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Synthesis, Characterization, and Photocrosslinking of Acrylated and Methacrylated Polyethylene Diepoxymethylene Tartramides

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ABSTRACT

Polyethylene tartramide (PT) containing free hydroxyl groups was prepared by the reaction of diethyl tartrate (DT) with the diamine, 1,2-diaminoethane at room temperature without the use of any solvent or catalyst. The reaction of PT with epichlorohydrin produces polyethylene diepoxymethylene tartramide (PDT). The photocrosslinkable acrylated and methacrylated monomers namely, poly[*N*-aminoethyl-(di-β-hydroxy-α-acryloyl)tartramide] (APDT) and poly[*N*-aminoethyl-(di-β-hydroxy-α-methacryloyl)tartramide] (MAPDT) were synthesized by the ring-opening reaction of PDT with acrylic acid and methacrylic acid, respectively. All the synthesized compounds were characterized by infrared (IR), ^{1}H-NMR, and ^{13}C-NMR spectra. The photocrosslinking properties of the monomers have been studied by irradiating the monomers under a medium pressure mercury vapor lamp using 1-hydroxycyclohexyl phenyl ketone as a free radical photoinitiator at different time intervals and different initiator concentration. The rate of disappearance of the acrylate and methacrylate functional group during irradiation was observed by measuring the absorption intensity due to C=C stretching frequency of the crosslinked polymers using FT-IR spectra. The photocrosslinking studies indicate that the methacrylated monomer exhibit higher double bond conversion than the acrylate monomer. The values of the hardness and density of the photocrosslinked polymers were measured and it was

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observed that the hardness and density values are higher for the polymers obtained from the methacrylated monomer than the acrylated monomer. The solubility of the photocrosslinked polymers were tested and these polymers were found to be insoluble in most of the organic solvents and the observation indicates, that all the polymers were swollen in the solvent, dimethylformamide (DMF), dimethyl sulfoxide, and methyl alcohol. The swelling studies of the photocrosslinked polymers were carried out and the results like swelling coefficient, crosslink density, molecular weight between crosslinks, and percent gel content of the crosslinked polymers were discussed.

Key Words: Photocrosslinkable monomers; IR, ^{1}H-NMR, and ^{13}C-NMR spectra; Irradiation of monomers; Percentage conversion; Hardness; Density; Solubility; Crosslink density; Gel content.

INTRODUCTION

Radiation processing is a relatively sophisticated industrial technique that can be economically substituted for conventional, thermal, and chemical processes. Photocrosslinking polymerization is a well-established technology for many industrial applications. Many reactive monomers and efficient photoinitiators have been synthesized and are also available commercially for photocrosslinking. Many reports have been published in applications to microlithography,[1–3] printing materials,[4] and liquid crystalline and non-linear optical materials.[5,6] In the coating industry, fast drying UV-curable varnishes, inks or paints are employed to improve the surface properties of all kinds of materials, such as metals, plastics, paper, wood, and textiles.[7–9]

Photocrosslinking of acrylic resins was carried out by introducing allyl ester groups into poly(methyl acrylate) and methyl acrylate–styrene copolymers. Photocrosslinkable elastomers with pendent acrylate groups have been synthesized by ring-opening reaction of epoxidized natural rubber with acrylic acid and its curing studies were preformed in the presence of free radical photoinitiator.[10]

The photoinitiated crosslinking of polyethylenes and subsequent chemical analysis and determination of physical properties have been extensively investigated. The processes involve the use of photoinitiator, mainly aromatic ketones.[11–14]

Photoinitiated free-radical polymerization involving crosslinking of multifunctional vinyl monomers and oligomers (prepolymers) is currently enjoying a commercial interest on account of its potentially large number of applications.[10] The present work deals with the synthesis, characterization studies related to photocrosslinking of newly synthesized acrylated polyethylene diepoxymethylene tartramide (APDT) and methacrylated polyethylene diepoxymethylene tartramide (MAPDT) by photochemical reaction in the presence of the initiator, 1-hydroxycyclohexyl phenyl ketone (Irgacure 184).

EXPERIMENTAL

Reagents and Materials

The reagent, triethylamine (CDH) was heated under reflux over sodium wire for 8 h, distilled, and finally collected over fresh sodium wire. Ethyl alcohol was refluxed with

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calcium oxide for 6 h and allowed to stand overnight and distilled.[15] 1,2-Diaminoethane (Merck), tartaric acid (CDH), and epichlorohydrin (Merck) were used without further purification. Acrylic acid (Merck) and methacrylic acid (Merck) was used after removal of the inhibitor for acrylation reactions. The commercial solvents, benzene, acetone, toluene, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide, and methyl alcohol were purified appropriately before use. The photoinitiator, 1-hydroxycyclohexyl phenyl ketone (Aldrich) was used as received.

Synthesis of Diethyl Tartrate

A mixture of tartaric acid (100 g, 0.67 mol), purified ethyl alcohol (159 g, 3.45 mol), sodium-dried benzene (350 mL), concentrated hydrochloric acid (5 mL), and dried magnesium sulfate (30 g) was taken and the mixture was refluxed for 10 h, cooled, and magnesium sulfate was filtered off. The benzene solution and unreacted ethyl alcohol were removed by distillation under reduced pressure; the azotrope mixture of ethyl alcohol–benzene passed over first, followed by benzene. Finally, the residue was distilled under reduced pressure, the diethyl tartrate (DT), a colorless viscous liquid was collected boiling point 280°C.[15,16]

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Synthesis of Polyethylene Tartramide

The diamine, 1,2-diaminoethane (3.005 g, 0.05 mol) was mixed with the reagent, DT (10.3 g, 0.05 mol) and the reaction mixture was stirred at room temperature for about 5 h using magnetic stirrer. The product, polyethylene tartramide (PT) was washed with ethyl alcohol and dried under vacuum at room temperature overnight.[17,18]

Synthesis of Polyethylene Diepoxymethylene Tartramide

The PT (7.552 g, 0.0434 mol) and the solvent acetone (200 mL) were mixed thoroughly to get a clear solution. Triethylamine (8.77 g, 0.0868 mol) was added into the reaction vessel and the contents were mechanically stirred for 1 h. Epichlorohydrin (8.03 g, 0.0868 mol) was then added rapidly into the reaction vessel while stirring. The temperature was maintained at 30°C throughout the reaction. The reaction was stopped after 8 h. The epoxy compound was obtained from the filtrate after evaporating the solvent, acetone and dried under vacuum.[19]

Synthesis of Photocrosslinkable Acrylated and Methacrylated Monomers

Polyethylene diepoxymethylene tartramide (PDT) (50 g, 0.1748 mol) was dissolved in toluene and acrylic acid (25.18 g, 0.3496 mol) was then introduced into the reaction vessel. The mixture was mechanically stirred at constant rate and the temperature was kept constant at 35°C throughout the reaction time. Under these conditions, the ring opening of epoxide group by acrylic acid occurred after stirring for 16 h. Acrylated polyethylene

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diepoxymethylene tartramide was obtained as liquid after evaporating the solvent, toluene and dried under vacuum.[8,10] A similar procedure was employed for the synthesis of MAPDT by using methacrylic acid.

Photocrosslinking of Acrylated and Methacrylated Polyethylene Diepoxymethylene Tartramides

Photocurable formulations containing the monomer (APDT/MAPDT) and the photoinitiator, 1-hydroxycyclohexyl phenyl ketone (0.0375 g, 0.25%) were placed in a quartz tube. The contents were exposed to UV-radiation of a medium pressure mercury vapor lamp to the power output of 125 W/linear centimeter at a distance of 3 cm from the source point for 10 min. All irradiation studies were carried out at room temperature in the presence of air by varying the photoinitiator concentrations at different time intervals.

