4-N-phenylmaleimide) (pBMI) has been studied. Polycyanurate thermosets undergo ammonolytic degradation to the level of oligomeric soluble products already at room temperature, complete degradation to bisphenol-A and melamine, however requires supercritical conditions (160 °C) and longer reaction times. Polyimides prepared by free radical polymerisation after ammonolysis at 160 °C give the corresponding amines and linear polymers with unsubstituted imide and diamide units. SEC of the polymer analogous (with respect to the carbon chain) reaction products and of linear pPMI shows that the polymers have a polymodal molar mass distribution with a high molar mass and an oligomeric fraction.

Keywords: ammonolysis; dicyanate thermoset; polyimides; recycling

Introduction

Recycling of thermosetting polymers is more challenging than that of thermoplastic polymers since materials recycling is not an option for thermosets because of their cross-linked nature. First choice for non-contaminated thermoplastics is materials recycling, followed by chemical recycling including pyrolysis and energy recycling as last option. Cross-linked polymers cannot be reprocessed without decomposition, hence materials recycling is not an option for this class of polymeric materials. Chemical recycling to give useful monomeric and other low molar mass compounds also requires thermoset polymers that contain functional groups amenable to controlled chemical reactions.

Pyrolysis of thermosets, which can be used to recover the inorganic fraction (glass fibres, magnetic metals etc.), has been studied.[1–3] Chemical recycling of ester group containing thermosets by alcoholysis,[4] glycolysis,[5] and acetolysis[6] has been reported in the literature. Braun et al. described hydrogenolysis of anhydride cured epoxy resins, phenolic resins, melamine formaldehyde and unsaturatated polyester thermosets.[7]

In our studies with ammonia as reaction medium[8] and reagent[9] we found that bisphenol-A-polycarbonate can be chemically recycled in liquid ammonia under mild conditions with high rate to give urea and bisphenol-A[10], while an aliphatic polycarbonate required supercritical conditions (200 °C, 1000 bar) and long reaction times.[11] Supercritical with respect to liquid conditions have the advantage of reduced viscosity and a 10 to 100 fold higher diffusivity depending on density in either phase. [12] No discontinuous change, e.g., in reaction rate or activation energy upon transition from a liquid to a supercritical phase has been observed in our studies. Hence, in our work the supercritical state follows from the necessity to achieve reasonable reaction rates by increasing temperature.

The results from ammonolysis of bisphenol-A-polycarbonate led us to study

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ammonolysis of thermosetting polymers that have functional groups prone to nucleophilic attack and cleavage. Candidates meeting these requirements are polycyanurates, polyisocyanurates and maleimides all of which have technical and commercial applications. Chemical recycling of these materials to the best of our knowledge has not been reported in the literature so far.

In the present paper we describe ammonolytic cleavage of polycyanurates, isocyanurates and bismaleimide thermosets. Intermediate products have been determined as a function of time and conversion to shed light on the reaction steps and mechanisms involved.

Experimental Part

Ammonolysis of poly-BPA-cyanurate was done in an autoclave or in a continuous reactor at room temperature, 120, 140 and 200 °C. Details of experimental setup and techniques have been reported in previous papers.[10–11] Autoclave content or fractions were collected, dissolved in acetonitrile or THF and analyzed with HPLC.

Ammonolysis of polymaleimides was made in an autoclave at 160 °C for 3.5 h; ammonia was released after cooling, solids were transferred into a flask and treated with boiling methanol to dissolve and separate the amine from the linear polymer (pMI).

HPLC consisted of an Agilent Technologies 1100 series binary LC pump, equipped with a vacuum degasser, auto-sampler, thermostatically controlled column compartment and UV diode array detector fitted with a standard flow cell (10 mm, 13 μL) and employed ChemStation Rev. A software. HPLC/ESI-mass spectroscopy used the electrospray interface, fragmentation voltage was 70 V, m/e range 150–2500. The column was a Jupiter C18 300 Å reversed phase. Injection volumes varied from 0.1 to 100 μL. Solvents for elution were gradient grade acetonitrile and bidistilled water both containing 0.05 weight percent trifluoroacetic acid. Total flow rate was 1 mL per minute. The gradient used started from 5% acetonitile with a linear increase to 100% within 14 min, followed by 2 min with 100% acetonitrile. A blank run was made after each injection of a sample to prove that no material was left on the column. Calibration curves were used for quantization of bisphenol-A, monoadduct of bisphenol-A and melamine, aniline and 4,4′-diaminodiphenylmethane.

