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ORIGINAL PAPER

Synthesis, characterization, and polymerization of vinylmelamines

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Abstract Vinyl functionalized melamine derivatives for cross-linking based on polymerization were synthesized as potential substitutes for harmful formaldehyde in melamine resins. Methylmelamines undergo direct vinylation with acetylene to the corresponding vinylmelamines in more than 95% conversion. Their chemical structures were fully characterized by mass spectrometry, Fourier transform infrared (FTIR) spectroscopy, elementary analysis, ^{1}H, ^{13}C, and 2D correlation nuclear magnetic resonance (NMR) experiments. Linear and cross-linked polymers were prepared by free radical polymerization neat and in solution and characterized by size exclusion chromatography (SEC) and matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectrometry.

Keywords Heterocycles · Melamine · Methylmelamine · Polymerizations · Spectroscopy · Vinylation

Introduction

About 100 years after Justus von Liebig [1] successfully synthesized 2,4,6-triamino-1,3,5-triazine (melamine) by heating a mixture of potassium thiocyanate and ammonium chloride in 1834, melamine found industrial applications in the production of melamine-formaldehyde (MF) resins [2, 3]. Since that time melamine has become an increasingly important chemical commodity, mainly in the fabrication of MF resin-containing products. In the late 1990s volatile organic compounds (VOC) and therefore formaldehyde as part of the MF resins were of increasing public interest that reached a maximum in 2004 when formaldehyde gained the status of suspected carcinogen [4]. Concurrently, the prescriptive limits were lowered drastically and the search for alternative cross-linking agents, to replace formaldehyde, was promoted with the development of novel melamine derivatives and their insertion into new markets. However, a serious substitute for formaldehyde has not been found to date. Our research group is interested in the preparation of novel melamine derivatives bearing functional groups applicable in alternative cross-linking reactions that avoid the use of formaldehyde.

The direct vinylation of heterocyclic compounds, e.g., pyrrolidone, with acetylene is well known [5] but there is no reported evidence of the successful vinylation of melamine. In the early 1960s the preparation of exocyclic *N*-alkylated melamine derivatives, the methylmelamines, was reported first [6, 7] and only recently several synthesis routes have been established [8–10]. Although the methylmelamines have been known for more than 50 years, no systematic study of the physicochemical properties and their typical reactions is published. Nevertheless, methylmelamines show excellent properties in their application in formaldehyde-based resins [11–13] and therefore constitute interesting starting materials in synthesis. Because of the important differences to melamine concerning their high solubility in common organic solvents and the increased reactivity of the exocyclic nitrogens, we successfully applied them to the direct vinylation with acetylene and present their use as monomers in a free radical polymerization.

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Results and discussion

The direct vinylation of the methylmelamines containing one [2,4-bis(dimethylamino)-6-(methylamino)-1,3,5-triazine (**1**)], two [2-(dimethylamino)-4,6-bis(methylamino)-1,3,5-triazine (**2**)], and three [2,4,6-tris(methylamino)-1,3,5-triazine (**3**)] methylamino groups with acetylene was studied (Fig. 1). The methylmelamines **1**–**3** were chosen to prepare polymerizable monomers that afforded linear thermoplasts and highly cross-linked thermosets both from homo- and copolymerization.

Pentamethylmelamine (**1**) reacts with acetylene under atmospheric pressure in dimethyl sulfoxide (DMSO) as the solvent and potassium *tert*-butanolate (*t*-BuOK) as the catalyst at a temperature above 140 °C to afford 2,4-bis(dimethylamino)-6-(methylvinylamino)-1,3,5-triazine (**4**) (Scheme 1). It should be mentioned that the catalyst and the solvent provide a superbase system [14]. To minimize side reactions of DMSO and alkaline hydrolysis of **1** that were observed at prolonged reaction times, the formation of **4** was monitored with gas chromatography–mass spectrometry (GC–MS) and stopped at a conversion higher than 95%. The distribution of acetylene in the solvent highly depended on the synthesis scale and a strong influence on the reaction time was observed. Thus, the conversion of vigorously stirred experiments with less than 50 cm^3 solvent was finished within 15 min, whereas batches of 300 cm^3 prolonged the reaction time to 1 h, both for single addition of catalyst.