Characterization Methods

Infrared (IR) spectra were recorded on a Perkin–Elmer Model 782 and Brukker IFS66V FT-IR for the characterization of synthesized compounds and for double bond conversion into crosslinked polymers, respectively. ^{1}H-NMR and ^{13}C-NMR were run on an AMX 400 MHz NMR spectrometer at room temperature in DMSO-d_6 using TMS as the internal standard. A medium pressure mercury vapor lamp with the power output of 125 W/linear centimeters was used for the photocrosslinking study. The solubilities of the crosslinked polymers were examined using 0.003 g polymer in 5 mL of solvent at room temperature for 24 h. The hardness of the photocured film was determined by A-Type JIS K6301 hardness tester. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were collected using a Mettler TA 3000 thermogravimetric analyzer and Perkin–Elmer DSC 7 differential scanning calorimeter, respectively at a heating rate of 20°C/min in N_2 atmosphere.

Measurement of Density

The density data for the photocured polymers were obtained by hanging each of the cured polymers (0.1 g) in isopropyl alcohol; the data on density were derived from the weight loss.

Swelling Study

The swelling studies for the photocured polymers were obtained by adding each polymer sample (50 mg) with DMF (7 mL). The amount of superficially swollen samples was taken out for different time intervals (04, 09, 16, 22, 28, 35, 40, 47, 51, 57, 60, 64, 72 h). The amount of maximum swelling was obtained by making a plot of the amount of swollen samples against time. From the weight of maximum swelling and the initial

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weight, the swelling coefficient was calculated. Crosslink density and molecular weight between crosslinks were also calculated.

Gel content of the photocured polymers were estimated as follows: 50 mg of the cured polymer was added to DMF (7 mL) and the mixture was allowed to stand for 74 h. The swollen sample was isolated and subjected to vacuum drying for a sufficiently long time to ensure complete drying. The percent gel content was determined from the weight difference between the initial weight and to the weight of sample after drying. All the swelling characteristics were measured at room temperature in the presence of air.

RESULTS AND DISCUSSION

Scheme 1 represents the synthesis of acrylated/metharcrylated prepolymers employing tartaric acid, epichlorohydrin, and 1,2-diaminoethane using acrylic/methacrylic acids.

The structural elucidation of DT, PT, PDT, APDT, and MAPDT were confirmed by IR spectra (Fig. 1) as follows:

Diethyl tartrate—The absorption band at 3350 cm^{-1} is due to the presence of –OH group and 1765 cm^{-1} is due to C=O stretching in DT. The absorption at 2990 and 2900 cm^{-1} are assigned for the presence of C–H stretching vibration of the methylene and methyl groups respectively.

Polyethylene tartramide—The amide I band (C=O group) appears at 1680 cm^{-1}. The broad single band between 3330 and 3150 cm^{-1} is due to the presence of –OH and –NH (amide II) groups. The bands at 2930, 2856, 1355, 1109, and 1072 cm^{-1} are due to $-CH_2$ groups.[18,20] Compared to DT, the spectral data of PT shows the disappearance of the characteristic absorption of methyl group (2900 cm^{-1}) of DT and the appearance of the band at 1680 cm^{-1} characteristic of the formation of amide unit.

Polyethylene diepoxymethylene tartramide—The symmetrical and asymmetrical stretching of the epoxy ring occurs at 1275 and 875 cm^{-1}, respectively. The C–H stretching vibration of the epoxy ring occurs at 3000 cm^{-1}. The band at 1160 cm^{-1} is due to the presence of C–O–C stretching. A broad band for amide II (–NH stretching) and amide I band (C=O) appears at 3145 and 1678 cm^{-1}, respectively. The –CH stretching of the –CH and $-CH_2$ groups appeared at 2930, 2855, 1356, 1110, and 1075 cm^{-1}.

Acrylated polyethylene diepoxymethylene tartramide—Marked difference appear after acrylation of PDT with acrylic acid.[10,20–22] The decrease of the peaks at 1275 and 875 cm^{-1} due to the epoxy ring of PDT and an increase of band at around 3350 and 1710 cm^{-1} for –OH and ester C=O in APDT is evidence for the formation olefinic group. Several new bands which are directly related to the acrylic function, mainly at 1190 cm^{-1} (C–O–C ester and at 805 cm^{-1} ($=CH_2$ twisting) indicates the formation of acrylates. Presence of a strong absorption band at 1630 cm^{-1} indicates the presence of olefinic C=C bond. The bands 1680 and 1156 cm^{-1} are assigned for amide carbonyl and C–O–C groups. C–H and CH_2 frequencies appear at 2927, 2853, 1355, 1108, and 1071 cm^{-1}.

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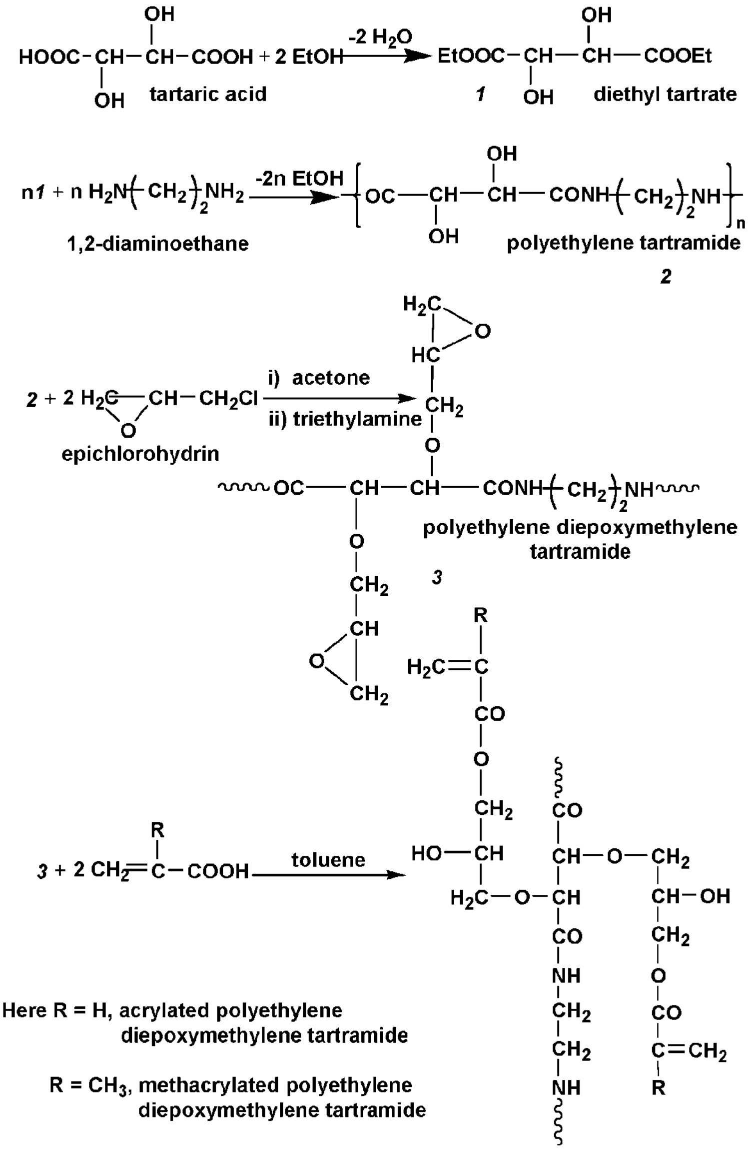

Scheme 1. Synthesis of APDT and MAPDT.

