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Highly branched melamine-phenolic novolaks

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Summary

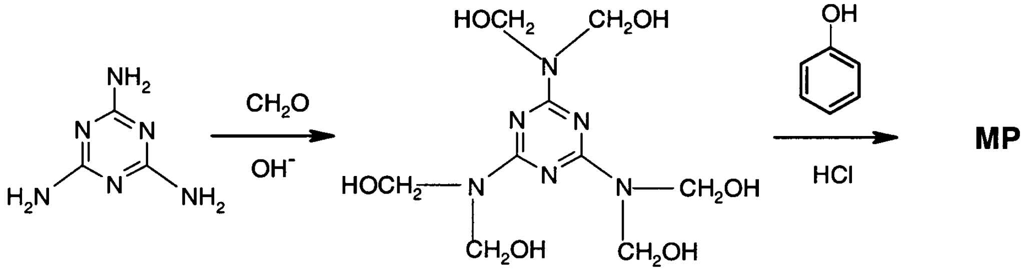
A convenient synthesis of highly branched melamine-formaldehyde-phenolic oligomers, which can be applied as precursors for dendritic macromolecules, is described. The synthesis comprises the condensation of methylolated melamines with phenol in the presence of stoichiometric amounts of hydrochloric acid (similarly to the Mannich's reaction conditions). A mixture of hydroxyphenylmethylmelamines was obtained of an average content corresponding to the five substituted melamine ring. NMR and mass spectrometry (LSIMS/FAB) analysis showed the products to be almost free of neat melamine–formaldehyde and phenol–formaldehyde condensates.

Introduction

Synthesis of polymers based on well-known monomers but endowed with a new macromolecular architecture, has received much attention recently. The examples may be dendrimers and hyperbranched polymers, which are of high interest because of the unusual properties arising from their globular structure [1-10]. Highly branched macromolecules exhibit low viscosity, high solubility, and enhanced reactivity as compared with their linear or statistically branched analogues. There are many papers on synthesis of hyperbranched polycondensation resins [6-10], especially polyesters in view of their applications in coatings and composites [e.g. 11-13].

Melamine- and phenol-formaldehyde resins belong to the oldest commercial polymers. Amino- and phenoplasts are entering the second century of their history, however they continue to be the subject of investigations with regard to their structure and crosslinking mechanism as well as various technological processes [14]. Generally, novolak-type phenolic resins exhibit a linear (especially ortho-novolaks) or a slightly branched structure, cyclic phenol-formaldehyde oligomers are also known [15]. The preparation of well-defined novolak resins with low polydispersity have been the subject of interest, especially for photoresist applications [e.g. 16,17]. Some model novolac compounds consisting of up to eight phenolic units were synthesized using "step-by-step" method [18].

The present work continues our previous investigations on highly branched phenol-formaldehyde resins [19]. Our goal was the application of dendrimer synthesis sequence for the inexpensive monomers. However, we aimed rather at highly branched novolaks than perfect dendrimers. This paper describes the use of melamine, a hexafunctional compound, as a core substance to produce the branched novolaks



Scheme 1. Reaction sequence for the synthesis of branched melamine-phenolic novolak **MP**

Even under specific conditions, the reaction of melamine and phenol with formaldehyde leads to blends of melamine-formaldehyde and phenol-formaldehyde resins that predominate over genuine copolycondensation products [20,21]. This is so because the reactivity of phenol and N-amides (like melamine or urea) with formaldehyde depends on pH in the opposite way. In an alkaline medium, self-condensation of phenol-formaldehyde resol dominates the analogous reaction of amino resin. Under acidic conditions the reactivity of phenol is reduced and mainly amino-formaldehyde resin is formed and further crosslinking takes place [20].

The main problem we faced in the present investigation was to prevent the self-condensation of methylolmelamines and to make them react with phenol to produce hydroxyphenylmethylmelamines (as a dendrimer-like substance **MP**). We presumed that using hydrochloric acid, in stoichiometric rather than catalytic amounts towards methylol groups (similarly to the conditions of Mannich reaction) would suffice to reach the target. Although dendrimerization was here in mind, the hydroxyphenylmethylmelamines can also be applied for a general synthesis of genuine melamine-phenolic resins. They can replace blends of melamine-formaldehyde and phenol-formaldehyde resins in some applications, especially in the wood adhesives industry [21,22].