Size exclusion chromatography (SEC): PSS-System 2000 consisting of a UV-detector Lambda 1010 and RI-detector Shodex RI71. Eluent: N,N-dimethyl acetamide; column: PSS-SDV/5 (7.8 × 300 mm, 5 μm particle size, linear 105–10^3 Å); polystyrene standards. Flow rate was 1 mL per minute.

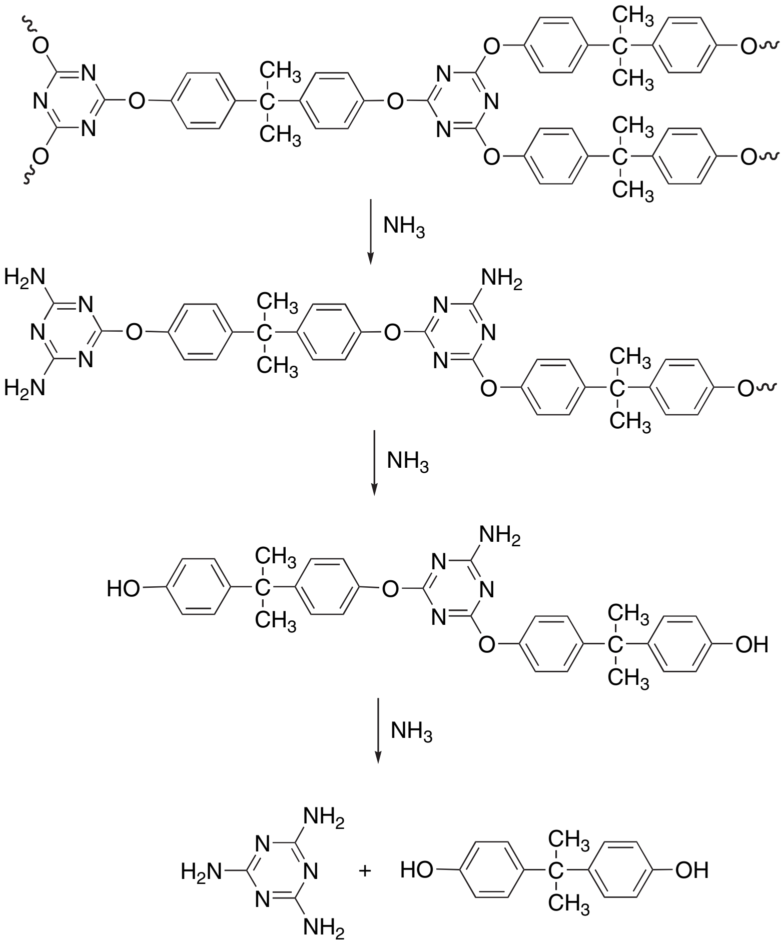
Results and discussion

Ammonolysis of Cyanurate and Isocyanurate Thermosets

Polycyanurates and polyisocyanurates are obtained from cyclotrimerisation of diisocyanates or dicyanates. Both reactions are base catalysed. The most commonly used monomers are 2,2-bis(4-cyanatophenyl)-propane (bisphenol-A-dicyanate) for cyanurates and MDI or polymeric MDI for isocyanurates. Isocyanurates normally are part of rigid foams used for thermal insulation, polycyanurates find applications in aviation and aeronautical industries.

Ammonolysis of a cyanurate thermosets involves nucleophilic attack of the 1,3,5-triazine ring by ammonia releasing a phenolic group under incorporation of an amino group. Final products of ammonolysis are the phenols from which the cyanate esters have been obtained and melamine. Two moles of ammonia per monomer (bisphenol-A-dicyanate) and three moles per triazine ring are required for complete ammonolysis. The reaction sequence of ammonolytic cleavage of polycyanurate is shown in Scheme 1.