Methacrylated polyethylene diepoxymethylene tartramide—The olefinic C=C absorption band occur at 1615 cm^{-1}. All the other absorption bands are nearly similar which are assigned for APDT.

The ^1H-NMR spectra of PT, PDT, APDT, and MAPDT are presented in Figs. 2 and 3.

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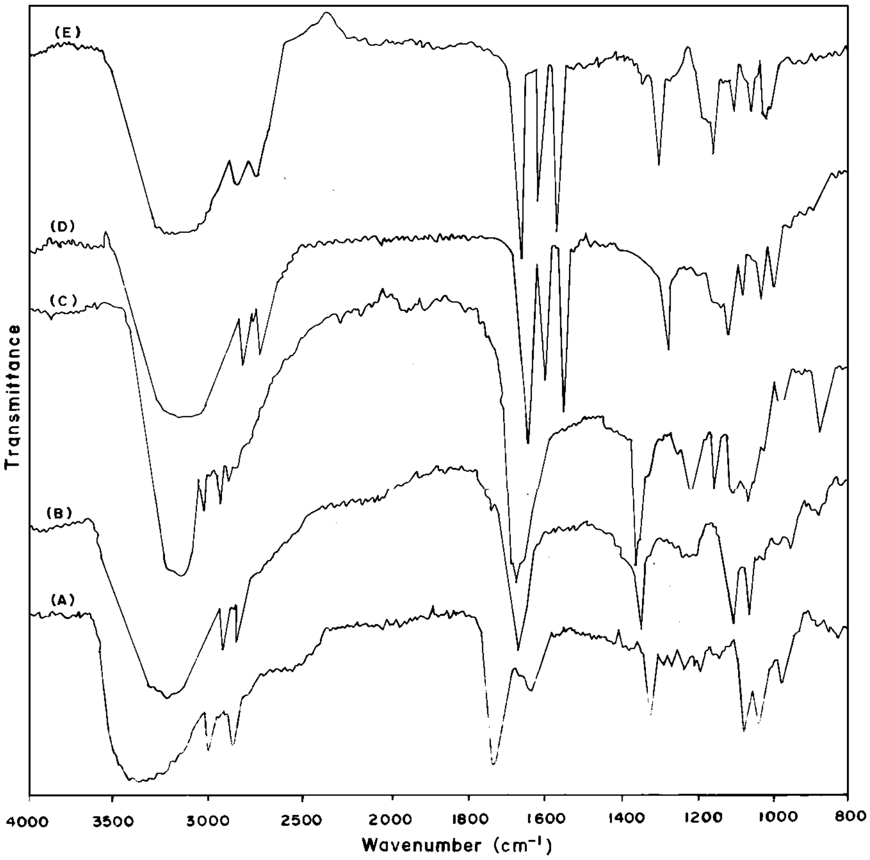

Figure 1. The IR spectra of (A) DT, (B) PT, (C) PDT, (D) APDT, and (E) MAPDT.

Diethyl tartrate—The methyl group appears as a triplet at 1.22 δ, while methylene protons appear as a quartet at 4.22 δ. The singlet at 4.70 δ can be assigned to the hydroxyl protons and methane protons appear at 3.36–3.54 δ as a doublet.[20]

Polyethylene tartramide—The –NH proton appears at 7.50 δ as a triplet. The singlet at 4.25 δ indicates the presence of –OH proton. The doublet at 3.00–3.20 δ shows the presence of –CH proton in the main chain and the multiplet at 3.54–3.80 δ shows the presence of amide methylene protons.

Polyethylene diepoxymethylene tartramide—The signal due to the –NH and chain –CH protons appears at 7.20 δ and 3.67–3.84 δ, respectively. The $-OCH_2$ protons appear as doublet of a doublet at 2.38 δ. The resonance signals for the –CH and CH_2 protons of epoxy ring appear at 3.23–3.53 δ as multiplet and 2.60 δ as a distorted triplet. The amide methylene protons appears as multiplet at 2.82–3.16 δ.

Acrylated polyethylene diepoxymethylene tartramide—The –NH proton appears as at 7.15 δ as a triplet. Alkylene group protons give three signals at 6.29–6.51, 6.04–6.23, and 5.76–5.98 δ as multiplets for the three different protons H_a, H_b, H_c. The values 4.19–4.59 (*m*), 3.60–3.83 (*d*), 2.55–2.70 (*m*), and 3.25–3.57 δ (*m*) are

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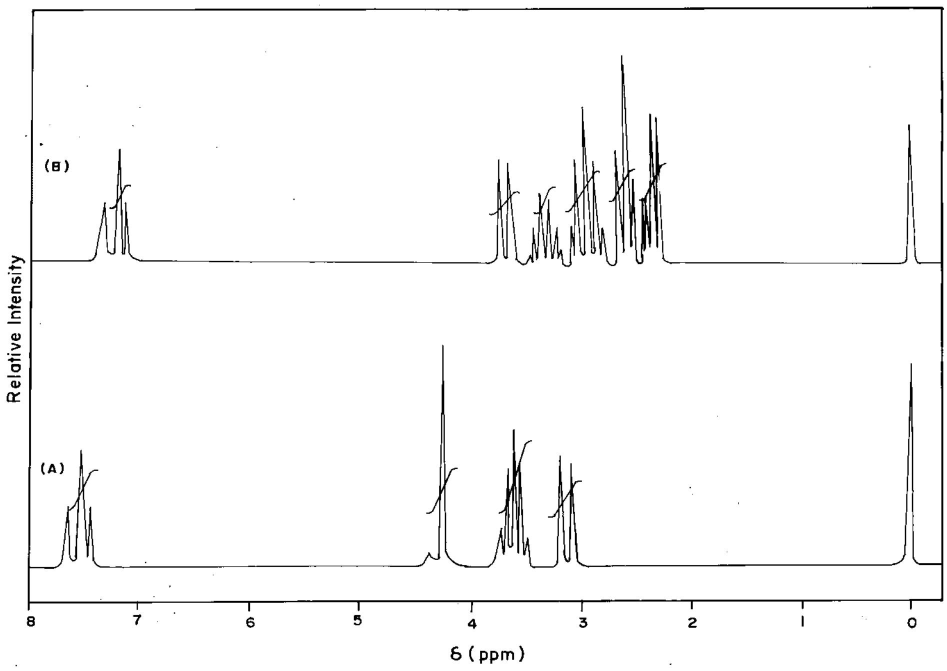

Figure 2. The ^{1}H-NMR spectra of (A) PT and (B) PDT.