Under the same reaction conditions with double the reaction time, **2** and **3** afforded 2-(dimethylamino)-4,6-bis(methylvinylamino)-1,3,5-triazine (**5**) and 2,4,6-tris(methylvinylamino)-1,3,5-triazine (**6**), respectively (Scheme 2).

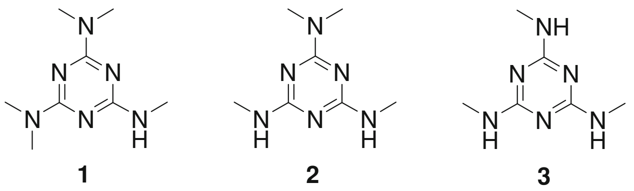
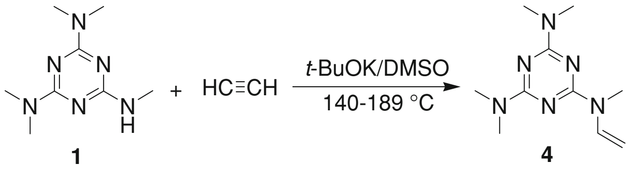
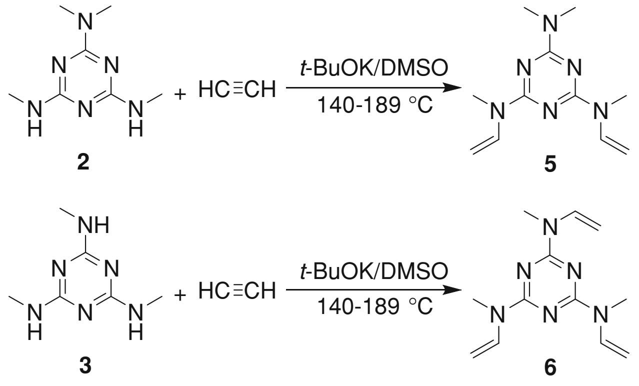


Fig. 1 The starting materials applied in direct vinylation: 2,4-bis(dimethylamino)-6-(methylamino)-1,3,5-triazine (**1**), 2-(dimethylamino)-4,6-bis(methylamino)-1,3,5-triazine (**2**), and 2,4,6-tris(methylamino)-1,3,5-triazine (**3**)



Scheme 1



Scheme 2

The starting materials **2** and **3** are characterized by two and three possible reaction sites, respectively, and therefore in the syntheses of **5** and **6** it was possible to observe the formation of their corresponding intermediates. Starting from tetramethylmelamine (**2**), the occurrence of 2-(dimethylamino)-4-(methylamino)-6-(methylvinylamino)-1,3,5-triazine (**7**) could be monitored with GC–MS, and both possible intermediates 2,4-bis(methylamino)-6-(methylvinylamino)-1,3,5-triazine (**8a**) and 2-(methylamino)-4,6-bis(methylvinylamino)-1,3,5-triazine (**8b**) were identified in the reaction mixture when trimethylmelamine (**3**) was applied as starting material in the vinylation (Fig. 2). It was possible to synthesize **7**, **8a**, and **8b** by quenching the reaction solution but the pure compounds were not isolated. GC–MS data showed a distribution of starting materials, intermediates, and product. Compounds **7**, **8a**, and **8b** were identified by interpretation of their electron impact mass spectra from GC–MS.