Surprisingly ammonolysis to soluble products proceeds already at room temperature with high rate. In Fig. 1 the extracted mass



Scheme 1.
Ammonolysis of a bisphenol-A-cyanurate thermoset.

from a room temperature experiment as a function of reaction time shows that 90% of the theoretically expected material (complete ammonolysis) were dissolved and transported in liquid ammonia after less than 2 hrs. No residual material was found in the extraction device. Melamine, one of the final products of ammonolysis is rather insoluble in ammonia,

Table 1.
Ammonolysis of BPA-polycyanurate.

No	T/°C	p /bar	t /h	Found %			Residue[a] %
				BPA	Mono[b]	Homologues	
307	25	8	1	22.4	3.3	≈60	13.2
305	25	8	1.5	32.6	8.5	≈50	6.2
281	120	180	2	67.8	26.3	-	56 Melamine
241	140	200	18	89.0	7.6	-	74 Melamine

[a] insol. in THF.
[b] homologous series (2), n = 1, Scheme 2.

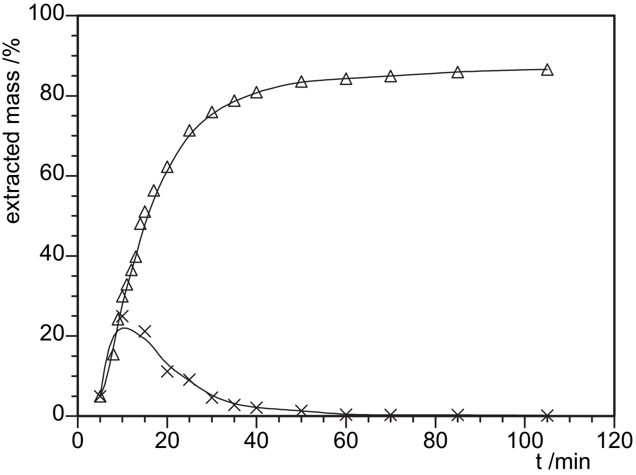


Figure 1.
Relative and integral mass-% of fractions from ammonolysis of poly-BPA-cyanurate at room temperature (x: individual fractions; Δ: cumulative mass).

hence it would have remained in the reactor. Cleavage of only 1 of the three triazine oxygens by ammonia will give a mass increase that corresponds to 93% of full ammonolysis. This suggests that only partial ammonolysis is required to obtain ammonia soluble products.

HPLC-analysis in combination with electro spray mass spectroscopy revealed that not only the end products of ammonolysis (bisphenol-A) were extracted. The HPLC chromatogram in Figure 2 shows a large number of peaks, which are caused by oligomeric ammonolysis products. According to Scheme 2 at least three homologous series can be formed, one with two bisphenol-A end groups, the second with

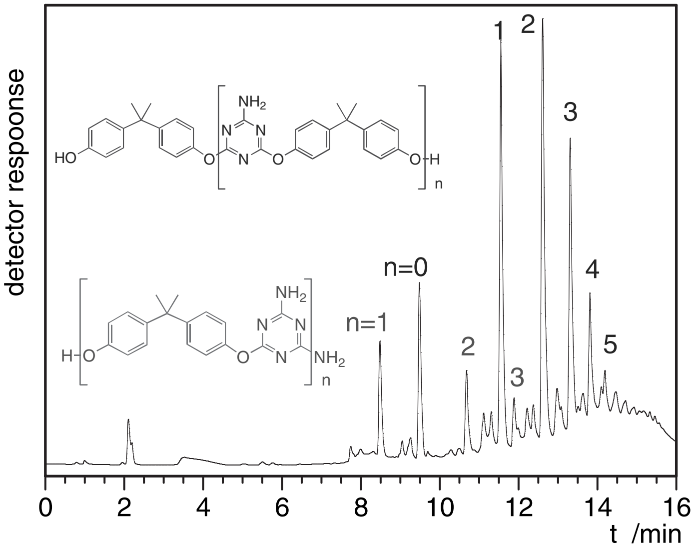
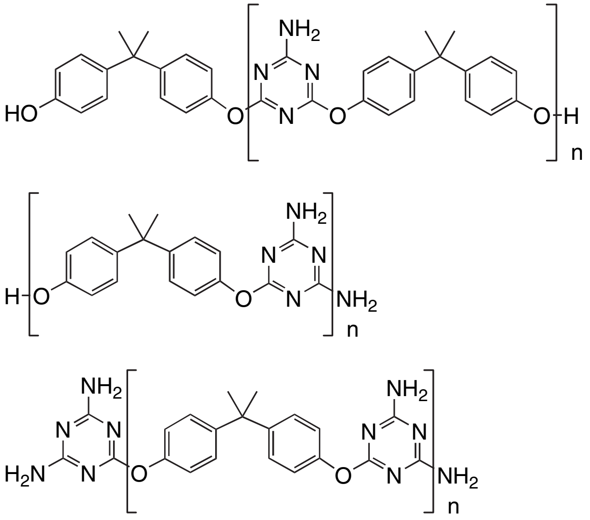


