Synthesis, Characterization, and Utilization of Methacrylic Esters of Polyhydric Alcohols

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Synopsis

Dimethacrylic esters of di-, tri-, and tetraethylene glycols; trimethacrylic ester of trimethylolpropane and tetramethacrylic ester of pentaerythritol were prepared by a commercially viable process in high yields and purity. These methacrylic esters were systematically characterized by infrared, ^{1}H and ^{13}C nuclear magnetic resonance and mass spectroscopic methods. Anaerobic adhesive compositions were made based on each monomer, and their torque strengths were compared.

INTRODUCTION

The synthesis of some of the dimethacrylic esters of polyhydric alcohols was reported in the literature[1-3] earlier by the transesterification method, in which a lower alkyl ester of methacrylic acid was reacted with a polyhydric alcohol or an alkali metal alcoholate in the presence of an ester linkage catalyst, polymerization inhibitor, and an inert diluent. However, unsatisfactory yields of the esters were obtained due to excessive polymerization during the reaction. Therefore, the following was suggested: (1) the use of a column packed with copper gauge to prevent polymerization of the reactants during the progress of the reaction and (2) the addition of small amounts of monomers from the dropping funnel into a claisen flask so as to avoid prolonged heating of the monomers during distillation.[4]

However, these methods did not work satisfactorily when these monomers are to be prepared on moderately large scale. In this communication, we are reporting the synthesis of di-, tri-, and tetramethacrylic esters on pilot plant scale in high conversions and in high purity. These were characterized by various spectroscopic methods and were evaluated as anaerobic adhesives.

EXPERIMENTAL

Preparation of Diethylene Glycol Dimethacrylate

In a stainless steel reaction kettle of 10 L capacity, diethylene glycol (15 mol, 1590 g), a polymerization inhibitor (45.0 g), and an esterification acidic catalyst (45.0 g) were charged. An inert solvent such as benzene (2800 mL) and a small amount of a chain terminating solvent such as carbon tetrachloride

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TABLE I
Physicochemical Characteristics of Methacrylic Esters of Polyhydric Alcohols

Methacrylic ester	Yield (%)	GLC analysis		Iodine value		Refractive index (°C)	Density [g/mL (°C)]	Melting point (°C)
		Retention time (min)	Purity (%)	Obtained	Theory			
DEGDMA	92.0	1.47	92.0	193.0	209.9	1.4565 (29)	1.100 (28)	—
TEGDMA	94.0	3.32	91.7	162.9	177.6	1.4577 (30)	1.070 (28)	—
TETEGDMA	94.0	7.46	92.5	142.4	153.9	1.4607 (24)	1.020 (28)	—
TMPTMA	93.0	9.58	93.0	209.6	225.4	1.4700 (24)	—	—
PETETMA	80.0	17.40	87.0	216.6	249.0	—	—	54.5

(100 mL) were then added into the kettle. The contents were heated to reflux temperature (90°C) under slow stirring. Methacrylic acid (33.0 mol, 2840 g) was then added slowly, using a dropping funnel, to the charge of the kettle over a period of 4 h. The water of reaction formed was continuously removed azeotropically with benzene through a Dean and Stark trap. The amount of water (30 mol, 540 mL) was collected in an 8-h reaction period, indicating the completion of the reaction.

The crude reaction product in benzene was then transferred to another kettle and washed with 2 × 10 L water to remove the acidic catalyst and part of the unreacted and excess methacrylic acid. The remaining methacrylic acid was removed by washing the product with 5% sodium carbonate aqueous solution (20 L) and finally washed with another 20 L of water till the washings were neutral. At this stage, the benzene solution containing the crude product, which was dark in color, was bleached by adding a bleaching earth and stirring it at 50°C for 30 min. The solution was then allowed to stand still for 1 h, and the solution was decanted neatly. The benzene was then stripped off under reduced pressure using water suction. Thus 1900 mL benzene was recovered out of a total charge of 2800 mL.

The crude diethyleneglycol dimethacrylate (DEGDMA) was golden yellow in color and weighed 3340 g (percent yield 92). The purity of the product was 92% as determined by gas liquid chromatography (GLC) and iodine value. The iodine value was determined by the pyridine sulfate dibromide method.[5]

Using the same procedure, triethylene glycol dimethacrylate (TEGDMA) and tetraethylene glycol dimethacrylate (TETEGDMA) were prepared. Trimethylol propane trimethacrylate (TMPTMA) and pentaerythritol tetramethacrylate (PETETMA) were prepared using 3.30 and 4.40 mol of methacrylic acid per 1 mol of corresponding polyhydric alcohols, respectively.

Physicochemical properties of these technical grade methacrylic esters are reported in Table I.

Evaluation of Purity By Thin Layer Chromatography (TLC) and Gas Liquid Chromatography (GLC)

TLC Technique was used to check qualitatively the conversion of polyhydric alcohol to corresponding methacrylic ester. The TLC plates coated with silica gel G were developed with an n-hexane; ethyl ether (50:50 v/v) solvent system, and the plates were exposed in an iodine chamber. The polyhydric

alcohols appeared at 0–10 ($R_f \times 100$) and corresponding methacrylic esters appeared at 70–80 ($R_f \times 100$).

GLC technique was used to estimate quantitatively the purity of the methacrylic esters. The chromatographic column used in this study was a glass capillary column of 6 mm diam and 2 m long, packed with diethylene glycol succinate supported on Chromosorb W. Carrier gas nitrogen (41.0 mL/min) and flame ionization detector (FID) were used. Injection port and FID temperature 300°C each were maintained. The retention time in minutes for each methacrylic ester is reported in Table I.

Spectroscopic Studies of Purified Methacrylic Esters

Small amounts (10 g) of each monomer were purified by passing them through a column packed with silica gel and eluting them with *n*-hexane. These purified monomers were used for spectroscopic studies.

