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UV-curable coatings of highly crosslinked trimethylmelamine based acrylates and methacrylates

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ABSTRACT

The synthesis and characterization of N^1,N^2,N^3-trimethylmelamine based (meth)acrylates and their application as components of UV-curable lacquers is described. A pre-condensed oligomeric mixture with a degree of condensation up to five is obtained via a one-pot conversion. Dividing the synthesis into two steps gives access to the mostly monomeric tris(meth)acrylates in overall yields higher than 76%. In general, the prepared compounds can easily be applied on glass, metal, and polystyrene glass affording highly transparent, hard, and scratch resistant coatings after UV-curing. The UV-cured monomeric trimethylmelamine trisacrylate was fully characterized by means of hardness, gloss, scratch-, abrasion-, and chemical resistance. Remarkably, the trimethylmelamine trisacrylate does not release cancerogen formaldehyde even at 150 °C.

1. Introduction

Highly resistant three-dimensional networks are obtained from the condensation of 2,4,6-triamino-1,3,5-triazine (melamine) and formaldehyde, the MF-resins, that were first commercially used by Henkel [1] in the mid-forties of the last century. Those MF-resins still play an important role in the wood-working industry until today [2]. Undesirably, these resins release formaldehyde during and even many years after the curing process. Albeit, formaldehyde is widespread in Nature and found as metabolite in animal and human bodies, in the early 1990s it was classified to be toxic and since 2004 of being carcinogenic to humans [3]. Thus, the emission of formaldehyde is a problem both at the stage of processing and in the final product. The development of formaldehyde-free, curable alternatives to MF-resins, while keeping the known advantages of market available products, is still of research interest. Most melamine produced worldwide is used for the manufacture of resins but further fields of applications are found in additives and coatings, adhesives, and varnishes [4–6]. The derivatization of the exocyclic nitrogens of melamine with polymerizable acrylic and methacrylic functionalities is found in patents [7–9] and Giacobbe et al. [10] published low radiation curable melamine based acrylates. The compounds found in literature are monomers to oligomeric mixtures, wherein the exocyclic nitrogens of melamine are connected via methylen or ether bridges and partially containing weakly bonded hydroxymethyl groups that, besides the ether bridges, are known to readily release formaldehyde. In general, melamine constitutes a problematic starting material showing various difficulties resulting from its poor solubility in most organic solvents, the low reactivity of the exocyclic amino functionalities, which are possessing amide-like reactivity, and out of these often yield reaction products of complex composition. Focused on the preparation of a pre-condensed oligomeric product mixture and monomers with exactly defined chemical structure our synthesis strategy based on the derivatization of

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the methylmelamine 2,4,6-tris(methylamino)-1,3,5-triazine (**1**). Trimethylmelamine (**1**) shows good to excellent solubility in most organic solvents, an increased reactivity compared to melamine, and provides a high degree of functionalization of the obtained cured product. Within this paper we present the synthesis of highly reactive multifunctional trimethylmelamine (**1**) based acrylates and methacrylates, we determined their UV-curing behavior, and investigated the formaldehyde release as well as the mechanical and physic-chemical properties of the cured coatings.

2. Materials and methods

All solvents and reagents were of p.a. quality and were used without further purification. Solvents and reagents were purchased from standard chemical suppliers. Photoinitiator Irgacure 500, dipropylene glycol diacrylate (Laromer DPGDA), and Ebecryl P 116 were purchased from Ciba Specialty Chemicals, BASF, and Cytec Surface Specialties. Melting points are uncorrected and were measured on a Leica Galen III microscope with a Kofler melting point unit. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra as well as 2D correlation NMR experiments were performed on a Brucker Avance DPX 200 MHz spectrometer using standard pulse sequences as provided by the manufacturer. Deuterated solvents were used as internal calibration standards for NMR spectroscopy. Fourier transform infra-red (FT-IR) and mass spectra were recorded using a Perkin Elmer Paragon 1000 PC FT-IR spectrometer and a Thermo Finnigan LCQ DECA XP$^{\text{plus}}$ with electro spray ion source (ESI) with sample delivered by a syringe pump at a flow rate of 5 mm^3 min^{-1}. UV curing was carried out in a Hoenle UVACUBE 100 and irradiation equipment from IST METZ GmbH using a mercury medium pressure lamp. Scratch resistance was measured on an Erichsen Universal Scratch Tester 413 using a test tip according to Bosch. Stain resistance against potassium permanganate was tested according Ref. [11] using a Gretag Macbeth Color Eye 7000 color analyzer. Pencil hardness was tested by the Erichsen Pencil Test model 318. Pendulum hardness was determined by the König method regarding to ISO 1522 using Byk-Gardner 5858 equipment. Gloss was measured at three different angles with an Erichsen PICOGLOSS 503 gloss meter. Abrasion resistance was tested with the Taber abraser 352 G instrument from Erichsen using S33 abrasive discs. The falling sand method was performed according to DIN 52348 or ASTM D 968 with an instrument from Qualtec Products Industry. 2,4,6-Tris(methylamino)-1,3,5-triazine (**1**) was synthesized by temperature controlled stepwise nucleophilic substitution of the chlorine atoms in cyanuric chloride with methylamine [12,13]. Crude **1** was recrystallized from 2-propanol.