Workup of the crude reaction solution was rather simple because all fully vinylated products show very poor solubility in water and could therefore be easily separated from the water-soluble starting materials and side products by several washing procedures. The crude vinylmelamines were recrystallized from acetone/water (20:80) to afford **4**, **5**, and **6** in 69, 82, and 65% yield, respectively, with purities higher than 99% according to GC–MS. All

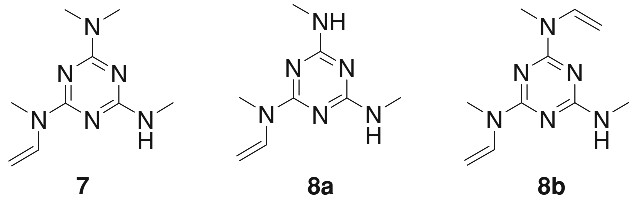


Fig. 2 Intermediates occurring in the direct vinylation of **2** and **3**: 2-(dimethylamino)-4-(methylamino)-6-(methylvinylamino)-1,3,5-triazine (**7**), 2,4-bis(methylamino)-6-(methylvinylamino)-1,3,5-triazine (**8a**), and 2-(methylamino)-4,6-bis(methylvinylamino)-1,3,5-triazine (**8b**)

products show excellent solubility in most organic solvents from protic to nonprotic and polar to nonpolar. Furthermore, the vinylmelamines are stable in air and show good stability in neutral and alkaline media. All products were fully characterized by mass spectrometry, FTIR spectroscopy, elementary analysis, ^{1}H, ^{13}C, and 2D correlation NMR experiments.

It was possible to scaleup the syntheses of the novel vinylmelamines **4–6** in a bubble reactor in quantities of 80 g starting material to obtain the monomers for basic investigations on material properties for commercial applications.

Polymerization of 2,4-bis(dimethylamino)-6-(methylvinylamino)-1,3,5-triazine (**4**) was accomplished neat and in solution with azoisobutyronitrile (AIBN) as initiator. Characterization of low molar mass samples with MALDI-ToF MS was done to determine the end groups. In the first case the polymer contained an isobutyronitrile start group and a hydrogen end group; in a second minor series isobutyronitrile start and end groups can be found, as would be expected (Fig. 3). When using xylene as solvent the initiator does not only react directly with the monomer but transfers the free radical to a solvent molecule, which acts as a start group for the polymer chain. Termination is again by a hydrogen transfer reaction (Fig. 4).

Size exclusion chromatography of the material obtained from the polymerization in solution, after removal of residual monomer by washing, gave M_n of 5,045 g mol^{-1} and M_w of 6,469 g mol^{-1} relative to polystyrene standards and a polydispersity index of 1.28 (Fig. 5), which is also in good agreement with the MALDI data presented in Fig. 4.

The multifunctional monomer 2,4,6-tris(methylvinylamino)-1,3,5-triazine (**6**) was polymerized neat using AIBN as initiator and gave a hard, solid material, which could not be dissolved or melted. Thermogravimetric analysis showed an excellent thermal stability with an onset temperature for the thermal degradation of above 450 °C.

Conclusion

Novel formaldehyde-free monomers based on melamine have been developed. The free imino groups of methylmelamines react readily with acetylene to afford the corresponding fully substituted derivatives in yields above 95%. Through selection of different methylmelamines it was possible to vary from monofunctional to trifunctional monomers, giving the option to produce either linear thermoplastic polymers or thermally very stable thermosets, the latter being a possible alternative to conventional melamine-formaldehyde resins. The linear polymers were investigated using MALDI-ToF MS and the polymerization mechanisms using different initiators could be explained. The new monomers offer a broad range of industrial application for melamine derivatives, not only in homopolymerization but also in the copolymerization with other monomers, which is currently under investigation.