Infrared Spectroscopy (IR)

The IR spectra were recorded using a Perkin-Elmer (Model 221) spectrophotometer. The IR spectra of all these monomers are quite similar and hence are not discussed in great detail for each monomer individually. For the same reason, only one IR spectrum is shown in Figure 1 of the monomer TEGDMA. Two characteristic C—H out-of-plane deformation vibration of methacrylic esters appear at 810 and 930 cm^{-1}. C=C stretching and C—H in plane deformation vibrations of methacrylic esters appear at 1630 cm^{-1} and as doublet at 1290 and 1320 cm^{-1}, respectively. C=O stretching vibration of ester appears as a strong band at 1720 cm^{-1} and C—O stretching vibrations of ether/ester are shown at 1110–1160 and 1040 cm^{-1}.

^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR)

^{1}H-NMR spectra of the monomers in carbon tetrachloride were recorded using FT-NMR-JEOL-FX-90-Q-MHZ NMR spectrophotometer, and the chemical shifts are recorded in δ values (ppm) with tetramethyl silane as internal standard. For all monomers, the spectra are consistent with the structures, and only the essential features are described below.

The ^{1}H-NMR spectra of DEGDMA, TEGDMA, and TETEGDMA are similar as their chemical structures are similar. Their general structure may be represented as

$$(a_1) \, H \diagdown \atop (a_2) \, H \diagup C = \underset{\underset{(b)}{CH_3}}{\overset{(c)}{C}} - CO - O - \overset{(d)}{CH_2} - \overset{}{CH_2} - O \left[\overset{(d)}{CH_2} - \overset{(d)}{CH_2} - O \right]_n$$

$$- \overset{(d)}{CH_2} - \overset{(c)}{CH_2} - O - CO - \underset{\underset{(b)}{CH_3}}{C} = C \overset{\diagup H \, (a_1)}{\diagdown H \, (a_2)}$$
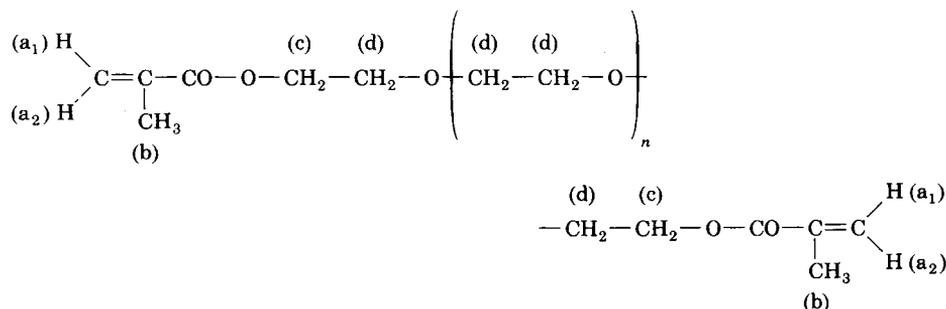
where n = 0 for DEGDMA, = 1 for TEGDMA, and = 2 for TETEGDMA. The ^{1}H-NMR spectra of DEGDMA and TETEGDMA only are shown in
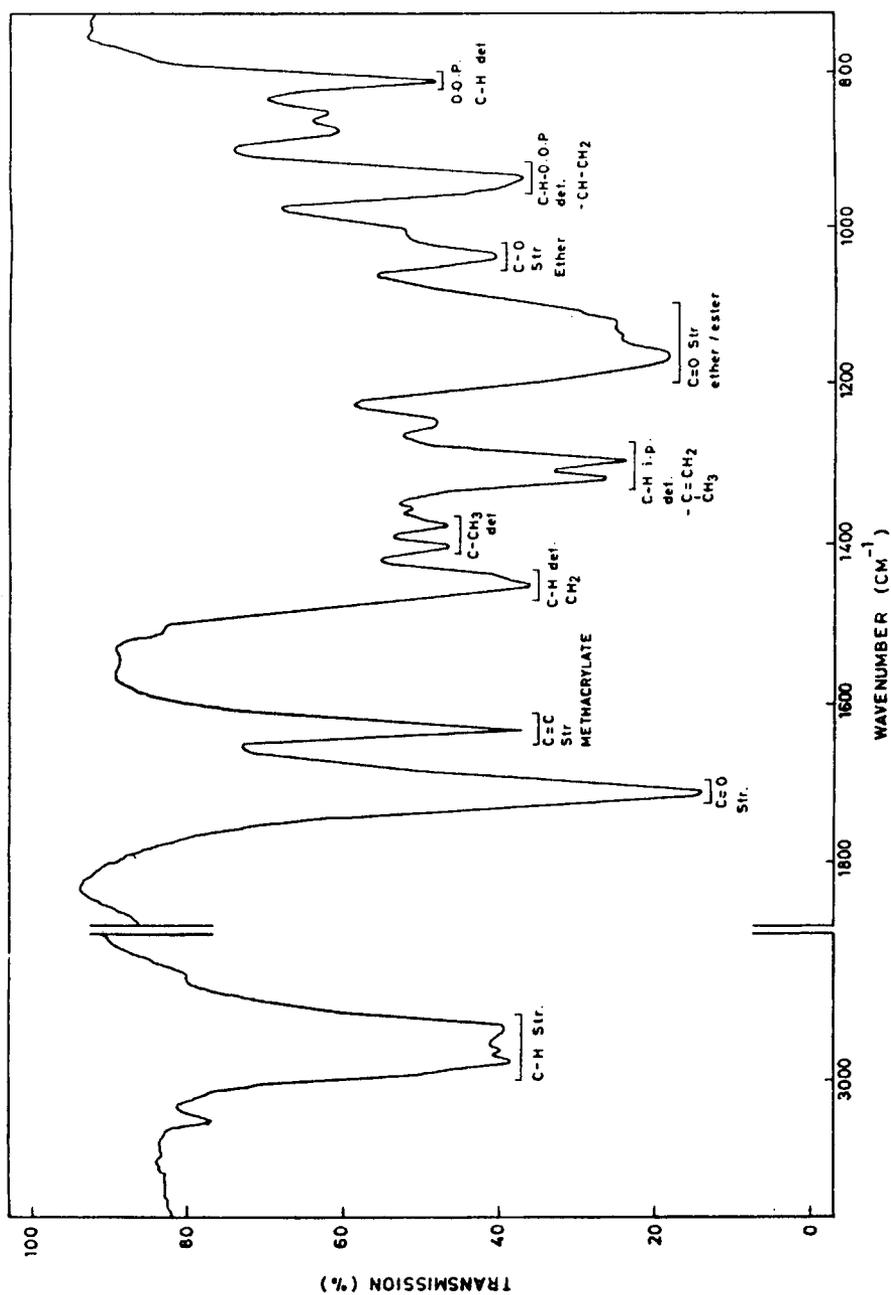
Fig. 1.   Infrared spectrum of triethyleneglycol dimethacrylate.