2.1. Potassium permanganate stain resistance test

An aqueous potassium permanganate solution (1 wt.%) is dropped onto the film surface and rinsed off with deionized water after five minutes. The color change is determined by the yellowness index of the stain using a color analyzer.

*2.2. Synthesis of ((((1,3,5-triazine-2,4,6-triyl)tris(methylazanediyl))tris(methylene))tris(oxy))tris(ethane-1,2-diyl) tris(2-methylacrylate) (**2**, $C_{27}H_{42}N_6O_9$)*

To a suspension of 100.0 g (0.387 mol) 2,4,6-tris[(hydroxymethyl)methylamino]-1,3,5-triazine (**7**) in 400 cm^3 THF at 0 °C are added 151.4 g (1.16 mol) 2-hydroxyethyl methacrylate and 0.37 g (3.01 mmol) 4-methoxyphenol (PMP) dissolved in 25 cm^3 THF. After stirring for 15 min a solution of 2.21 g (11.6 mmol) 4-toluenesulfonic acid in 25 cm^3 THF is added and the reaction mixture is stirred at 0 °C for further 12 h. The reaction solvent is evaporated, the crude product dissolved in toluene, washed with saturated sodium bicarbonate solution twice, and three times with deionized water. The separated organic layer is dried over a sodium sulfate/calcium chloride mixture and evaporation of the solvent yields 214.0 g **2** (93%) as a colorless, oily liquid.

^{1}H NMR (200 MHz, $CDCl_3$, 30 °C, δ): 6.13 (d, $J_1 = 2.0$ Hz, 3H, $C{=}\mathbf{CH_2}$), 5.57 (d, $J_1 = 2.0$ Hz, 3H, $C{=}\mathbf{CH_2}$), 5.18 (s, 6H, $N{-}\mathbf{CH_2}{-}O$), 4.28 (t, $J_2 = 6.1$ Hz, 6H, $\mathbf{CH_2}{-}OC(O)$), 3.72 (t, $J_2 = 6.1$ Hz, 6H, $O{-}\mathbf{CH_2}{-}CH_2$), 3.12 (s, 9H, $N{-}\mathbf{CH_3}$), 1.95 (s, 9H, $C{-}\mathbf{CH_3}$) ppm.

^{13}C NMR (50 MHz, $CDCl_3$, 30 °C, δ): 167.5 ($\mathbf{C}{=}O$), 166.3 ($N{-}\mathbf{C}{=}N$), 136.4 ($\mathbf{C}{=}CH_2$), 125.9 ($C{=}\mathbf{C}H_2$), 78.08 ($N{-}\mathbf{C}H_2{-}O$), 65.78 ($O{-}\mathbf{C}H_2{-}CH_2$), 63.99 ($\mathbf{C}H_2{-}OC(O)$), 33.13 ($N{-}\mathbf{C}H_3$), 18.49 ($C{-}\mathbf{C}H_3$) ppm.

FT-IR (film between CaF_2 windows, $\bar{\nu}$): 3420, 2951, 2895, 1716, 1637, 1539, 1494, 1453, 1393, 1318, 1295, 1163, 1125, 1093, 1011, 943, 861, 810, 739, 650 cm^{-1}.

ESI-MS ($CHCl_3$:MeOH = 1:1, $c \sim 10$ µg cm^{-3}, positive ion mode, m/z): 595.5 (100) [**2** + H]$^+$.

*2.3. Synthesis of an Oligomeric Mixture of Trimethylmelamine based Methacrylates (**2**–**6**)*

150.1 g (0.892 mol) 2,4,6-tris(methylamino)-1,3,5-triazine (**1**), 248.2 g (2.68 mol) 2-hydroxyethyl methacrylate, 80.3 g (2.67 mol) paraformaldehyde, and 0.36 g 4-methoxyphenol are heated in 200 cm^3 toluene with efficient stirring using a KPG stirrer while flushed with nitrogen through an inlet tube. After 20 min stirring at 85 °C the mixture is heated to 95 °C. During the second heating period 1.50 g (7.88 mmol) 4-toluenesulfonic acid are added in 30 cm^3 THF/toluene mixture (1:1, v:v). 95 °C are held for 20 min followed by heating to 105 °C. Toluene is then evaporated at 110 °C for 20 min yielding an oligomeric mixture of trimethylmelamine based methacrylates **2**–**6** as a colorless, highly viscous liquid. To obtain a solvent free product mixture it is necessary to remove toluene under vacuum between 105 and 115 °C for 20 min.

FT-IR (film between CaF_2 windows, $\bar{\nu}$): 3503, 2952, 2889, 1719, 1637, 1541, 1493, 1393, 1373, 1319, 1296, 1168, 1125, 1097, 1029, 944, 861 cm^{-1}.

*2.4. Synthesis of ((1,3,5-triazine-2,4,6-triyl)tris(methylazanediyl))trimethanol (**7**, $C_9H_{18}N_6O_3$)*

150.2 g (0.893 mol) 2,4,6-tris(methylamino)-1,3,5-triazine (**1**) and 17.1 g potassium carbonate are suspended in 520 cm^3 water. During 15 min and with efficient stirring