Experimental

All chemicals were of p.a. quality and used without further purification. Reagents were supplied by commercial

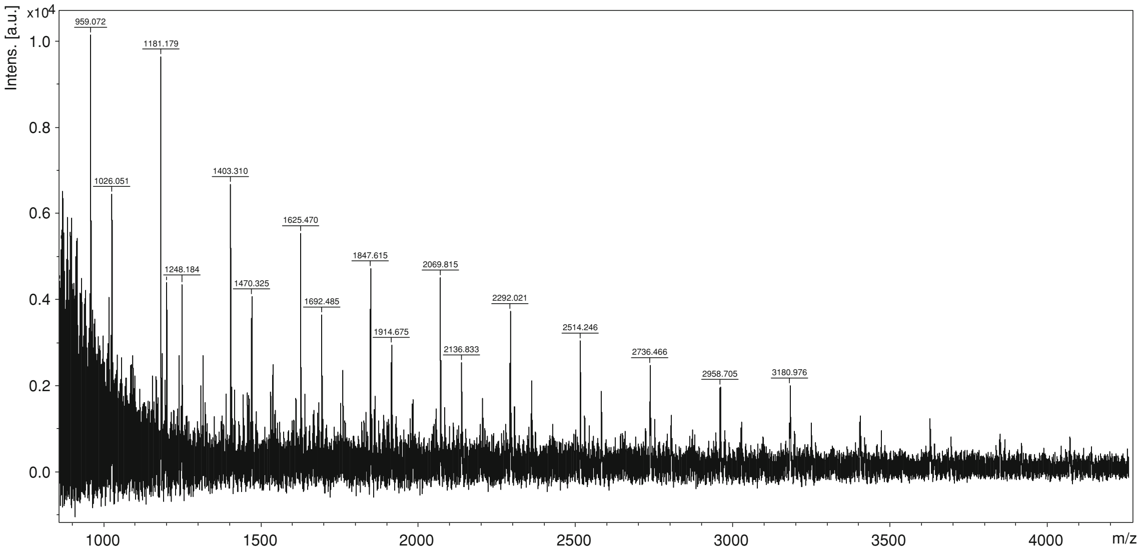


Fig. 3 MALDI-ToF mass spectra of poly(2,4-bis(dimethylamino)-6-(methylvinylamino)-1,3,5-triazine) polymerized neat using AIBN as initiator

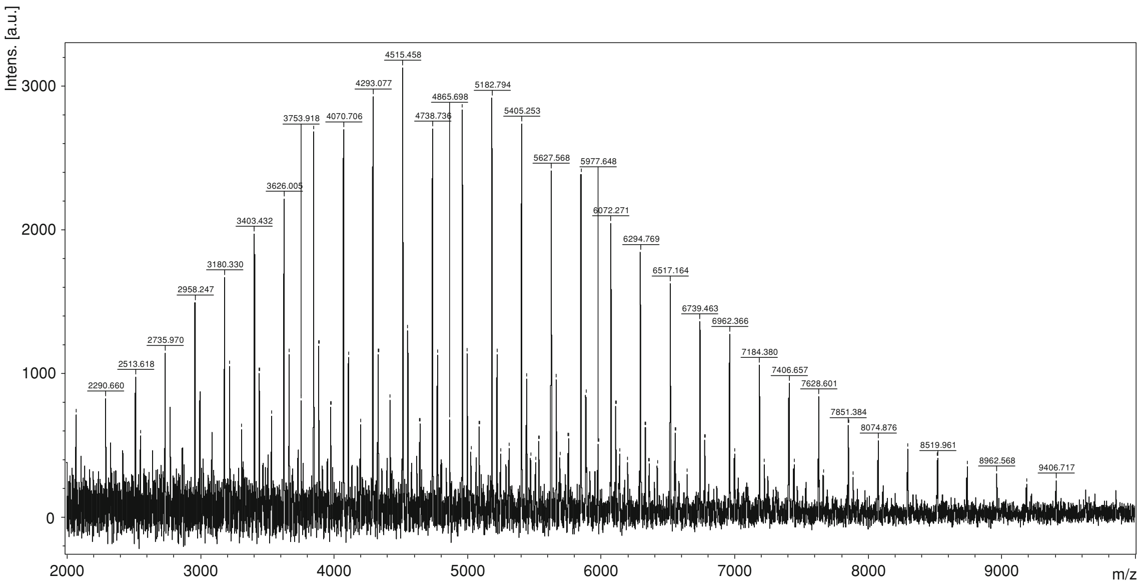


Fig. 4 MALDI-ToF mass spectra of poly(2,4-bis(dimethylamino)-6-(methylvinylamino)-1,3,5-triazine) polymerized in xylene using AIBN as initiator

