Syntheses of Monomers from Hydroxyethyl Acrylate and Methylolmelamine Which Polymerize by Low Doses of Radiation

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ABSTRACT: A process has been developed for the syntheses of monomers from 2-hydroxyethyl acrylate (HEA), hexamethylolmelamine, and another alcohol (optional). Two of the monomers, tris(acryloyloxyethoxymethyl)tris(methoxymethyl)melamine and hexakis(acryloyloxyethoxymethyl)melamine, were found to polymerize to dry, hard films when initiated by very small doses (0.1 and 0.04 Mrad, respectively) of high-energy electrons (2 Mev).

The growing interest in systems which can be cured by high-energy radiation prompted us to investigate monomers derived from melamine, formaldehyde, and hydroxyethyl acrylate (HEA). Radiation-initiated polymerizations have been the subject of numerous papers[1,2] and several patents.[3-6] Interest in radiation-initiated polymerizations partially stems from the speed of the process, the fact that solvents (a source of air pollution) are often not required, and that it is a facile method for coating solids.

Preparation of the Monomers

The preparation of new monomers which contained varying amounts of 2-hydroxyethyl acrylate residues attached to a melamine nucleus was approached by two routes. The first was an acid-catalyzed transetherification between hexakis(methoxymethyl)melamine and 2-hydroxyethyl acrylate. This transetherification procedure[7] was successfully employed for preparation of the compound which contained one HEA residue, pentakis(methoxymethyl)acryloyloxyethoxymethylmelamine. However, the preparation of compounds by this procedure which contained three or more HEA residues was unsuccessful. The reaction was very slow at room temperature and polymeric material was formed at elevated temperatures. Both concentrated hydrochloric acid and *p*-toluenesulfonic acid were employed as acid catalysts.

The second route to the desired monomers was an acid-catalyzed etherification of hexamethylolmelamine. This route provided an easy entry into a series of monomers which contained multiple HEA residues per melamine. The reactions were rapid (2–11 hr) at room temperature and the monomers were obtained in yields of 43–73%.

A comparison of the probable mechanisms of the two routes for monomer formation suggested that the acid-catalyzed etherification of hexamethylolmelamine (A) should be superior, since it was expected that water should be superior to methanol as a leaving group (see Scheme I). The superiority of the second route was proven experimentally.

Several acid catalysts (concentrated hydrochloric acid, picric acid, *p*-toluenesulfonic acid, and concentrated sulfuric acid) were used to catalyze the etherification of hexamethylolmelamine with 2-hydroxyethyl acrylate. Concentrated sulfuric acid was found to be a superior catalyst for the etherification.

The mixed ethers containing both alkoxy and acryloyloxyethoxy groups could be synthesized in a single-step procedure. This was accomplished by premixing the appropriate alcohol and HEA prior to reaction with hexamethylolmelamine. Table I lists the compounds prepared in this manner. Hammond has reported the reaction of hydroxylalkyl acrylates and hexamethylolmelamine to form monomers similar to those discussed in this report.[8]

The relative nucleophilicities of methanol and HEA were determined by competitive reactions between hexamethylolmelamine, methanol, and HEA. It was then possible to prepare a monomer containing a predetermined number of the methoxy and acryloyloxyethoxy groups. The ratio of methanol to HEA moieties on the methylmelamine nucleus could be approximated according to the equation

$$\frac{\text{HEA residues/melamine}}{\text{CH}_3\text{OH residues/melamine}} = \frac{\text{mol of HEA charged} \times 0.6}{\text{mol of CH}_3\text{OH charged}} \quad (1)$$

The substitution equation (1) was altered if the commercial grade HEA was not purified to remove acrylic acid. The relative reactivities of methyl, ethyl, *n*-propyl, and *n*-butyl alcohol in the etherification of hexamethylolmelamine have been accurately determined, and similar results were obtained by Anderson, Netzel, and Tessari.[9]

The monomers were easily purified by dissolving in benzene, extracting with water, and concentrating the benzene solution. The excess alcohols (HEA and methanol or butanol) were the major impurities and were extracted by water.