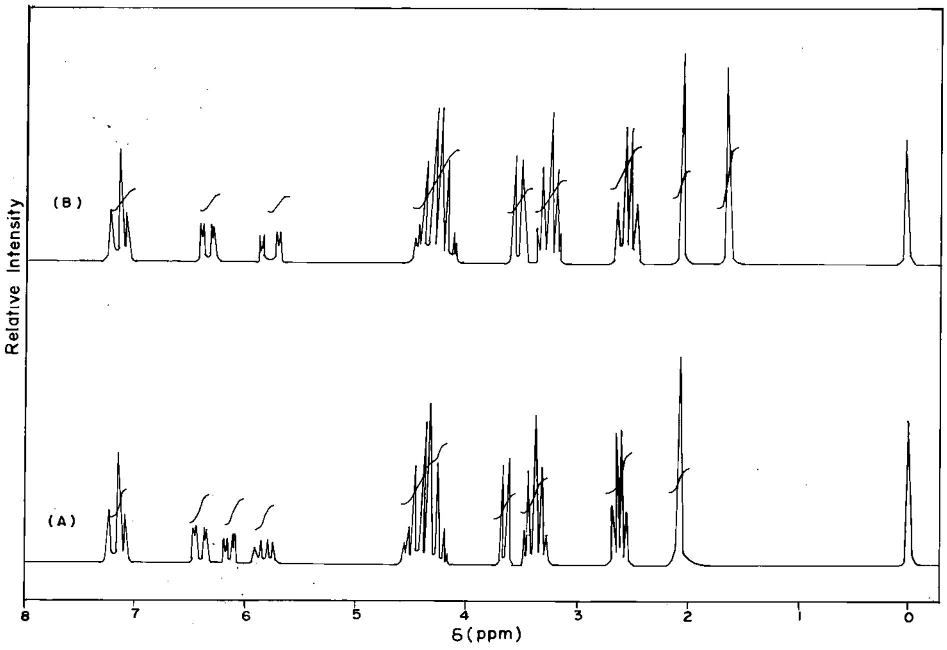

Figure 3. The ^{1}H-NMR spectra of (A) APDT and (B) MAPDT.

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assigned for the protons of acid ester and –CH proton attached to hydroxyl group, chain –CH, –OCH_2, and amide methylene, respectively. The hydroxyl group proton appears at 2.08 δ as a singlet.

Methacrylated polyethylene diepoxymethylene tartramide—The data assigned for APDT are nearly similar as for the compound MAPDT. The only difference is, the signal appeared at 1.70 δ as a singlet is assigned to methyl protons of alkene group.[23,24]

The proton decoupled ^{13}C-NMR spectra of PT, PDT, APDT, and MAPDT are given in Figs. 4–7.

Polyethylene tartramide—The three signals at 173.3, 72.8, and 37.8 ppm are assigned to C_1, C_2, and C_3 carbons.[23]

Polyethylene diepoxymethylene tartramide—There are six signals which appeared at 173.70, 51.00, 46.20, 45.51, 44.86, and 30.58 ppm are assigned to C_1–C_6 carbons of the epoxy compound. C_1 carbon of epoxy compounds is directly attached with nitrogen and the value is higher due to a deshielding effect.

Acrylated polyethylene diepoxymethylene tartramide—The observance of nine signals at 175.19, 170.49, 125.60, 132.40, 69.54, 59.89, 46.20, 45.27, and 33.40 ppm are respectively assigned to carbons C_1–C_9. Here, C_1 and C_2 carbons absorb at a lower field compared to others due to the deshielding effect.

Methacrylated polyethylene diepoxymethylene tartramide—The spectra of the methacrylated monomer compared to the signal observed in APDT, there is an

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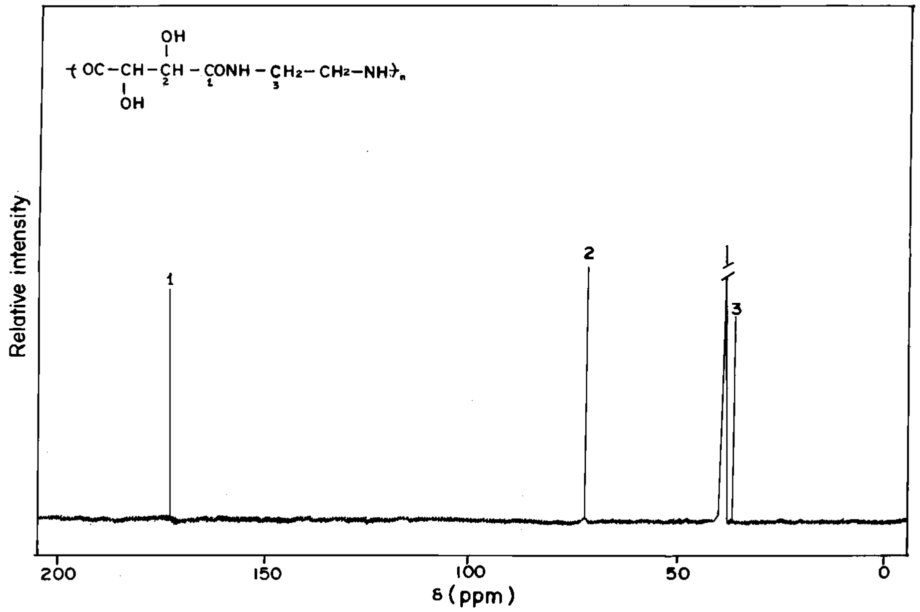

Figure 4. ^{13}C-NMR spectrum of PT.

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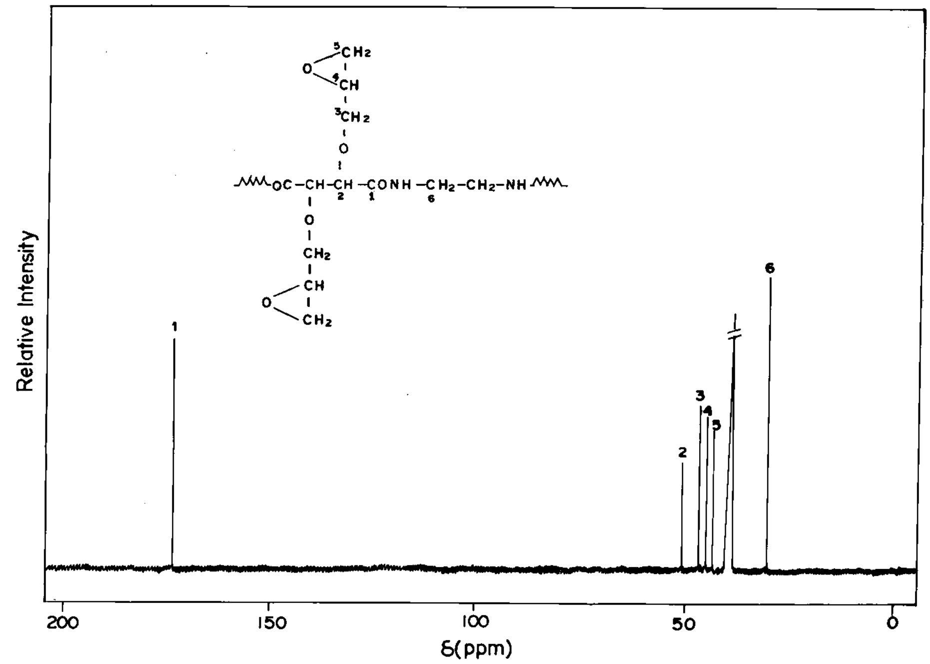

Figure 5. ^{13}C-NMR spectrum of PDT.