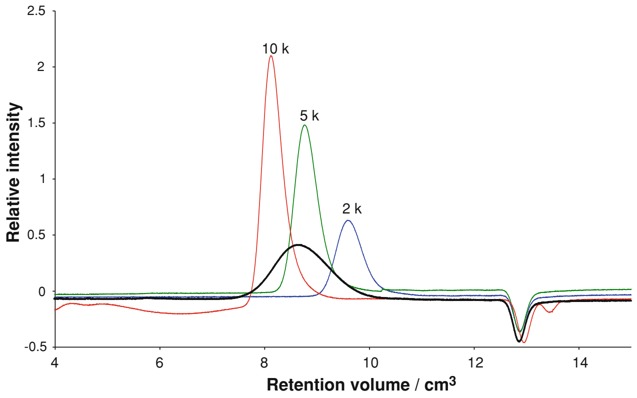


Fig. 5 SEC chromatogram of poly(2,4-bis(dimethylamino)-6-(methylvinylamino)-1,3,5-triazine) polymerized in xylene using AIBN as initiator compared to polystyrene standards (10k, 5k, and 2k)

sources and were used without further purification. The methylated melamines **1**–**3** were prepared according to Bořkovec and DeMilo from cyanuric chloride, methylamine, and dimethylamine [7].

Melting points were measured on a Leica Galen III microscope with a Kofler melting point unit. ^{1}H, ^{13}C, and 2D correlation NMR experiments were recorded on a Bruker Avance DPX 200 MHz spectrometer using standard pulse sequences as provided by the manufacturer. FTIR analyses were performed on a Thermo Fisher Scientific iN10 MX using attenuated total reflection (ATR) mode, elementary analysis was done on a Thermo Scientific Flash EA 1112, GC–MS was performed on a Thermo Trace GC hyphenated to a Finnigan MD800 mass spectrometer operating in electron impact mode (EI), and electrospray ionization (ESI) mass spectrometry was done on a Thermo Finnigan LCQ Deca XP plus in positive ion mode.

Analyses of the polymers were done using a Bruker Autoflex Smartbeam III MALDI ToF-ToF mass spectrometer in reflectron mode. The samples were dissolved in chloroform (10 mg cm^{-3}) and mixed with a solution of dihydroxybenzoic acid or indolylacrylic acid in tetrahydrofuran (10 mg cm^{-3}) in a ratio of 1:10. SEC was performed in dimethylacetamide as solvent with a flow rate of 0.35 cm^{3} min^{-1} using a set of three Phenomenex Phenogel columns with 10,000, 1,000, and 100 Å (4.6 × 300 mm, 5 μm) at a temperature of 60 °C and a refractive index detector. Calibration was done using polystyrene standards of 2,430, 5,460, and 10,850 g mol^{-1} with polydispersity indices of 1.06, 1.03, and 1.02, respectively.

General syntheses procedure for monomers

In a nitrogen-flushed three-necked round-bottom flask about 1.5 g methylmelamine in 15 cm^{3} DMSO was heated to 140 °C under a constant flow of acetylene (60 cm^{3} min^{-1}). Under vigorous stirring the reaction was started with the addition of *t*-BuOK (50 mol% calculated on the basis of methylmelamine) as the catalyst. The reaction was monitored with GC–MS and stopped at a conversion of 95% after 15–35 min. The reaction mixture was evaporated to dryness under high vacuum, the obtained residue dissolved in chloroform, and washed with water three times. Evaporation of the solvent and recrystallization from acetone/water yielded the vinylmelamine as a white solid (65–82%). All products were fully characterized with elemental analysis whose results agreed favorably with calculated values.