The monomers prepared by the reaction of HEA, hexamethylolmelamine, and another alcohol (optional) were

TABLE I

MONOMERS PREPARED FROM HEXAMETHYLOLMELAMINE (A)

R			
No. of alkoxy residues		No. of HEA residues	% yield
Methyl	0	6	73
	3	3	61
	3.4	2.6	
	4.2	1.8	59
Butyl	3.3	2.7	43

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(1) W. H. T. Davison, *J. Oil Colour Chem. Ass.*, **52**, 946 (1969).

(2) W. Vanderbie, P. Spencer, and C. Swanholm, *Paint Varn. Prod.*, **59** (3), 39 (1969).

(3) W. J. Burlant, U. S. Patent 3,437,514 (1969); to Ford Motor Company.

(4) P. Timmerman, U. S. Patent 3,467,488 (1969); to Radiation Processing, Inc.

(5) J. J. Brophy and R. R. Perron, U. S. Patent 2,668,133 (1954); to United Shoe Machinery Corp.

(6) W. H. T. Davison, British Patent 949,191 (1964); to T. I. (Group Services), Ltd.

(7) J. K. Magrane and R. E. Layman, U. S. Patent 3,020,255 (1962); to American Cyanamid Co.

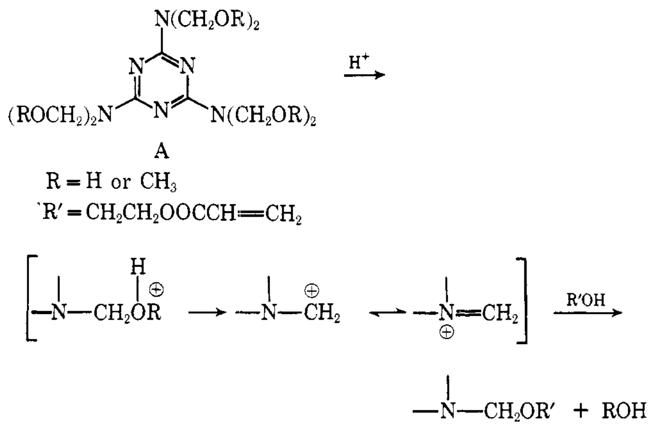
(8) R. Hammond, British Patent 628,150 (1949); to I.C.I., Ltd.

(9) D. G. Anderson, D. A. Netzel, and D. J. Tessari, *J. Appl. Polym. Sci.*, **14**, 3021 (1970).

TABLE II
RATIO OF NMR PEAK AREAS

Compound	Ratio	Theory	Found	Comments
1	(1) A/C	0.75	0.79	If <0.75, then some polymerization If >0.75, then diacrylate present
	(2) $(A + B)/B$	1.5	1.46	If >1.5, then contamination by HEA and/or methanol and/or diacrylate If <1.5, then some polymer formation and/or incomplete etherification
	(3) B/C	1	1	If >1, then incomplete etherification If <1, then diacrylate and/or HEA present
2	(4) A/C	0.75	0.76	Same as (1)
	(5) A/B	1.5	1.65	Same as (2)
	(6) B/C	0.5	0.46	If >0.5, then etherification not complete If <0.5, then contaminated with HEA and/or diacrylate.

SCHEME I
A PROPOSED MECHANISM FOR THE FORMATION OF THE MONOMERS



characterized by nuclear magnetic resonance (nmr) spectroscopy. Anderson, *et al.*,[9] also characterized their aliphatic melamine ethers by nmr spectroscopy. The nmr spectra of tris(acryloyloxyethoxymethyl)tris(methoxymethyl)melamine (**1**) and hexakis(acryloyloxyethoxymethyl)melamine (**2**) were selected as representative examples (see Figures 1 and 2).

These nmr spectra bear some additional comments. Various ratios of the peak areas could be obtained which provided some diagnostic information about the products. These ratios are collected in Table II. The signal at δ 7.15 (Figure 1) was ascribed to residual benzene, and the small (<2% of the total proton integration) signals at high field (δ >2.9) were probably due to polymeric materials. The presence of 1,2-bis(acryloyloxy)ethane (referred to as diacrylate in Table II) could be implied from the nmr data as an impurity in some of the monomers.