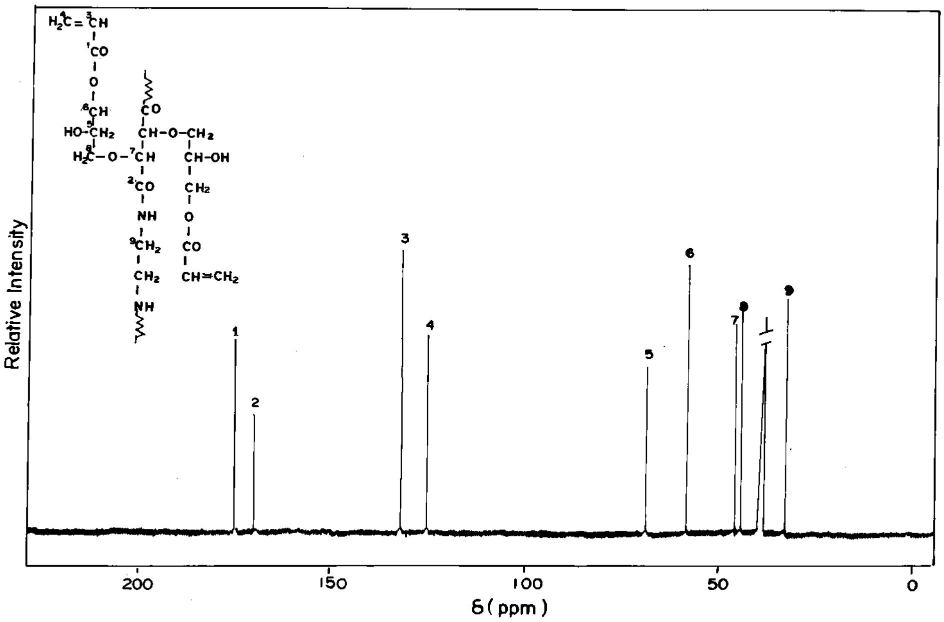

Figure 6. ^{13}C-NMR spectrum of APDT.

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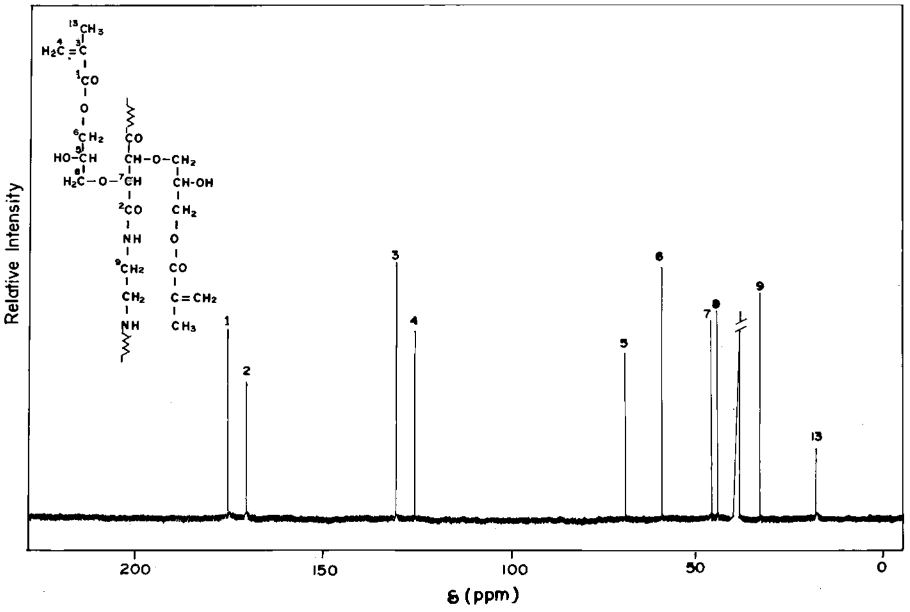

Figure 7. ^{13}C-NMR spectrum of MAPDT.

extra signal for methyl carbon (C_{13}) at 18.30 ppm and other spectral features are relatively the same with APDT.[20]

The list of photocrosslinked polymers and their nomenclature are presented in Table 1. It includes all the photocrosslinked polymers obtained from the monomers, APDT and MAPDT with respect to the initiator concentration and irradiation time.

The formation of probable network polymers from acrylated and methacrylated monomers involving 1-hydroxycyclohexyl phenyl ketone and UV light is given in Sch. 2.

Table 1. List of crosslinked polymers obtained from monomers.

Initiator concentration (%)	Crosslinked polymers obtained from monomers									
	APDT[a]					MAPDT[b]				
0.25	A_1	A_2	A_3	A_4	A_5	MA_1	MA_2	MA_3	MA_4	MA_5
0.50	A_6	A_7	A_8	A_9	A_{10}	MA_6	MA_7	MA_8	MA_9	MA_{10}
0.75	A_{11}	A_{12}	A_{13}	A_{14}	A_{15}	MA_{11}	MA_{12}	MA_{13}	MA_{14}	MA_{15}
1.00	A_{16}	A_{17}	A_{18}	A_{19}	A_{20}	MA_{16}	MA_{17}	MA_{18}	MA_{19}	MA_{20}
Irradiation time (min)	10	20	30	40	50	5	10	15	20	25

[a] Acrylated polyethylene diepoxymethylene tartramide.

[b] Methacrylated polyethylene diepoxymethylene tartramide.

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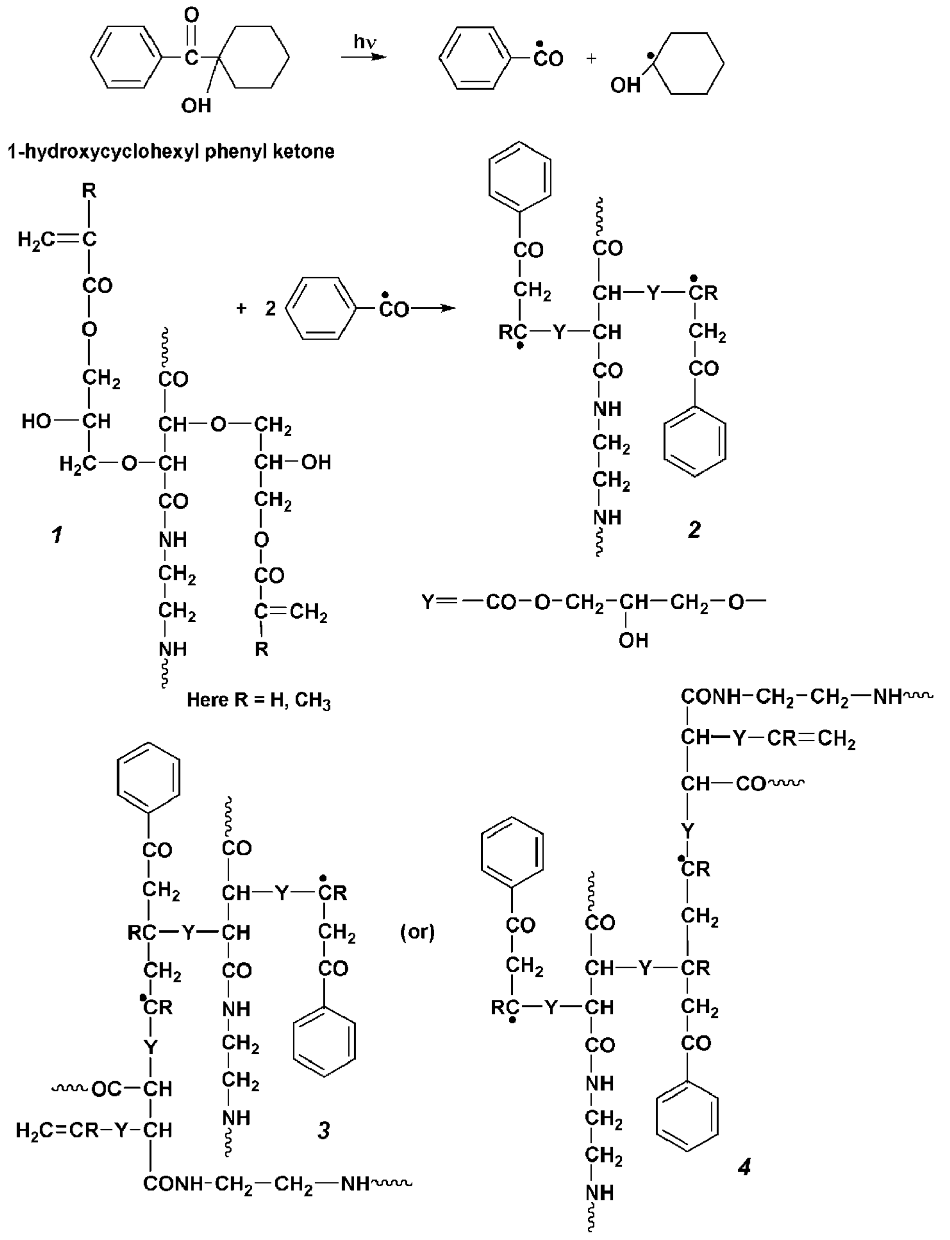