Experimental

Materials

Melamine (Nitrogen Works – Kędzierzyn), phenol (Reactivul) as aqueous 90 wt. % solution and formaldehyde (POCh, as 37 % formalin) were used.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on Varian INOVA 500 and Bruker WP-100FY spectrometers. Samples were dissolved in acetone-d_6 or DMSO-d_6 and TMS was used as an internal reference.

Liquid Secondary Ion Mass Spectrometry / Fast Atom Bombardment (LSIMS/FAB) spectrum was recorded on a Finnigan MAT 95 spectrometer with m-nitrobenzyl alcohol as a matrix. A sample was ionized with Cs+ of 13 keV. Temperature of ion source: 40 °C. Ten measurements were made to produce an average spectrum.

Gel Permeation Chromatography (GPC) analysis was carried out on a Shimadzu C-R4A Chromatopac equipped with two columns (250x 7.4). Column set: Microstyragel 5 m (mixed bed). Tetrahydrofuran as eluent and a refractive index detector was used. GPC calibration curve was obtained using polystyrene standards.

Differential scanning calorimetry (DSC) traces were recorded on a Perkin-Elmer DSC-7 instrument operated at a heating rate of 20°C / min.

Infrared spectra (KBr pellets) were obtained with Perkin Elmer System 2000 FT-IR spectrometer. The IR peak assignments were made based on [23]. The number-average molecular weights were determined with a Hewlett Packard 302 Vapor Pressure Osmometer (with tetrahydrofuran as solvent). The intrinsic viscosity of novolak solutions in ethanol was measured by means of an automatic viscometer AVS 400 Schott Geräte at 30°C.

*Synthesis of melamine-phenolic novolak (***MP***)*

Formalin (600 mL, 8 mol formaldehyde) was placed in the reactor and pH was adjusted to 8-8.5 with aqueous 10 wt. % NaOH. Temperature was raised to 85 °C and melamine (126 g, 1 mol) was added with stirring until all the melamine was dissolved. After additional 15 min at 85°C, the reaction mixture was cooled and the resulting precipitate filtered off and dried. The resulting methylolated melamine had a melting point 156-170 °C; total formaldehyde content was 49.4 wt. %, corresponding to degree of methylolation n = 4.69, with the molecular formula assumed to be $C_3N_6H_{6-n}(CH_2OH)_n \cdot H_2O$ [24]. ^{1}H-NMR spectrum (DMSO-d_6): 5.4 (OH), 4.9-5.1 (N-CH_2-O) was consistent with the literature data.

Methylolated melamine (150 g) was stirred in 600 mL of 18 wt % hydrochloric acid until a homogeneous solution was obtained, which was subsequently added to 650 g (an excess) phenol. The mixture was stirred at ambient temperature for 90 min, then neutralized. As a result, a water layer separated, which was decanted and the excess of phenol was removed under reduced pressure and finally by steam distillation. The product was yellow-brown solid (225 g). The number-average molecular weight Mn determined by VPO was 650 g/mol. GPC measurements gave Mn = 470 g/mol and polydispersity Mw/Mn = 1.3.

The curing of novolak MP was performed by heating from 100°C to 270°C at the rate of 1-2 °C/min.

Discussion

We correctly presumed that the use of the stoichiometric amounts of hydrochloric acid and some excess of phenol would restrain self-condensation of methylolmelamines. As it is commonly assumed, under strong acidic conditions the methylol groups transform into NCH_2^+ cations, which, as we have found, readily undergo condensation with phenol. Thus, a mixture of hydroxyphenyl-methylmelamines was obtained, which almost did not contain neat melamine-formaldehyde condensation products nor phenol-formaldehyde ones.

The resulting branched melamine phenolic novolak **MP** can be presented as in Figure 1 which shows an exemplary structure with five substituents. The result is corroborated by LSIMS/FAB spectrum, gel permeation chromatography, molecular weight determination, chemical analysis and NMR spectroscopy.

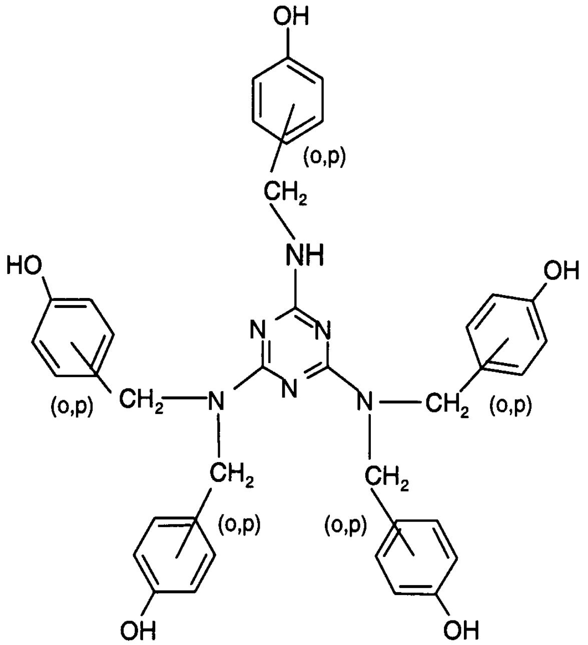


Figure 1. An approximate structure of the melamine-phenolic novolak **MP**.