Electron-Beam Curing of the Monomers

Electron-beam-induced polymerization of tris(acryloyloxyethoxymethyl)tris(methoxymethyl)melamine (**1**) and hexakis(acryloyloxyethoxymethyl)melamine (**2**) was found to proceed at very low dose levels. When films of **1** and **2** were subjected under a nitrogen atmosphere to a beam of 2-MeV electrons from a Van de Graaf accelerator, both materials polymerized to form dry, clear, nonscratchable coatings with dose levels of 0.1–0.2 and 0.04–0.06 Mrad, respectively, using a beam current of 10 μA.

The low doses necessary to cure hexakis(acryloyloxyethoxymethyl)melamine (**2**) compare very favorably with the doses required to cure various acrylate and methacrylate monomers.[10]

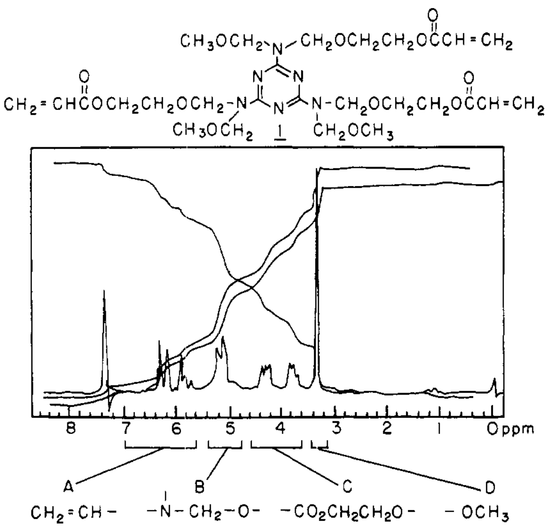


Figure 1. The nmr spectrum of the tris(acryloyloxyethoxymethyl)tris(methoxymethyl)melamine (**1**). The structure shown above indicates the average composition of the monomer; see text.

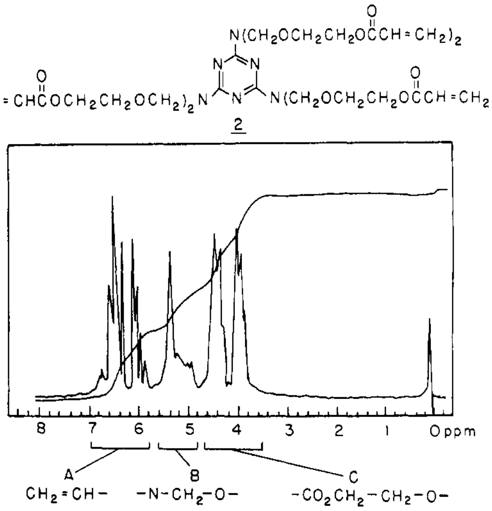


Figure 2. The nmr spectrum of hexakis(acryloyloxyethoxymethyl)melamine (**2**).

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(10) T. J. Miranda and T. F. Huemmer, *J. Paint Technol.* **41**, 118 (1969).

Experimental Section

All solvents were distilled prior to use. Infrared spectra were recorded with a Perkin-Elmer Infracord spectrometer. The nmr spectra were recorded with Varian A-60A or T-60 recording spectrometers, and peak positions were recorded in parts per million (δ) relative to tetramethylsilane used as an internal standard. Evaporations at reduced pressure were accelerated with a warm bath which was at 40° or below. Melting points were taken on a Fisher-Johns melting point apparatus. Room temperature was 23 ± 2°. HEA (Dow Chemical Co.) was purified by passing through an alumina column (9 in. × 1 in. i.d., Fisher 80–200 mesh, used for 45 ml of HEA). 4-Methoxyphenol was obtained from Eastman Organic Chemicals, and it was used to inhibit polymerization during preparative reactions. Sulfuric acid (Mallinckrodt Chemical Works) was 95–98% analytical reagent.