Scheme 2. Photocrosslinking of APDT and MAPDT.

The FT-IR spectra reveals that the rate of disappearance of the double bond for the reactive acrylated and methacrylated monomers during crosslinking at different irradiation time intervals for different concentrations of the photoinitiator were determined using the formula.[25]

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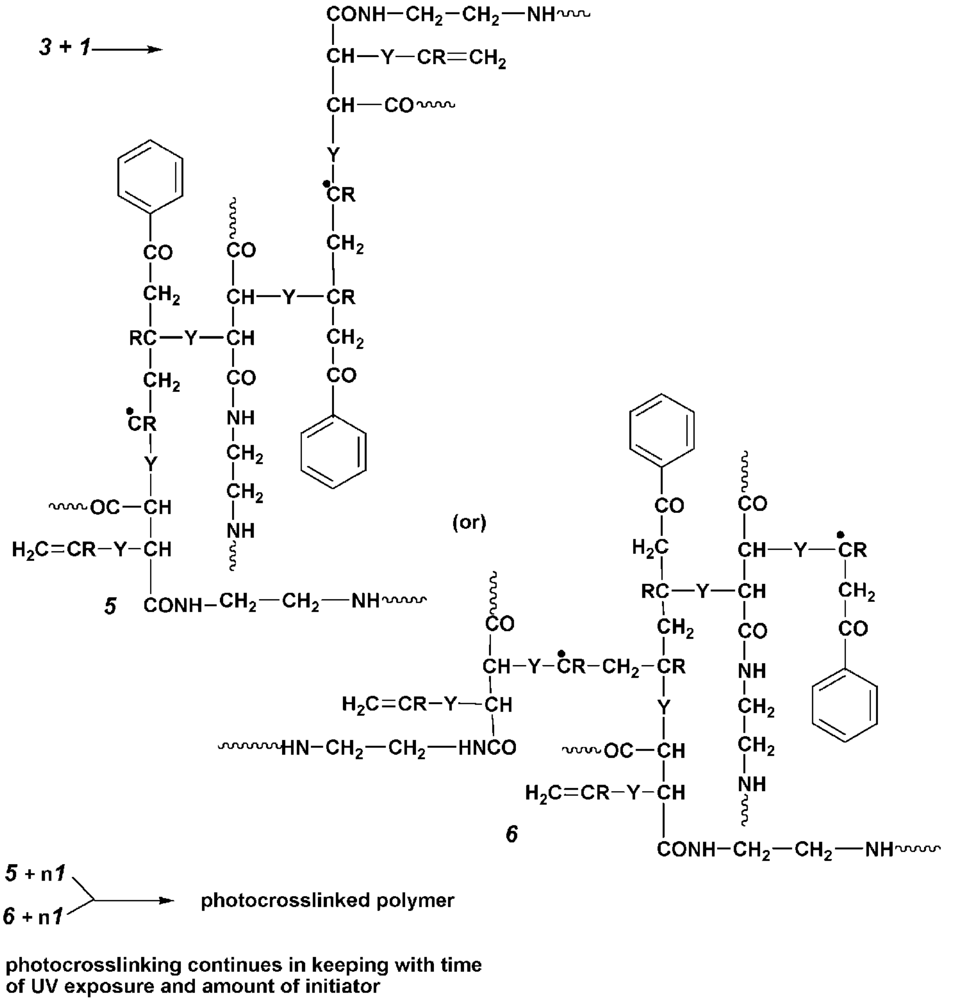

Scheme 2. Continued.

For acrylated:

$$\text{Percent double bond reacted} = \left(1 - \frac{(A_{\text{acrylateC=C}}/A_{\text{CO}})\text{polymer}}{(A_{\text{acrylateC=C}}/A_{\text{CO}})\text{monomer}}\right) \times 100$$

For methacrylated:

$$\text{Percent double bond reacted} = \left(1 - \frac{(A_{\text{methacrylateC=C}}/A_{\text{CO}})\text{polymer}}{(A_{\text{methacrylateC=C}}/A_{\text{CO}})\text{monomer}}\right) \times 100$$

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Table 2. Percentage conversion into crosslinked polymers obtained from APDT, polymer density, and hardness.

Polymer code no.	Conversion (%)					Density gm/cc (hardness)				
A_1–A_5	22.7	31.5	36.0	39.4	42.2	0.894 (47)	1.003 (56)	1.112 (61)	1.205 (64)	1.252 (68)
A_6–A_{10}	29.3	40.4	45.1	49.0	50.4	0.925 (54)	1.105 (63)	1.120 (66)	1.212 (72)	1.278 (77)
A_{11}–A_{15}	34.8	47.8	54.6	57.1	58.5	1.119 (60)	1.125 (73)	1.148 (78)	1.232 (79)	1.296 (81)
A_{16}–A_{20}	43.1	58.9	65.4	67.9	69.5	1.122 (68)	1.283 (84)	1.292 (86)	1.326 (87)	1.315 (88)

Here, $A_{\mathrm{acrylateC=C}}$ represents absorption intensity of the acrylated monomer $A_{\mathrm{methacrylateC=C}}$ represents absorption intensity of the methacrylated monomer A_{CO} refers to absorption intensity of ester carbonyl group.

In both acrylated and methacrylated prepolymers, the absorption due to ester carbonyl occurs at $1710\,\mathrm{cm}^{-1}$. The acrylated and methacrylated monomers shows a decrease in intensity for C=C absorptions at 1630 and $1615\,\mathrm{cm}^{-1}$, respectively. The percentage conversion of double bond for acrylated monomer at different irradiation time (10, 20, 30, 40, and 50 min) and different initiator concentrations (0.25%, 0.50%, 0.75%, and 1.00%) are given in Table 2. The percentage conversion is found to increase with increasing the initiator concentrations and irradiation time. The initiator concentration, and the corresponding maximum percentage double bond conversion for acrylated monomer are as follows: (0.25, 42.2); (0.50, 50.4); (0.75, 58.5); and (1.00, 69.5). The values of percentage conversion of the crosslinked polymers obtained from methacrylated monomer are given in Table 3. The polymers MA_1–MA_{20} obtained at different irradiation time (05, 10, 15, 20, and 25 min) and different initiator concentrations (0.25%, 0.50%, 0.75%, and 1.00%). The percentage conversion of the polymer MA_{20} is found to be 90.2 for 1.00% initiator concentration and at an irradiation time of 25 min.[26]

Table 3. Percentage conversion into crosslinked polymers obtained from MAPDT, polymer density, and hardness.