Figure 2.
HPLC-chromatogram of extraction experiment at 25 °C (fraction 40–50 min).



(1)

(2)

(3)

Scheme 2.
Possible homologous series in partial ammonolysis of cyanurate thermosets.

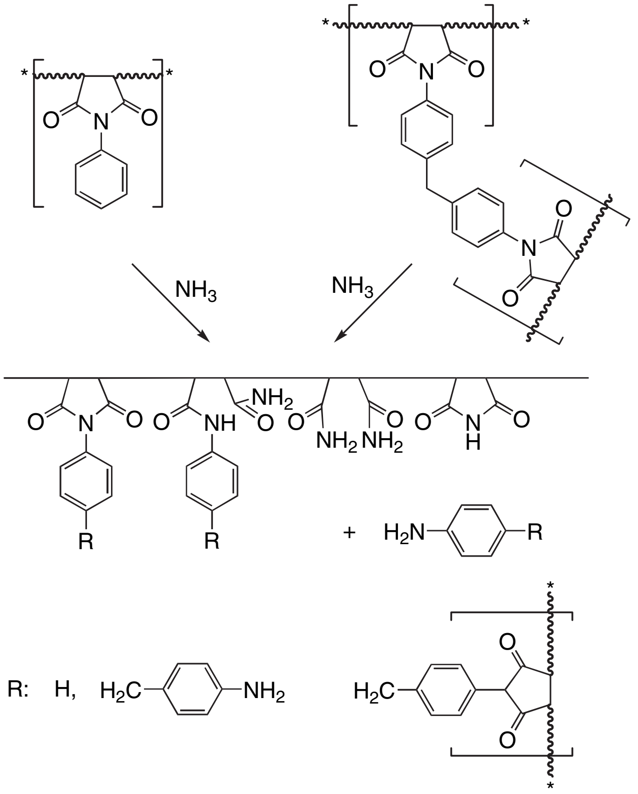
one bisphenol-A and one diaminotriazine end group, the third one having two diaminotriazine end groups.

From HPLC-MS homologous series 1 and 2 could be identified in the soluble fractions: up to $n = 5$ for series 1, up to $n = 3$ for series 2. Relative amounts of bisphenol-A and the first homologue decrease with time in the extracted fractions while those of higher homologues increases. Relative amounts of the first two homologues of series 2 also increase with time. The third homologous series could not be detected. There are further small peaks in the chromatogram which may originate from branched oligomers containing trisaryloxytriazine moieties that have not been attacked by ammonia. These results suggest that ammonolysis of the trisaryloxy-s-triazine ring (cyanurate ring) proceeds very fast even at room temperature, followed by attack of the amino-diaryloxy-s-triazine which is slower but still faster than the third ammonolysis step of the diamino-aryloxy-s-triazine to yield melamine. These findings are in agreement with results reported by Bauer for reaction of 2,4, 6- triphenoxy-1, 3,5- triazine with n-octylamine, where $k1 > k2 > k3$. [13]

Based on the decreasing reactivity of aminotriazines the first step is formation of diaryloxytriazine and phenolic groups. This reaction causes linearization of the cross-linked thermoset leaving primarily phenolic end groups (series 1) with a large amount of bisphenol-A. The second ammonolysis step decreases the degree of polymerisation of the linear macromolecules with formation of homologues of series 2. From series 3 only the first member with $n = 1$ should be formed. Under these conditions melamine should not be formed either.