δ 1·93 (b)

(b)
CH₃
(a) H C=C—C—O—CH₂—CH₂—O—CH₂—CH₂—O—C—C=C H(a₂)
H ‖O (c) (d)   (d) (c) ‖O H(a₁)
(b) CH₃

42

28

28

δ6·09 (a₁)   28   δ5·57 (a₂)   δ4·36   (c)   (d) δ3·76

IOC sweep

No. PROTONS   4   4   4   6
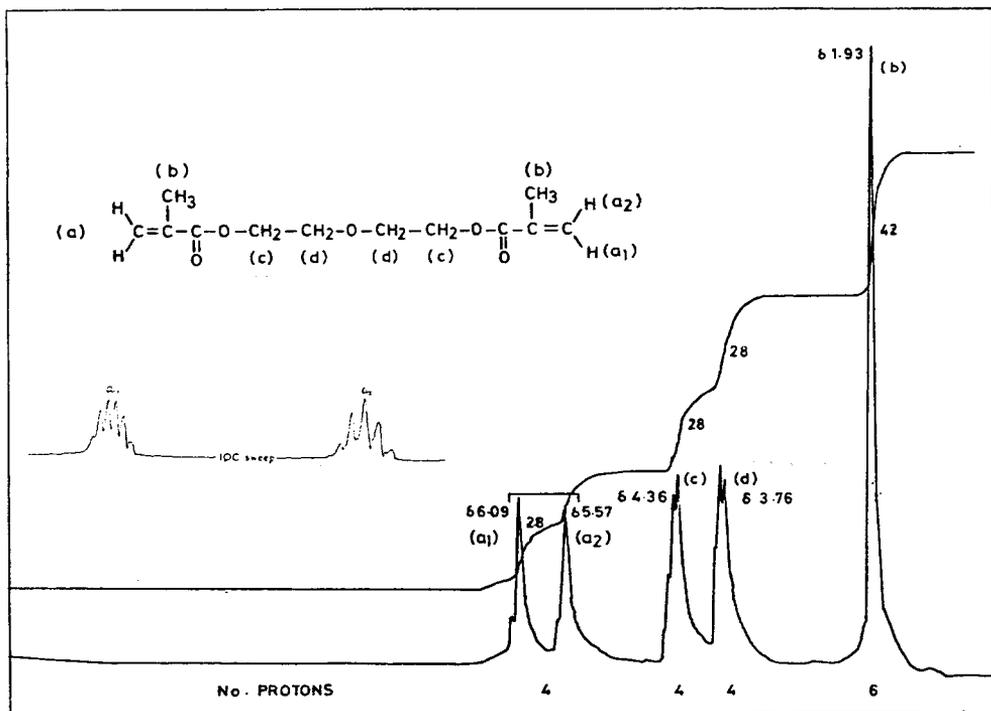
Fig. 2. ¹H-NMR spectrum of diethyleneglycol dimethacrylate.

Figures 2 and 3, respectively, for ready reference. The protons corresponding to b, a_1, and a_2 appear to constitute an A_3xy system. Protons b are coupled with both protons a_2 (*cis*-allylic coupling) and a_1 (*trans*-allylic coupling) and therefore appear as a quartet at 1.93. In fact, a careful scanning of this region at a 250-s sweep showed a triplet with a larger central peak. Protons corresponding to a_1 and a_2 are seen as nonidentical multiplets in the regions 6.09 and 5.57, respectively. The protons c appear at 4.36 as a triplet being adjacent to an oxygen atom and methylene protons d. The protons d also appear as a triplet at 3.76, being adjacent to oxygen and also methylene protons. The intensity of the peak at 3.76 (protons d) increased with increase in value n, i.e., chain length. This can be seen clearly in Figure 3.

The ¹H-NMR spectrum of TMPTMA (Fig. 4) appeared naturally different from earlier spectra:

(b)
(c)   CH₃   H(a₂)
CH₂—O—CO—C=C
(b)   H(a₁)

H₃C—CH₂—C—CH₂—O—CO—C=C H(a₁)
(e)   (d)   (c)   H(a₁)
                        CH₃

(b)
CH₂—O—CO—C=C H(a₁)
(c)   H(a₂)
                    CH₃
(b)