GPC chromatogram of novolak **MP** is characterized by a fairly narrow band (Fig 2) of low polydispersity (Mw / Mn = 1.3). This indicates a quite uniform substance, though GPC measurements based on calibration with linear polystyrene standards can give somewhat misleading results in the case of branched molecules with lower hydrodynamic volume. Some amount of dihydroxydiphenylmethane formed as a by-product (GPC peak at 12,6 mL) may be washed out with hot water.

If chemical composition is taken into account (11.9 wt. % nitrogen), there are on the average five phenol units per one melamine molecule in the product (calcd. 12.8 wt. % nitrogen). This is in good agreement with the hydroxyl number determination of 445 (calcd. 428). The molecular weight measured by VPO (Mn = 650 g/mol) also corresponds well to the structure in Figure 1 (calcd. MW 656 g/mol). For comparison, the GPC curve for the conventional phenol-formaldehyde novolak is shown in Figure 2. The intrinsic viscosity of **MP** in ethanol is equal to 3.8 mL/g, compared to 5.5 mL/g for the conventional novolak with Mn=750 g/mol.

The mass spectrum (Figure 3) of positive ions exhibits several dominating peaks, which must be undoubtedly ascribed to the hydroxyphenylmethylmelamines. Peaks (M+1) at masses of 551.4, 657.5, and 763.5 correspond to tetra-, penta-, and hexa(hydroxyphenylmethyl)melamine, respectively. The peak 443.3 is most likely to correspond to the penta- derivative cation, which has lost two hydroxyphenylmethyl substituents (2×107). Only some peaks of very low intensity in the spectrum can be ascribed to molecules of higher masses of resinous substances.

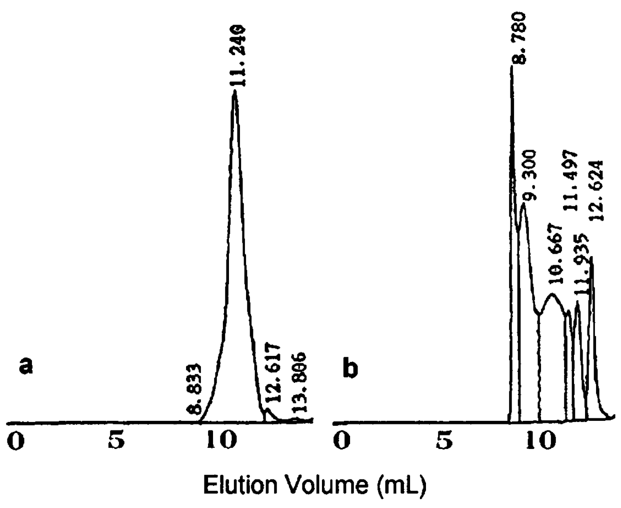


Figure 2.
Gel permeation chromatograms of:
a) melamine-phenolic novolak **MP**
b) conventional novolak resin