Condensation of Formaldehyde and Melamine. Hexamethylolmelamine. The procedure employed was essentially the one described by Sorenson and Campbell.[11] The reaction product was collected by filtration and the filter cake was washed twice with fresh portions of ethanol and three times with dichloromethane. The filter cake was granulated and placed under vacuum (15 mm) at room temperature for 15 hr to yield 80.5 g (88%) of a white solid identified as hexamethylolmelamine, mp 159–163° (Fisher–Johns, block setting 30), lit.[11] mp ~150°.

Reaction of 2-Hydroxyethyl Acrylate, Methanol, and Hexamethylolmelamine. Tris(acryloyloxyethoxymethyl)tris(methoxymethyl)melamine (1). A solution of methanol (17.6 ml, 0.435 mol) and 2-hydroxyethyl acrylate (79 ml, 0.75 mol) was added to a mixture of hexamethylolmelamine (25.5 g, 0.083 mol) and 4-methoxyphenol (300 mg) in a 250-ml round-bottomed, single-necked flask fitted with a magnetic stirrer. The mixture was stirred until the particles were dispersed (1 min), and then sulfuric acid (3 ml) was added. The reaction vessel was fitted with a drying tube containing calcium chloride and was allowed to stir at room temperature for 2 hr. The reaction solution was diluted with 500 ml of benzene and the benzene solution was extracted with two 100-ml portions of a saturated, aqueous solution of sodium bicarbonate and then with four 100-ml portions of water. The benzene solution was dried by passing it through a mixed bed of anhydrous calcium sulfate and sodium sulfate in a cone of fluted filter paper. The dried benzene solution was concentrated under reduced pressure and finally using a vacuum pump (1 mm) at room temperature for 2 hr to yield 32.6 g (61%) of a viscous, water-white liquid identified as tris(acryloyloxyethoxymethyl)tris(methoxymethyl)melamine: ir max (film) 1735 (ester $C{=}O$), 1650 (shoulder, $C{=}C$), 1550 cm^{-1} (melamine aromatic $C{=}N$); nmr δ 6.2 (9 H, multiplet, CH_2CH), 5.2 (12 H, multiplet, $N{-}CH_2{-}O$), 4.1 (12 H, multiplet, $O{-}CH_2CH_2{-}O$), 3.33 (9 H, s, $O{-}CH_3$).

The ratio of methoxy to acryloyloxyethoxy groups in the final product was varied from an average of 4.2 methoxy and 1.8 acryloyloxyethoxy groups to no methoxy and 6 acryloyloxyethoxy groups per melamine moiety. The desired degree of substitution on the product could be predetermined (see text). The isolation of the other products was identical with that of the procedure described above.

Reaction of 2-Hydroxyethyl Acrylate and Hexamethylolmelamine. Hexakis(acryloyloxyethoxymethyl)melamine (2). 2-Hydroxyethyl acrylate (40 ml, 0.379 mol) was added to a mixture of hexamethylolmelamine (10 g, 0.0327 mol) and 4-methoxyphenol (75 mg) in a 100-ml, round-bottomed, single-necked flask fitted with a magnetic stirrer. The mixture was stirred until the particles were dispersed (1 min), and then sulfuric acid (1 ml) was added. The reaction vessel was fitted with a drying tube containing calcium chloride and was allowed to stir at room temperature for 11 hr. The reaction was diluted with a two-component solvent consisting of ethyl acetate (150 ml) and hexane (75 ml). The reaction solution was extracted twice with 50-ml portions of a saturated, aqueous solution of sodium bicarbonate, then with four 50-ml portions of water. The organic layer was dried by passing it through a mixed bed of anhydrous calcium sulfate and sodium sulfate in a cone of fluted filter paper. The dried solution was concentrated under reduced pressure and finally using a vacuum pump (1 mm) for 4 hr to yield 21.2 g (73%) of a water-white liquid identified as hexakis(acryloyloxyethoxymethyl)melamine: ir max (film) 1730 (ester $C{=}O$), 1640 (shoulder, $C{=}C$), 1550 cm^{-1} (melamine aromatic $C{=}N$); nmr δ 6.2 (18 H, multiplet, $CH_2{=}CH$-), 5.17 (12 H, multiplet, $N{-}CH_2{-}O$), 4.3 (12 H, multiplet, -OCH_2CH_2OCO-), 3.8 (12 H, multiplet, -OCH_2CH_2OCO-).