Polymer code no.	Conversion (%)					Density gm/cc (hardness)				
MA_1–MA_5	47.2	52.9	56.1	57.2	59.1	1.135 (77)	1.175 (81)	1.186 (82)	1.265 (84)	1.288 (85)
MA_6–MA_{10}	58.3	68.0	69.0	69.7	70.8	1.268 (82)	1.286 (87)	1.293 (87)	1.309 (88)	1.326 (89)
MA_{11}–MA_{15}	70.5	79.2	81.1	82.1	83.2	1.334 (85)	1.345 (89)	1.364 (89)	1.372 (90)	1.394 (91)
MA_{16}–MA_{20}	79.8	88.5	89.3	89.9	90.2	1.369 (90)	1.370 (91)	1.374 (91)	1.419 (92)	1.428 (92)

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Comparing the values of maximum percentage conversion of the acrylated monomer and those of the methacrylated monomer under identical conditions, lower double bond conversion is observed for the acrylated than the methacrylated monomer. Here, the photoinitiator, 1-hydroxycyclohexyl phenyl ketone on exposure to UV light of wavelength $\lambda = 340\,\text{nm}$ produces benzoyl radical, which on reaction with the acrylated prepolymer, APDT produces a less stable secondary species, while the methacrylated prepolymer, MAPDT produces a more stable tertiary species, which continues the reaction further and makes the conversion higher in case of MAPDT than APDT.[27]

The hardness values of photocrosslinked polymers A_1–A_{20} obtained from acrylated monomer are measured and presented in Table 2. Polymers obtained for 0.25%, 0.50%, 0.75%, and 1.00% initiator concentrations at 10 min irradiation time are designated as A_1, A_6, A_{11}, and A_{16}. It is observed that the hardness of the crosslinked polymer increases with increasing initiator concentration. The hardness of the polymers MA_1–MA_{20} obtained from methacrylated monomer are measured and their data are presented in Table 3. It was observed that the hardness of the crosslinked polymers increases with increasing initiator concentrations. Comparison of the values of hardness for the crosslinked polymers from acrylated monomer (A_1, A_6, A_{11}, and A_{16}) and from the methacrylated monomer (MA_1, MA_6, MA_{11}, and MA_{16}) indicates that the crosslinking process is faster in the case of polymers from methacrylated monomer than those of acrylated monomer. The increased hardness of methacrylated polymers are due to the presence of methyl groups at the reactive carbon center resulting closer packing of chains, which increases the chain stiffness of the methacrylates by restricting the free rotation by steric hindrance. Hence, the polymers from methacrylates are more rigid, hard, and less flexible than the acrylates.[28]

The density of the crosslinked polymers was measured using the formula:

$$\text{Density of crosslinked polymer} = \left[\frac{a}{(a-b)} \times \text{density of the solvent}\right]$$

where, a = weight (g) of crosslinked polymer in air, b = weight (g) in isopropyl alcohol.

Values of density for all the polymers A_1–A_{20} and MA_1–MA_{20} were presented in Tables 2 and 3, respectively. In all the cases, it is observed that the density increases with increasing irradiation time, also with the increase of photoinitiator concentration. In comparison of the density of the polymers obtained from acrylated monomers (A_1–A_{20}) and methacrylated monomers (MA_1–MA_{20}), the methacrylated polymers are rigid and less flexible and show higher crosslink density due to higher percentage conversion.

The solubilities of all the photocrosslinked polymers were tested in DMF, dimethyl sulfoxide, methyl alcohol, chloroform, carbon tetrachloride, diethyl ether, isopropyl alcohol, tetrahydrofuran, benzene, and toluene. The polymers are found to be insoluble in all the solvents however in DMF, dimethyl sulfoxide, and methyl alcohol the process is limited to swelling. The swelling studies were carried out for the photocrosslinked polymers using the solvent DMF. The study on swelling coefficient, crosslink density, and molecular weight between crosslinks were also carried out.

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The swelling coefficient (Q) of the photocrosslinked polymers, A_1–A_5, A_6–A_{10}, MA_6–MA_{10} and MA_{11}–MA_{15} were determined using the formula:[29]

$$Q = \frac{\text{Weight of DMF in the swollen polymer}}{\text{Weight of the polymer before swelling}} \times \frac{\text{Density of DMF}}{\text{Density of polymer}}$$

The crosslink density (υ) and molecular weight between crosslinks (MW_c) were determined by using Flory-Reihner's equation:[29]

$$\upsilon = -\frac{V_r + xV_r^2 + \ln(1 - V_r)}{d_r V_0 (V_r^{1/3} - V_r/2)}$$

$$MW_c = \frac{1}{\upsilon}$$

$$V_r = \frac{1}{1+Q}$$

where, υ is the crosslink density (effective number of moles of crosslinked units per gram of crosslinked polymers), V_r is the volume fraction of polymer, d_r is the density of polymer, x is the polymer–DMF interaction parameter (lattice constant 0.34, for $\delta s = \delta p$), and V_0 is the molar volume of DMF.

The data of the Q, υ, MW_c of the polymers obtained from APDT and MAPDT monomers are presented in Table 4. The swelling coefficients of the polymers A_1–A_5, are 15.8, 10.1, 18.9, 7.0, and 6.6; A_6–A_{10} are 14.8, 8.5, 8.0, 6.2, and 5.5. The corresponding crosslink density and molecular weight between crosslinks data are presented. It was observed that the swelling coefficient decreases, the crosslink density increases, whereas the chain length between crosslinks decreases indicating the decrease in molecular weight between the crosslinks.[29,30] Identical observations were made for the polymers MA_6–MA_{10} and MA_{11}–MA_{15}. The following observations were also made: (i) as the irradiation time increases, the crosslink density increases whereas swelling coefficient and molecular weight between crosslinks decreases, (ii) as initiator concentration increases, the crosslink density increases whereas swelling coefficient and molecular weight between crosslinks decreases, and (iii) as the percentage crosslinking increases, the crosslink density increases whereas swelling coefficient and molecular weight between crosslinks decreases.

The percent gel content of the crosslinked polymers A_1–A_{20} and MA_1–MA_{20} were determined by using the formula:[31]

$$\text{Gel content (\%)} = \left[\frac{W_1}{W_0} \times 100\right]$$

where W_0 is the weight of polymer taken and W_1 is the weight of the extracted sample.

Figures 8 and 9 shows the percent gel content of the polymers A_1–A_{20} and MA_1–MA_{20}, respectively. The percent gel content increases with increasing irradiation time.[31] It was also observed that the percent gel content is proportional to the percentage crosslinking.

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Table 4. Swelling coefficient, crosslink density, and molecular weight between crosslinks data of crosslinked polymers, A_1–A_5, A_6–A_{10}, MA_6–MA_{10}, and MA_{11}–MA_{15}.