Fig. 3. ¹H-NMR spectrum of tetraethylene glycol dimethacrylate.
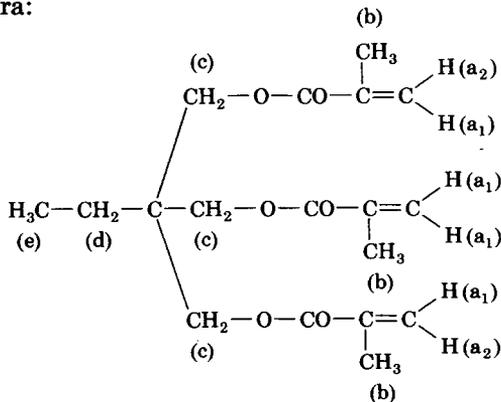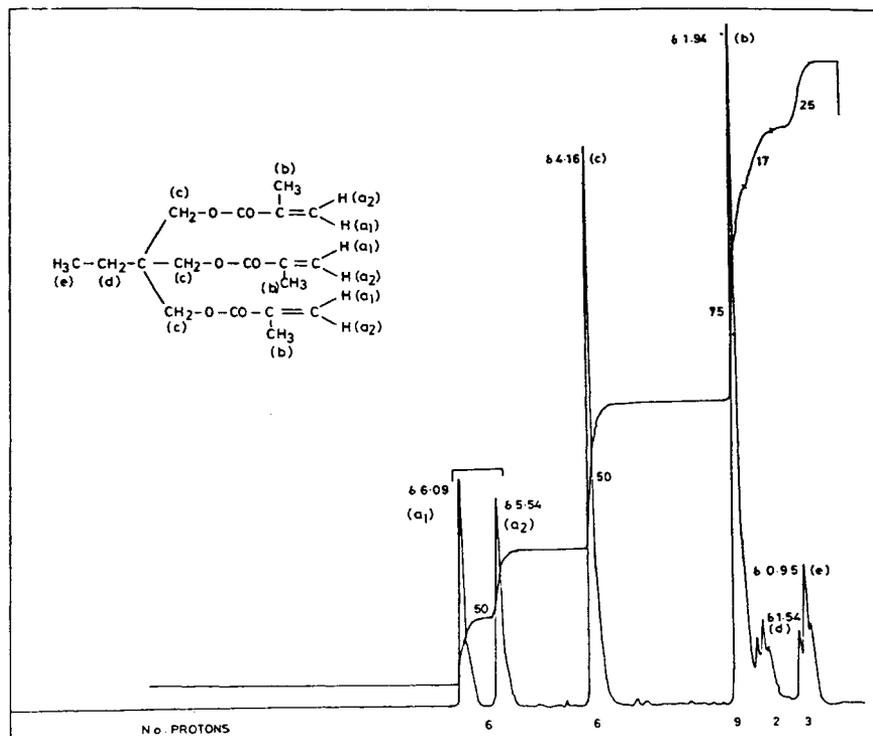
Fig. 4. ^{1}H-NMR spectrum of trimethylolpropane trimethacrylate.

The methylene protons c appeared as a singlet at 4.16, being adjacent to oxygen and a tertiary carbon atom. The methyl protons e form a part of an A_3B_2 system and are seen as a distorted triplet at 0.9–1.0, being coupled with the adjacent methylene group. The methylene protons d appeared as a quartet at 1.54 partly merged with protons b. In the ^{1}H-NMR spectrum of PETETMA, naturally, the peaks at 0.95 and 1.54 corresponding to protons e and d were absent as expected, and the rest of the peaks a_1, a_2, b, and c appeared at 6.09, 5.54, 1.94, and 4.16, respectively.

^{13}C Nuclear Magnetic Resonance Spectroscopy (^{13}C-NMR)

^{13}C-NMR spectra of these monomers seem to have not been reported earlier in the literature. All the spectra of the monomers in deuterated chloroform solution with TMS as internal standard were recorded using an FT-NMR JEOL-FX-90-Q-M HZ spectrophotometer, and the chemical shifts are recorded in ppm. Comparative chemical shifts of ^{13}C nuclei of typical methacrylic and acrylic esters are given in Table II.

^{13}C-NMR spectra of DEGDMA, TEGDMA, and TETEGDMA are similar, and therefore only a typical spectrum of TEGDMA is given in Figure 5, and a corresponding triethylene glycol diacrylate (TEGDA) spectrum is given in Figure 6. Similarly, the spectra of trimethylol propane trimethacrylate (TMPTMA) and triacrylate (TMPTA) are given in Figures 7 and 8, respectively, for comparative study. All the spectra are adequately explained in the

TABLE II
Comparative Chemical shifts (ppm) for ^{13}C in Methacrylic
and Acrylic Esters

Functional groups	Chemical shifts (ppm) in methacrylic/acrylic esters				
	TEGDMA	TEGDA	TMPTMA	TMPTA	PETETMA
$\underline{CH_3}-CH_2-$	—	—	7.33	7.04	—
$CH_3-\underline{CH_2}-C-$	—	—	23.28	22.26	—
$-CH_2-\underline{C}\diagup\diagdown-$	—	—	41.16	40.52	42.22
$-C-\underline{CH_2}-O-$	—	—	64.27	63.70	64.10
$-O-\underline{CO}-C\diagup\diagdown-$	166.79	165.14	166.79	165.15	166.82
$\underline{C}\overset{CH_3}{=}CH_2$	135.76	—	135.89	—	135.93
$-C=\underline{CH_2}$	18.67	—	18.07	—	18.20
$-\underline{C}\overset{CH_3}{=}\underline{CH_2}$	123.07	—	128.18	—	129.20
$-CO-O-\underline{CH_2}-CH_2-O-$	70.20	69.80	—	—	—
$-O-CH_2-\underline{CH_2}-O-CH_2-$	68.72	68.24	—	—	—
$-CO-\underline{CH}=CH_2$	—	127.45	—	127.79	—
$-CO-CH=\underline{CH_2}$	—	130.19	—	130.42	—
$-CH_2-CH_2-O-\underline{CH_2}-CH_2-$	63.34	62.98	—	—	—

figures by assigning chemical shift in ppm for each carbon atom in the molecule.