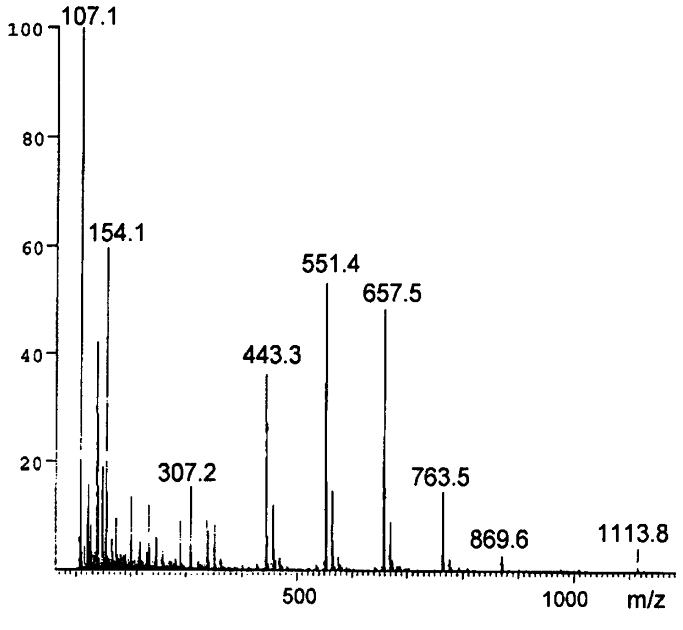


Figure 3. LSIMS/FAB MS spectrum of melamine-phenolic novolak **MP**

The ^{13}C-NMR spectrum of novolak **MP** (Table 1) corresponds well to hydroxyphenylmethylmelamines. The signals within the range of 40-50 ppm may be assigned to methylene carbons of N-**C**H_2-Ph groups. This is consistent with Tomita and Matsuzaki's work on copolycondensation of phenol, formaldehyde, and urea [20] . A weak signal at 73.4 ppm is present in the spectrum, which can be ascribed to N-**C**H_2O**C**H_2-N carbons. This shows a presence of small amounts of resinous products.

Table 1. ^{13}C-NMR data (40-50 ppm range) for melamine-phenolic novolak **MP**

Structure	chemical shift (ppm)	
-NH-**C**H_2-(o)PhOH	41.1	(40.6)*
-NH-**C**H_2-(p)PhOH	44.2	(44.2)
-N(CH_2)**C**H_2-(o)PhOH	45.6	(46.4)
-N(CH_2)**C**H_2-(p)PhOH	48.5	(49.2)

* values in parentheses: by Tomita [20]

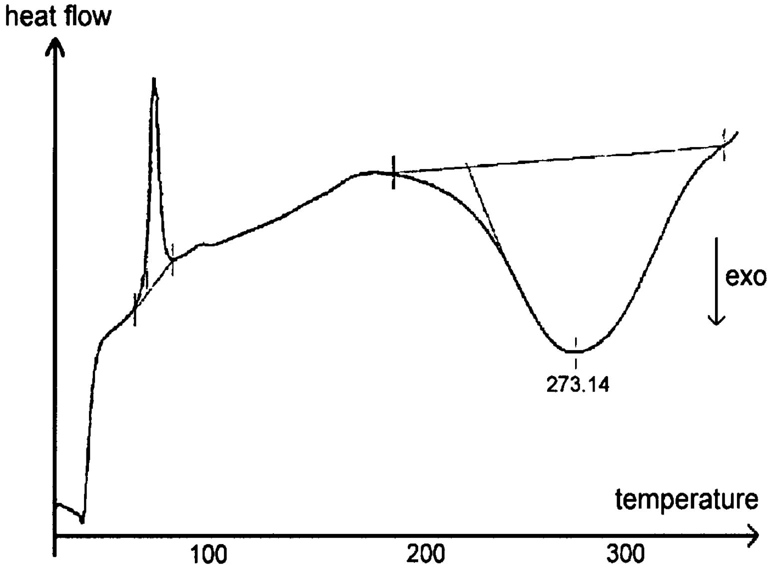


Figure 4. DSC of melamine-phenolic novolak **MP**

The DSC thermogram (Figure 4) shows the product **MP** to melt in the range 65°-83°C (peak temperature 75°C), and to be stable below 180-190 °C. At higher temperatures hydroxyphenylmethylmelamines undergo a hardening reaction (an exotherm in the

DSC curve with an extreme at 273 °C). The second heating DSC trace shows the glass transition temperature of the cured product at 118°C. The crosslinking is accompanied with the changes in the infrared spectrum (Figure 5).

The changes in position and intensity of the absorption peaks in the 1400-1600 cm^{-1} range, corresponding to the aromatic ring breathing and NH groups vibrations, are observed. The peak at 1610 cm^{-1}, grows in the intensity and appears as a well-defined band, which may be assigned to the NH deformation vibration. At the same time the intensity of the absorption at 1300-1350 cm^{-1}, attributed to the CN stretching vibration, decreases. The bands at 1550 cm^{-1} and 810 cm^{-1}, related respectively to in-plane and out-of-plane vibrations of triazine ring, increase their intensities. The latter band may overlap with the absorption due to CH deformation vibration of benzene ring (1,4 or 1,2,4 substitution type). Thus, changes in the arrangement of methylene bridges may influence the band pattern in this region, too.