Reaction of 2-Hydroxyethyl Acrylate, *n*-Butyl Alcohol, and Hexamethylolmelamine. A premixed solution of *n*-butyl alcohol (13.7 ml, 0.15 mol) and 2-hydroxyethyl acrylate (15.8 ml, 0.15 mol) was added to a mixture of hexamethylolmelamine (5.1 g, 0.0167 mol) and 4-methoxyphenol (60 mg) in a 50-ml, round-bottomed flask fitted with a magnetic stirrer.

The mixture was stirred until the particles were dispersed (1 min), and then sulfuric acid (0.16 ml) was added. The reaction vessel was fitted with a drying tube containing calcium chloride and was allowed to stir at room temperature for 3.75 hr. The reaction solution was diluted with 150 ml of benzene and the benzene solution was extracted with one 50-ml portion of a saturated, aqueous solution of sodium bicarbonate, then with five 50-ml portions of water. The benzene solution was dried by passing it through a mixed bed of anhydrous calcium sulfate and sodium sulfate in a cone of fluted filter paper. The dried benzene solution was concentrated under reduced pressure finally using a vacuum pump (1 mm) at room temperature for 2 hr to yield 5.9 g (47%) of a viscous, water-white liquid. The nmr identified the material as a mixture whose average composition was 3.3 butoxy and 2.7 acryloyloxyethoxy groups per melamine moiety: ir max (film) 1730 (ester $C{=}O$), 1650 (shoulder, $C{=}C$), 1560 cm^{-1} (melamine aromatic $C{=}N$); nmr δ 6.2 (ten-line multiplet, $CH_2{=}CH$-), 5.3 (multiplet, $N{-}CH_2{-}O$), 4.3 (four-line multiplet, CH_2CH_2OCO-), 3.8 (four-line multiplet, -OCH_2CH_2OCO-), 3.52 (triplet, spacing = 6 Hz, $OCH_2CH_2CH_2CH_3$), 1.8 (multiplet, $OCH_2CH_2CH_2CH_3$), 0.9 (triplet, spacing = 7 Hz, -CH_2CH_3).

Electron-Beam Polymerization of Hexakis(acryloyloxyethoxymethyl)melamine (2) and Tris(acryloyloxyethoxymethyl)tris(methoxymethyl)melamine (1). Hexakis(acryloyloxyethoxymethyl)melamine (approximately 10 g) was coated on a 4 in. × 12 in. × 0.03 in. polished steel "Q" panel with a 7-mil clearance draw bar. The space above the panel was continuously flushed with nitrogen while the panel passed through a beam of 2-MeV electrons from a Van de Graaf accelerator filtered with aluminum metal (0.33 g/cm^2). A 10-μA beam current and conveyor speed of 3.4 cm/sec delivered a dose of 0.02 Mrad for each pass through the beam. Three passes (0.06 Mrad) through the beam caused the hexakis(acryloyloxyethoxymethyl)melamine coated on the Q panel to become a dry (nontacky), clear, nonscratchable (with fingernail) film. When the dose level was reduced to 0.04 Mrad a dry, clear film also resulted, but it could be scratched (with difficulty).

Tris(acryloyloxyethoxymethyl)tris(methoxymethyl)melamine was coated on steel Q panels and irradiated under a nitrogen atmosphere as described above. The material formed a dry (nontacky), clear, nonscratchable (with fingernail) film with a dose of 0.2 Mrad. When the dose level was reduced to 0.1 Mrad, a dry, clear film also resulted, but it could be scratched.

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(11) W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," Interscience, New York, N. Y., 1968, pp 460–461.