Mass Spectroscopy (MS)

The mass spectra of these methacrylic esters were recorded using a Micromass VG 7070 H United Kingdom mass spectrophotometer. Mass spectra of DEGDMA and TETEGDMA at 70 eV are shown in Figures 9 and 10. The fragmentation pattern of polyethyleneglycol dimethacrylates is shown below.

$$H_2C=\underset{CH_3}{\underset{|}{C}}-CO-O-CH_2-CH_2-$$

$$-O\!\!\left(CH_2-CH_2-O\right)_{\!n}\!-\!\Big|\,CH_2-CH_2-O\!\Big|\,CO\!\Big|\,\underset{CH_3}{\underset{|}{C}}\!=\!CH_2$$
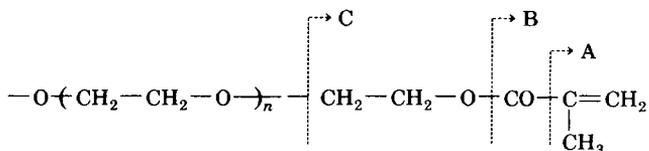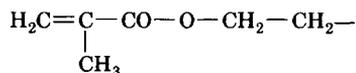
where $n = 0$ for DEGDMA, $= 1$ for TEGDMA, and $= 2$ for TETEGDMA. In all the three spectra of DEGDMA, TEGDMA, and TETEGDMA, molecular ion (M^+) peaks are noticed. Fragments A, B, and C appeared at m/z 41, 69, and 113. A very interesting fragmentation pattern was noticed in three spectra. The fragmented ion B (m/z 69) formed a base peak in the spectra of DEGDMA and TEGDMA, whereas, in the case of the TETEGDMA, the
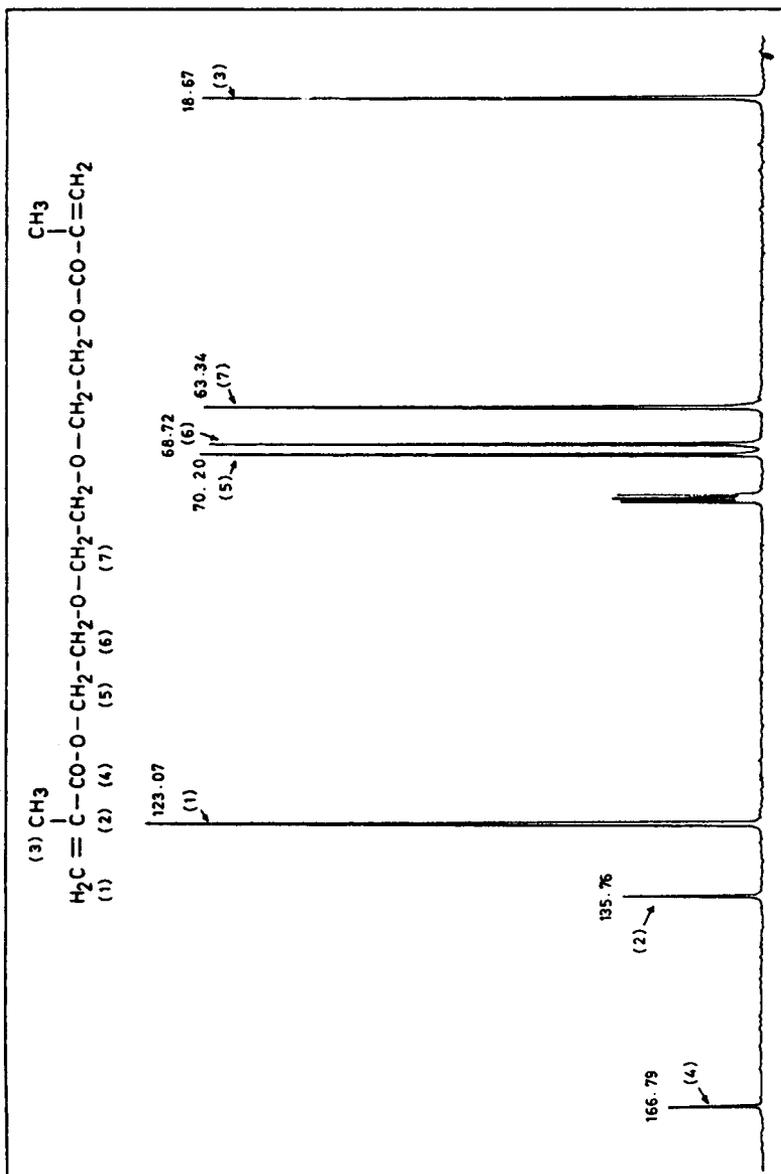
Fig. 5. ^{13}C-NMR spectrum of triethyleneglycol dimethacrylate.
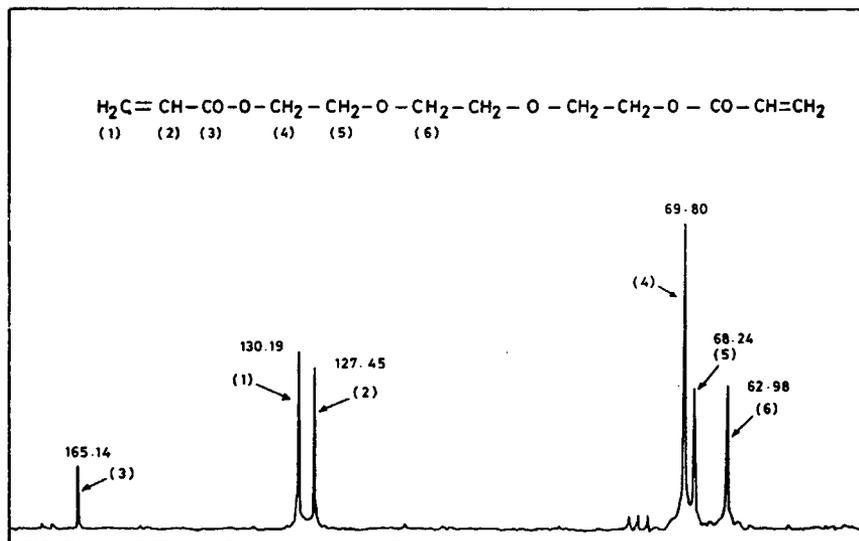
Fig. 6. ^{13}C-NMR spectrum of triethyleneglycol diacrylate.

fragmented ion C (m/z 113) appeared as base peak. The percent abundance ratio of fragmented ions B and C (B/C) decreased uniformly with the increase in the value of n, i.e., a uniform decrease of 0.220 for every increase of one unit of [CH_2—CH_2—O] link in the chain (Table III). Similarly the intensity ratio of A/B fragments reduced uniformly with the increase in chain length (Table III). These observations are not reported earlier in the literature. For reconfirming these observations, diethyleneglycol diacrylate (DEGDA) triethyleneglycol diacrylate (TEGDA) and tetraethyleneglycol diacrylate (TETEGDA) were prepared and purified by our standardized procedure described in this communication, and the mass spectra were recorded. The percent abundance ratios of fragments B and C (B/C) and A and B (A/B) decreased uniformly with the increase in the [CH_2—CH_2—O] units in the chain (Table III). The mass spectrum of TETEGDA only is shown in Figure 11 for ready reference and to show that the base peak is of fragment C (CH_2—CH_2—O—CO—CH=CH_2) at m/z 99 as is the case in TETEGDMA spectrum.