Experiments at elevated temperature with liquid or supercritical ammonia resulted in cleavage of the third phenoxy group and formation of melamine. At 140 °C in an autoclave without continuous removal of soluble compounds melamine could be recovered to 74 and bisphenol-A to 89%, however still contaminated by small amounts of the mono- and of the bisadduct.

A similar experiment with phenylisocyanurate as model of polyisocyanurates at 120 °C showed cleavage of the triazinetrione ring and stepwise formation of aniline and urea as final products.



Scheme 3.
Ammonolysis of N-arylmaleimide polymers (pPMI, pBMI).

Ammonolysis of Bismaleimide Thermosets

Thermoset polymers from bismaleimides are another class of high performance materials used in aviation and aerospace applications.[13] They can also serve as an example of ammonolysis of linear polyimides used for adhesives or other applications. Ammonolysis will lead to a linear polymer with unsubstituted imide and diamide as comonomers while the amines will be regenerated. In terms of recycling only the amines will be of immediate use while the linear polymers do not have applications so far. Beyond recycling the analytical aspect is also important since characterisation of the resulting linear polymer will give information on the degree of polymerisation of the maleimide moieties in the thermoset. Structure of polymers and expected products of ammonolysis are shown in Scheme 3.

Polymers studied were a linear poly(N-phenylmaleimide) (pPMI) and a thermoset polymer based on the bismaleimide of MDA, 4,4′-methylenbis-(4-N- phenylmaleimide) (pBMI). PMI was polymerised using

Table 2.
Ammonolysis of pPMI and pBMI (autoclave, 160 °C, 200 bar, 3,5 h).

Polymer	Starting mat.	Ammonolysis products/mg (%)		
	/mg	pMI	Amine	Oligomers
pPMI	600	316 (87)	282 (87)	80 (12%)
pBMI	1040	603 (103)	490 (85)	-

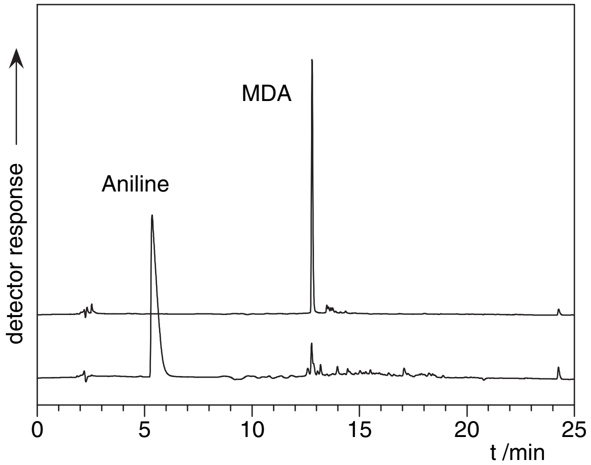


Figure 3.
HPLC-chromatogram methanol soluble fractions of polyimides (pPMI, pBMI).

cumolhydroperoxide as initiator in a sealed glass tube at 150 °C for 2 h and at 280 °C for another 15 h; the resulting pPMI was treated with boiling methanol to remove residual monomer and soluble oligomers. BMI was polymerised under similar conditions but without addition of an initiator. The resulting monolithic body of pBMI was crushed to a size below 1 mm (mesh size of the sieve).

Ammonolysis of polymaleimides was made in an autoclave at 160 °C for 3.5 h; Methanol soluble fractions contain the amines. MDA shows only the peaks of the two isomers 4,4-MDA and 2,4-MDA (4%) in the ratio present in BMI as shown in Figure 3. Aniline is contaminated with some oligomers (Figure 3) that contain aniline and maleimide groups as revealed by IR- and NMR-spectra.