2,4-Bis(dimethylamino)-6-(methylvinylamino)-1,3,5-triazine (**4**, $C_{10}H_{18}N_6$)

Pentamethylmelamine (**1**, 1.51 g, 7.7 mmol) was used as starting material, yielding after 15 min reaction time and recrystallization of the crude product 1.18 g (5.3 mmol) **4** (69%) as a white solid. M.p.: 102–103 °C; EI-MS: $m/z = 222$ (100), 221 (62), 207 (70), 195 (14), 178 (34), 164 (18), 151 (25), 137 (17); ESI-MS ($AcN/H_2O = 4:1$, $c \sim 0.1$ mg cm^{-3}): $m/z = 223.3$ $[\mathbf{4} + H]^+$; ^1H NMR (200 MHz, DMSO-d_6, 30 °C): $\delta = 7.83$ (dd, $J = 9.22$ Hz, 16.02 Hz, 1H, –CH=CH_2), 4.32 (d, $J = 16.02$ Hz, 1H, –CH=CH_2), 4.18 (d, $J = 9.22$ Hz, 1H, –CH=CH_2), 3.19 (s, 3H, –N(CH_3)vinyl), 3.06 (s, 12H, –N(CH_3)$_2$) ppm; ^{13}C NMR (50 MHz, DMSO-d_6, 30 °C): $\delta = 164.9$ (>C–N(CH_3)$_2$), 162.9 (>C–N(CH_3)vinyl), 133.9 (–CH=CH_2), 89.36 (–CH=CH_2), 35.51 (–N(CH_3)$_2$), 28.93 (–N(CH_3)vinyl) ppm; IR (ATR): $\bar{\nu} = 3{,}114$, 3,023, 2,925, 2,865, 2,787, 2,488, 1,620, 1,411, 1,483, 1,440, 1,421, 1,387, 1,323, 1,300, 1,285, 1,218, 1,188, 1,049, 986, 853, 843, 817, 804, 735, 680, 542, 602, 567, 558, 550, 539 cm^{-1}.

2-(Dimethylamino)-4,6-bis(methylvinylamino)-1,3,5-triazine (**5**, $C_{11}H_{18}N_6$)

Tetramethylmelamine (**2**, 1.59 g, 8.7 mmol) was used as starting material, yielding after 30 min reaction time and recrystallization of the crude product 1.67 g (7.2 mmol) **5** (82%) as a white solid. M.p.: 55–56 °C; EI-MS: $m/z = 234$ (55), 233 (46), 219 (100), 207 (17), 177 (26), 151 (21), 137 (36), 122 (20); ESI-MS ($AcN/H_2O = 4:1$, $c \sim 0.1$ mg cm^{-3}): $m/z = 235.3$ $[\mathbf{5} + H]^+$; ^1H NMR (200 MHz, DMSO-d_6, 30 °C): $\delta = 7.82$ (dd, $J = 9.21$ Hz, 15.92 Hz, 2H, –CH=CH_2), 4.41 (d, $J = 15.92$ Hz, 2H, –CH=CH_2), 4.27 (d, $J = 9.21$ Hz, 2H, –CH=CH_2), 3.22 (s, 6H, –N(CH_3)vinyl), 3.09 (s, 6H, –N(CH_3)$_2$) ppm; ^{13}C NMR (50 MHz, DMSO-d_6, 30 °C): $\delta = 164.6$ (>C–N(CH_3)$_2$), 162.9 (>C–N(CH_3)vinyl), 133.6 (–CH=CH_2), 90.61 (–CH=CH_2), 35.69 (–N(CH_3)$_2$), 29.19 (–N(CH_3)vinyl) ppm; IR (ATR): $\bar{\nu} = 3{,}107$, 2,921, 1,620, 1,556, 1,530, 1,475, 1,436, 1,408, 1,378, 1,317, 1,277, 1,230, 1,200, 1,053, 980, 838, 849, 807, 800, 682, 648, 631, 589, 571, 548, 540 cm^{-1}.