The fragmentation pattern of TMPTMA is given below:

Fig. 7. ^{13}C-NMR spectrum of trimethylolpropane trimethacrylate.

$$CH_2-O-CO-CH=CH_2$$

$$H_3C-CH_2-C-CH_2-O-CO-CH=CH_2$$

$$CH_2-O-CO-CH=CH_2$$
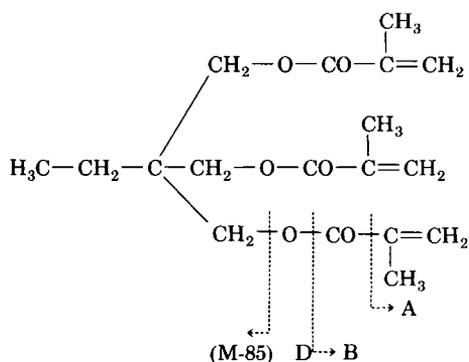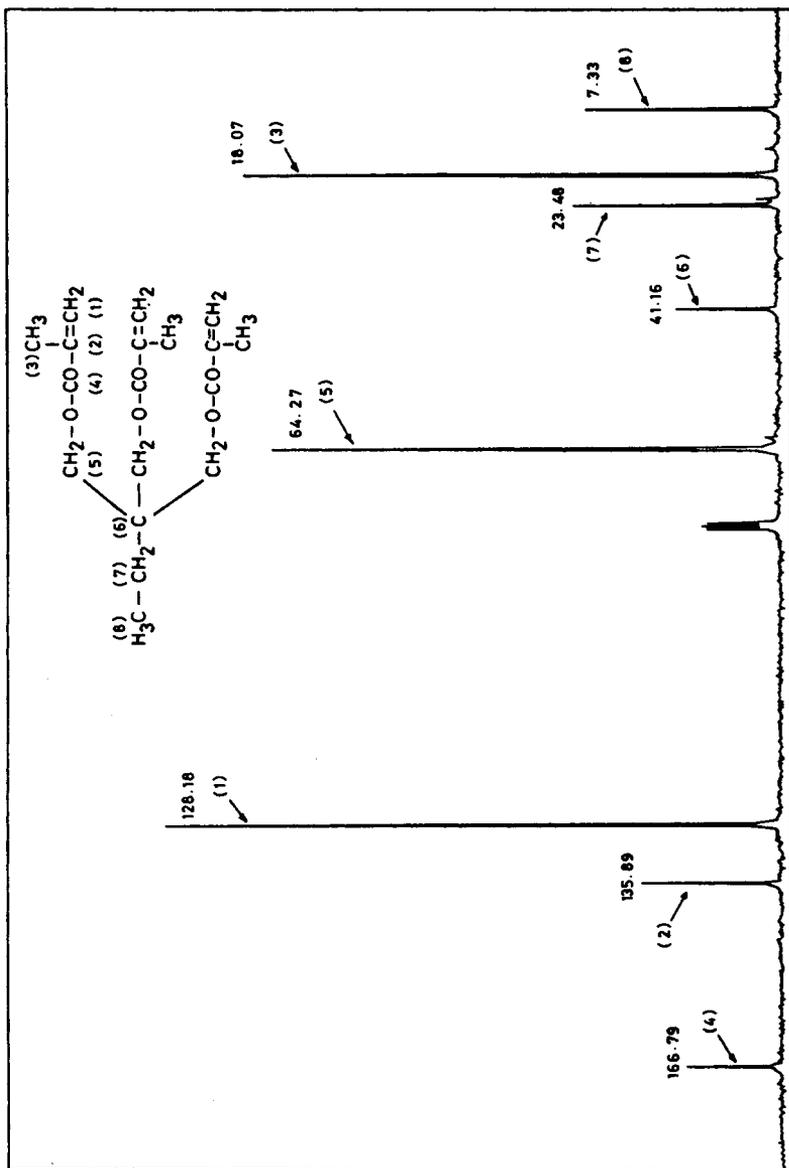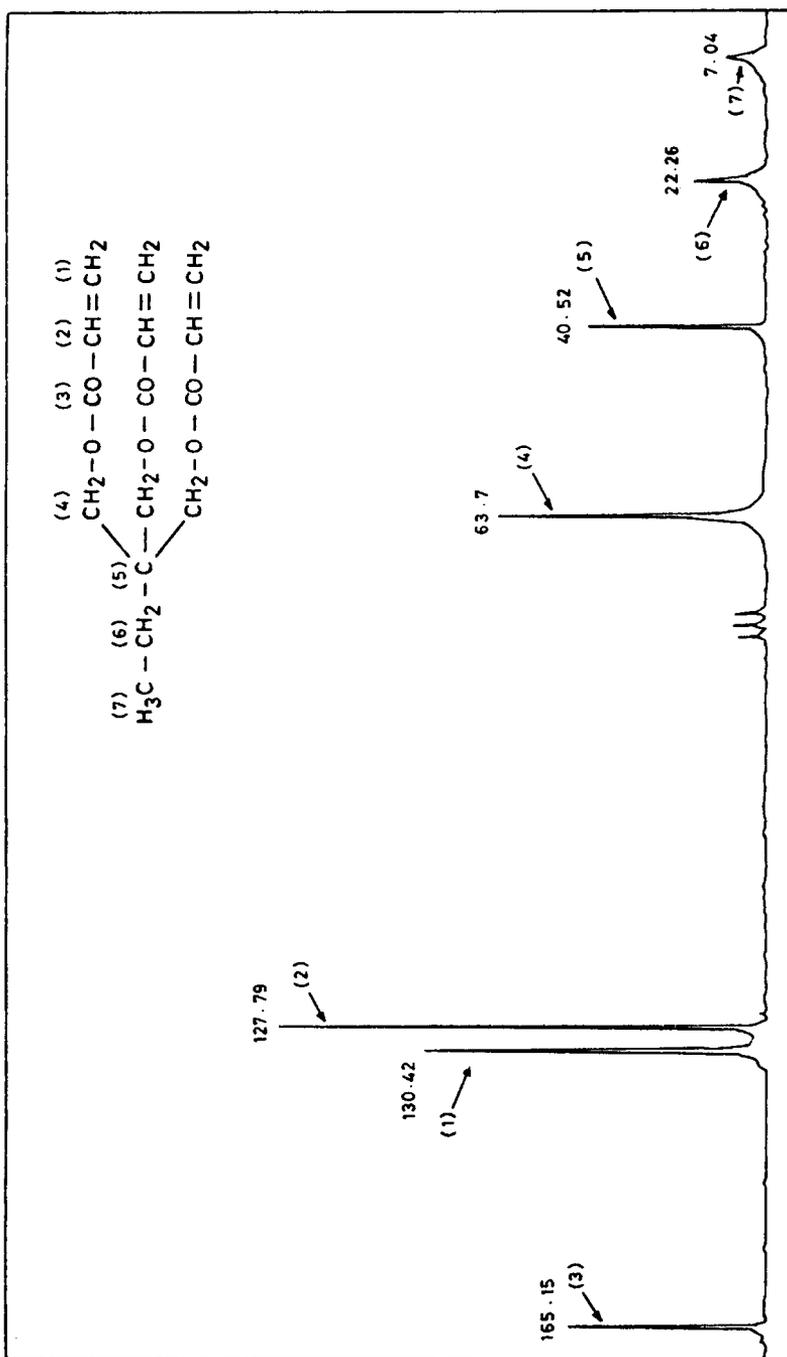
Fig. 8. ^{13}C-NMR spectrum of trimethylolpropane triacrylate.
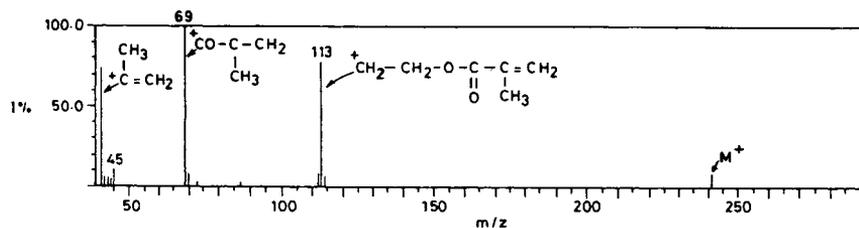
Fig. 9.   Mass spectrum of diethyleneglycol dimethacrylate.
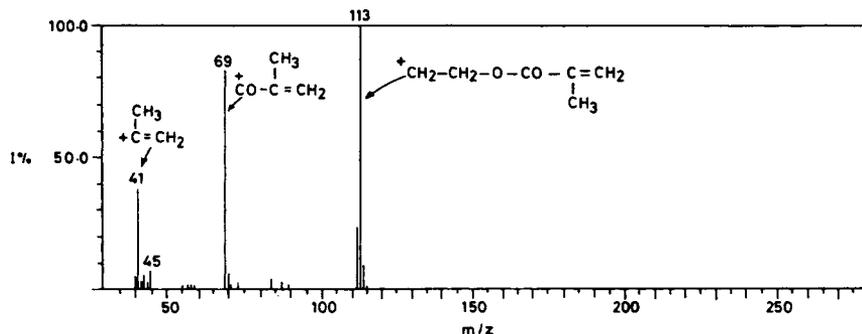
Fig. 10.   Mass spectrum of tetraethyleneglycol dimethacrylate.