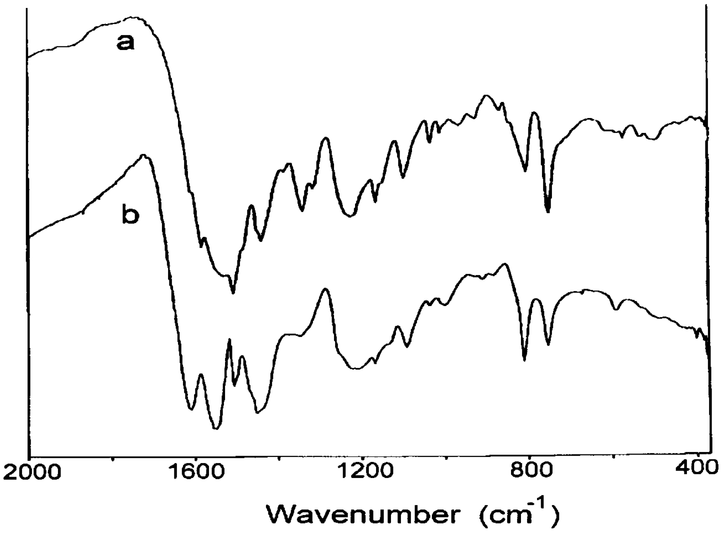


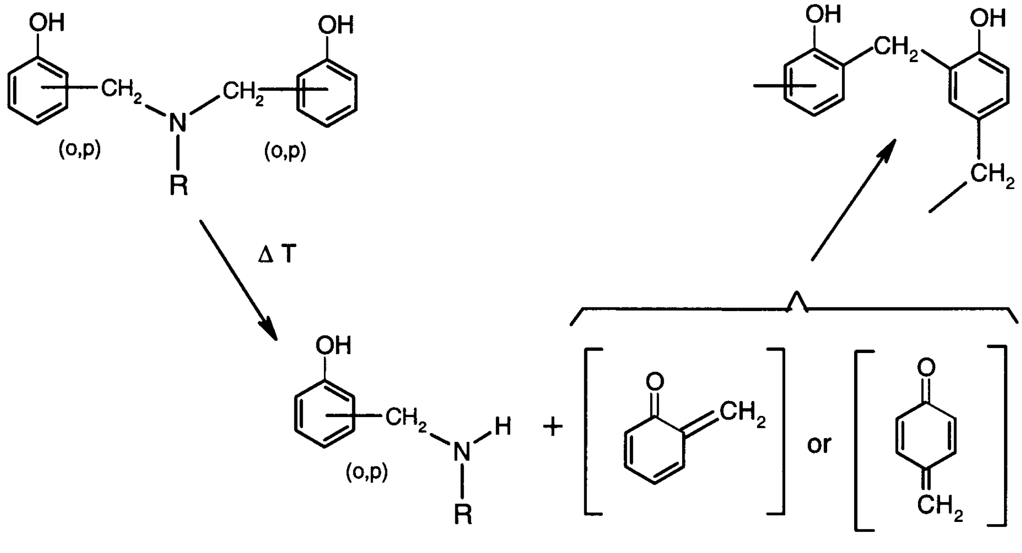
Figure 5. IR spectra of: a) melamine-phenolic novolak **MP** b) thermally cured **MP**

In conclusion, the infrared data may suggest that crosslinking proceeds through the rearrangement of the product MP structure. The mechanism for the cleavage of N-CH$_2$-Ph bond in aminomethylene bridged phenolic compounds at elevated temperatures was proposed by Kimura et al. [25]. The reaction leads to the reproduction of free amine groups and polycondensation of so formed quinone methide intermediates, as it is shown in Scheme 2.

Conclusion

It has been found that genuine co-condensation products of melamine, phenol, and formaldehyde can be obtained in high yield, when methylolated melamine react with phenol in the presence of a stoichiometric amount of hydrochloric acid, i.e., under conditions similar to those of the Mannich reaction. In this case, a mixture of individual hydroxyphenylmethylmelamines (HPMMs) was synthesized. It is almost certain that many other variations of genuine melamine – phenol – formaldehyde co-polycondensates can be obtained under applied conditions.

HPMMs are thermally stable up to 180-190 °C, at higher temperatures they undergo self-hardening, therefore unlike conventional novolaks they can be cured without using a crosslinking agent.



Scheme 2. Proposed thermal cure mechanism for melamine-phenolic novolak **MP**

HPMMs being a kind of multifunctional oligophenols can probably serve as low cost core substances for the controlled synthesis of phenol-formaldehyde type and other branched resins and polymers. Further work is in progress to use the method described above in the synthesis of more uniform oligophenols as well as the preparation of the next generations of dendritic molecules and will be reported later.

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