The resulting linear polymaleimides are soluble in DMSO and nmr-spectra reveal that virtually no aniline is left after ammonolysis of pPMI, while some MDA is left after ammonolysis of pBMI. IR-spectra of both compounds are quite similar; for pBMI and the resulting pMI IR-spectra are

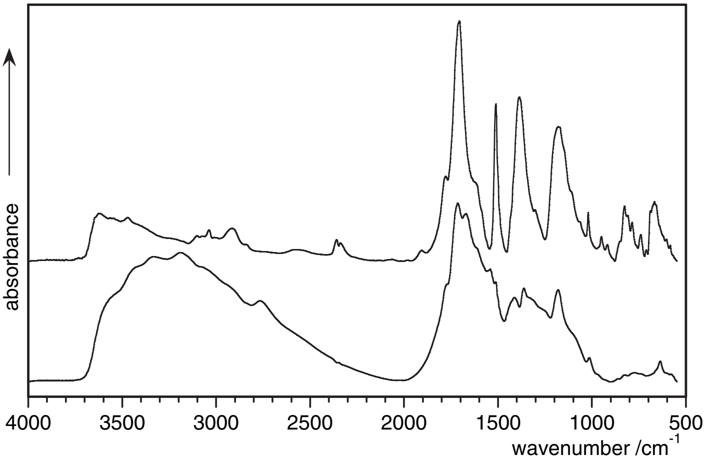


Figure 4.
IR-spectra (neat, ATR) of pBMI (upper) and its ammonolysis product (pMI).

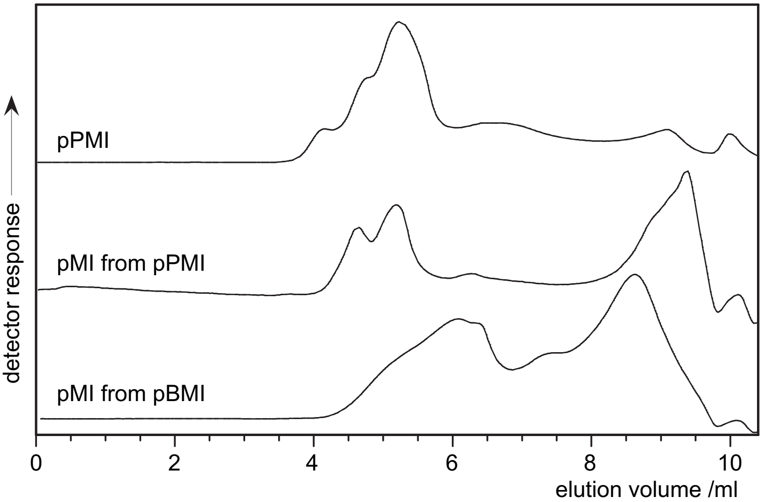


Figure 5.
SEC-chromatogram methanol soluble fractions of polyimides (pPMI, pBMI).

shown in Figure 4. Both spectra contain the typical carbonyl absorptions of the imide group, the aromatic C-C stretching vibration at 1600 cm^{-1} has disappeared and a strong N-H vibration is visible in the spectrum of pMI. Based on the elemental analysis approximately half of the N-arylmaleimide units have been transformed into unsubstituted maleimide units, the other half into diamide units which is also consistent with the carbonyl absorptions in the IR-spectrum.

The original pPMI and both ammonolysis products pMI were soluble in dimethylacetamide (DMAc). Size exclusion chromatograms of all three are shown in Figure 5. All polymers have a multimodal and broad molar mass distribution (MWD) with a maximum at high molar mass and another at lower molar mass (10 ml elution volume is very close to the exclusion limit). This broad MWD is the result of polymerisation (curing) conditions; it is also the first information on the MWD of the carbon chains of polymaleimides.

Conclusions

Ammonolysis of polycyanurate and poly-(4, 4′-methylenbis-(4-N-phenylmaleimide)) thermoset polymers can be performed at elevated temperature to give useful products for chemical recycling. Melamine and the bisphenol, from which the dicyanate has been made are final products of ammonolysis of cyanurate polymers, amines and linear polymers containing imide as well as diamide units are the ammonolysis products of polymaleimides. Ammonolysis of polycyanurates proceeds already at room temperature up to the level of the bisphenol and linear oligomers. Under these conditions no melamine is formed, the reaction seems to stop at the level of diaminoaryloxytriazines.

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