TABLE III

Comparative Fragmented Ions of Methacrylic and Acrylic Esters

Methacrylic/ acrylic esters	Fragmented ions [m/z (% I)]						
	M$^+$	A	B	C	A/B	B/C	D (M-85)
DEGDMA	242(10)	41(75)	69(100)	113(78)	0.750	1.282	—
TEGDMA	286(8)	41(60)	69(100)	113(95)	0.600	1.053	—
TETEGDMA	330(5)	41(38)	69(83)	113(100)	0.458	0.830	—
DEGDA	214(5)	27(36)	55(100)	99(67)	0.360	1.493	—
TEGDA	258(6)	27(29)	55(100)	99(97)	0.290	1.037	—
TETEGDA	302(2)	27(15)	55(68)	99(100)	0.220	0.680	—
TMPTMA	338(5)	41(32)	69(100)	—	—	—	253(45)
TMPTA	296(2)	27(22)	55(100)	—	—	—	225(18)[a]
PETETMA	408(0)	41(30)	69(100)	—	—	—	323(40)

[a] In acrylates fragment D is M-71.

The mass spectrum of TMPTMA is given in Figure 12. Fragments A and B appeared at m/z 41 and 69, respectively. Fragment B formed the base peak. Fragment D which is formed due to the loss of

$$^+O-CO-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2$$
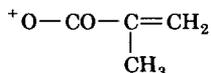
ion is in good abundance. To confirm this fragmentation pattern, a small amount of trimethylol propane triacrylate was prepared, purified, and its mass spectrum (Fig. 13) was taken. A similar fragmentation pattern was
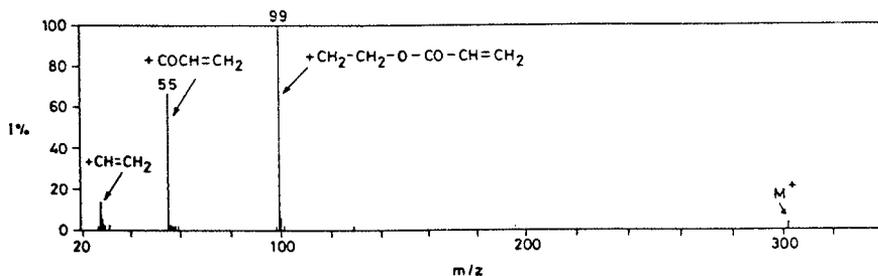
Fig. 11.   Mass spectrum of tetraethyleneglycol diacrylate.

observed, i.e., A (m/z 27), B (m/z 55), and D (M-71) (m/z 225). Molecular ion peaks of both these compounds TMPTMA and TMPTA are noticed at m/z 338 and 296, respectively.