2,4,6-Tris(methylvinylamino)-1,3,5-triazine (**6**, $C_{12}H_{18}N_6$)

Trimethylmelamine (**3**, 1.55 g, 9.2 mmol) was used as starting material, yielding after 35 min reaction time and recrystallization of the crude product 1.48 g (6.0 mmol) **6** (65%) as a white solid. M.p.: 96–97 °C; EI-MS: $m/z = 246$ (65), 245 (37), 231 (100), 219 (8), 204 (17), 188 (43), 174 (16), 163 (15); ESI-MS ($AcN:H_2O = 4:1$, $c \sim 0.1$ mg cm^{-3}): $m/z = 247.2$ $[\mathbf{6}+H]^+$; ^1H NMR (200 MHz, DMSO-d_6, 30 °C): $\delta = 7.90$ (dd, $J = 9.3$ Hz, 15.9 Hz, 3H, –CH=CH_2), 4.50 (d, $J = 15.9$ Hz, 3H, –CH=CH_2), 4.36 (d, $J = 9.3$ Hz, 3H, –CH=CH_2), 3.31 (s, 9H, –N(CH_3)vinyl) ppm; ^{13}C NMR (50 MHz, DMSO-d_6, 30 °C): $\delta = 163.8$ (>C–N(CH_3)vinyl), 134.2 (–CH=CH_2), 90.90 (–CH=CH_2), 29.87 (–N(CH_3)vinyl) ppm; IR (ATR): $\bar{\nu} = 3{,}110$, 2,923, 1,624, 1,540, 1,477, 1,439, 1,417, 1,378, 1,309, 1,284, 1,261, 1,206, 1,056, 978, 814, 799, 686, 631, 587, 573, 557, 550, 539 cm^{-1}.

2-(Dimethylamino)-4-(methylamino)-6-(methylvinylamino)-1,3,5-triazine (**7**, $C_9H_{16}N_6$)

EI-MS: $m/z = 208$ (50), 207 (100), 193 (31), 178 (18), 164 (19), 151 (26), 137 (28), 96 (45).

2,4-Bis(methylamino)-6-(methylvinylamino)-1,3,5-triazine (**8a**, $C_8H_{14}N_6$)

EI-MS: $m/z = 194$ (71), 193 (100), 179 (25), 167 (11), 137 (68), 123 (28), 96 (45), 82 (51).

2-(Methylamino)-4,6-bis(methylvinylamino)-1,3,5-triazine (**8b**, $C_{10}H_{16}N_6$)

EI-MS: $m/z = 220$ (62), 219 (69), 205 (100), 178 (10), 163 (33), 137 (44), 122 (25), 108 (17).

Polymer syntheses

2,4-Bis(dimethylamino)-6-(methylvinylamino)-1,3,5-triazine (**4**, 250 mg, 1.13 mmol) was mixed with 15 mol% azoisobutyronitrile (AIBN) and heated to 145 °C for 3 h under stirring. After cooling to room temperature the polymer was washed trice with methanol and dried in a vacuum oven.

To screen the polymerization in solution 400 mg 2,4-bis(dimethylamino)-6-(methylvinylamino)-1,3,5-triazine (**4**) was dissolved in 2 cm^3 xylene, 1 mol% AIBN added, and the solution heated to reflux for 5 h. The solvent was then removed under reduced pressure and the polymer washed trice with methanol and twice with warm ethanol.

As an example of the preparation of a cross-linked material 250 mg of 2,4,6-tris(methylvinylamino)-1,3,5-triazine (**6**) was mixed with 10 mol% AIBN and heated to 140 °C in an oven for 1 h.

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