In the mass spectrum of PETETMA only three fragments A (m/z 41), B (m/z 69) base peak, and M-85 (m/z 323) were noticed.

Utilization of Methacrylic Esters in Anaerobic Adhesive Compositions

There are several patents[6-8] available for the anaerobic adhesive compositions based on polyethyleneglycol dimethacrylates, useful as thread lockers and pipe sealants. However, we did not come across the use of trimethylolpropane trimethacrylate (TMPTMA) in such adhesive compositions. Therefore, we are now reporting the anaerobic adhesive compositions based on TMPTMA and compared with those based on DEGDMA, TEGDMA, and TETEGDMA. The anaerobic adhesive compositions based on these monomers, and their adhesive properties are given in Table IV. The monomer PETETMA could not be used in anaerobic adhesive compositions, as it is a solid having a melting point of 54.5°C.

Generally TETEGDMA-based adhesive formulations gave the best torque strengths of all the formulations based on other monomers studied in this investigation. TMPTMA-based anaerobic adhesive compositions are found to be good thread lockers and pipe sealants and are comparable with those based on DEGDMA and TEGDMA.

CONCLUSIONS

The dimethacrylic esters of di-, tri-, and tetraethylene glycols, trimethacrylic esters of trimethylolpropane, and tetramethacrylic ester of pentaerythritol could be synthesized in high yields and high purity by our modified esterification method. These esters could be used directly in anaerobic adhesive formulations without further purification. Conditions were standardized for all these monomers for their estimation of purity by gas liquid chromatography.

^{13}C-NMR spectral studies were made on these methacrylic esters, and chemical shifts for each carbon in its environment was assigned.

Mass spectral studies of dimethacrylic esters of di-, tri-, and tetraethylene glycols revealed very interesting results. The percent abundance ratio of
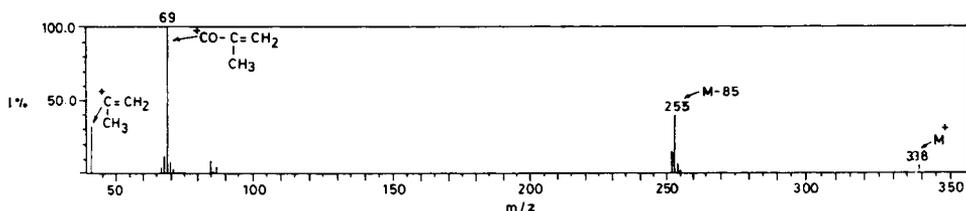
Fig. 12.   Mass spectrum of trimethylolpropane trimethacrylate.
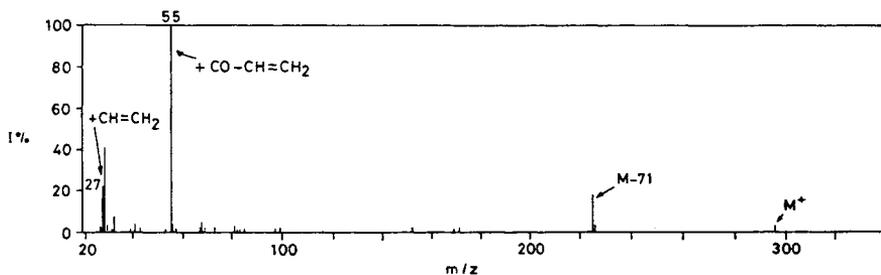
Fig. 13.   Mass spectrum of trimethylolpropane triacrylate.

(A/B) fragmented ions

$$^+C{=}CH_2 \text{ (A)} \quad \text{and} \quad {}^+CO{-}C{=}CH_2 \text{ (B)}$$
$$\underset{CH_3}{|} \qquad\qquad\qquad \underset{CH_3}{|}$$
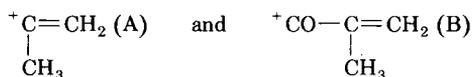
and also the ratio (B/C) of fragmented ions

$$^+CO{-}C{=}CH_2 \text{(B)} \quad \text{and} \quad {}^+CH_2{-}CH_2{-}O{-}CO{-}C{=}CH_2 \text{(C)}$$
$$\underset{CH_3}{|} \qquad\qquad\qquad\qquad\qquad \underset{CH_3}{|}$$
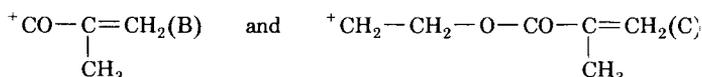
decreased with increase of every $[CH_2{-}CH_2{-}O]$ link in the chain. This phenomenon was also observed in the series of diacrylic esters of polyethyleneglycols.

TABLE IV
Anaerobic Adhesive Compositions and Their Torque Strength Values[a]

| Sample No. | Hydroperoxide (phm) | Accelerator (phm) | Torque strengths (kg M) (BT/PT) | | | |
			DEGDMA	TEGDMA	TETEGDMA	TMPTMA
1	2C	2T	1.50/1.60	1.60/1.70	2.60/2.70	1.30/1.40

Trimethylol propane trimethacrylate (TMPTMA) was effectively used in anaerobic adhesive compositions and tested as thread lockers and pipe sealants. Its performance is comparable with DEGDMA and TEGDMA.

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