Polymer code no.	Swelling coefficient (Q)	Crosslink density (υ) $\times 10^{-5}$	MW $M_c \times 10^4$
A_1–A_5	15.8	2.4	4.2
	10.1	5.1	2.0
	18.9	5.7	1.8
	7.0	7.9	1.3
	6.6	8.4	1.2
A_6–A_{10}	14.4	3.0	3.3
	8.5	6.1	1.6
	8.0	6.7	1.5
	6.2	9.7	1.0
	5.5	11.3	0.9
MA_6–MA_{10}	10.3	3.8	2.6
	6.9	7.6	1.3
	6.8	7.5	1.2
	5.3	11.6	0.9
	5.1	12.4	0.8
MA_{11}–MA_{15}	8.2	5.2	1.9
	5.3	11.6	0.9
	4.8	13.5	0.7
	4.3	16.1	0.6
	4.0	18.0	0.5

The thermogravimetric studies of the crosslinked polymers A_{12} and A_{14} obtained from APDT were performed in an nitrogen atmosphere at a heating rate of 20°C/min in order to evaluate their relative thermal stabilities. The TGA curves of the polymers are given in Fig. 10. The initial decomposition temperature (IDT) and the temperature

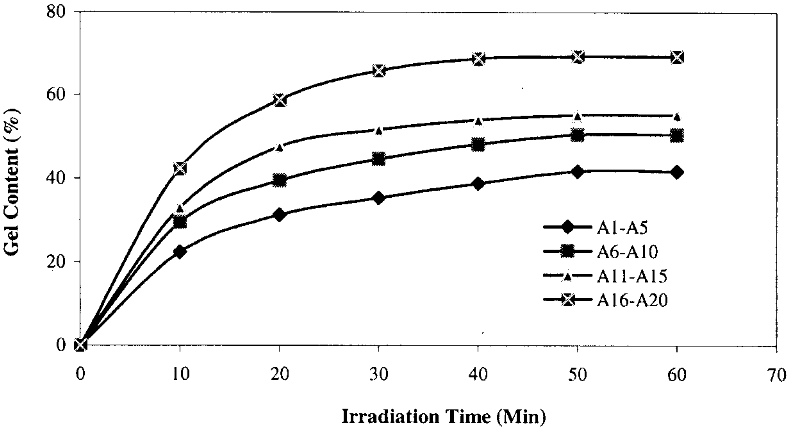

Figure 8. Gel content of crosslinked polymers, A_1–A_{20}.

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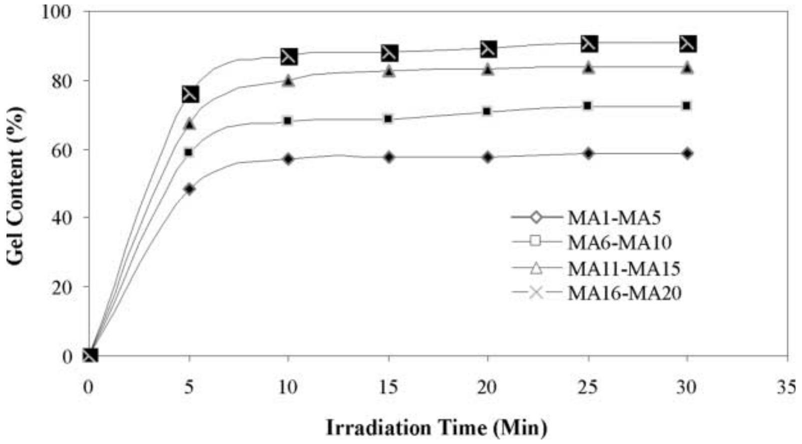

Figure 9. Gel content of crosslinked polymers MA_1–MA_{20}.

corresponding to 10% wt loss (T_{10}) of the polymers A_{12}: 172°C (205°C) and A_{14}: 179°C (213°C). The study reveals that the IDT and T_{10} increase with increasing irradiation time.

The DSC thermograms of the photocrosslinked polymers A_1–A_5 obtained from APDT at an initiator concentration of 0.25% and different intervals of exposure 10, 20, 30, 40, and 50 min are given in Fig. 11. Glass transition temperature (T_g) values for the

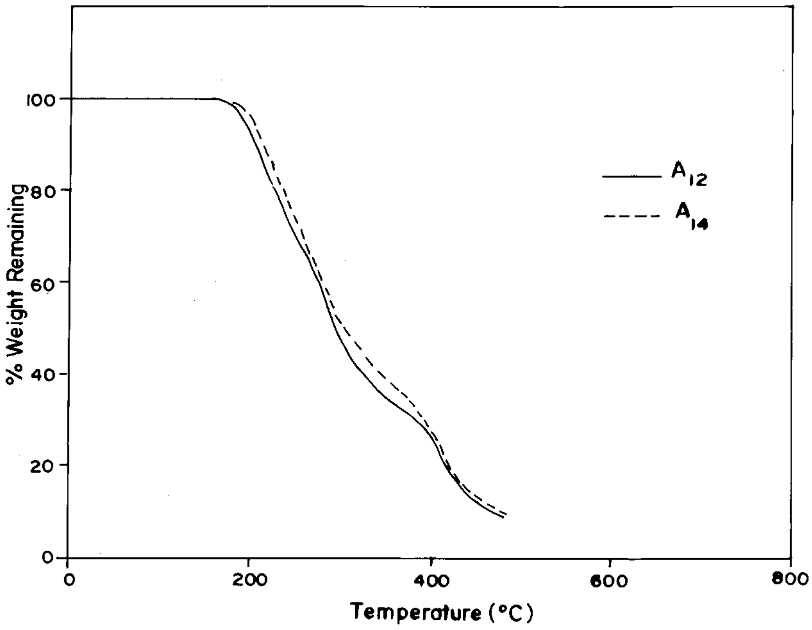

Figure 10. The TGA thermograms of crosslinked polymers, A_{12} and A_{14} measured at a heating rate of 20°C/min.

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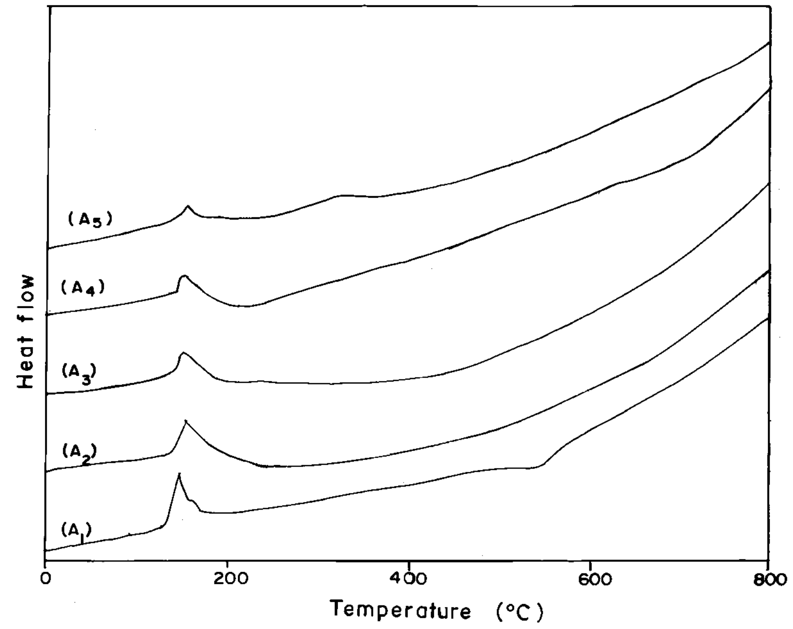

Figure 11. The DSC traces of crosslinked polymers, A_1–A_5.

polymers A_1 (149°C), A_2 (151°C), A_3 (148°C), A_4 (153°C), and A_5 (152°C) were compared and it was noticed that there was no marked difference in T_g values.

CONCLUSION

The photocrosslinkable monomers, APDT, and MAPDT were synthesized and confirmed by IR, ^{1}H-NMR, and ^{13}C-NMR spectra. Photocrosslinking behavior of the monomers have been studied by irradiating the monomers in the presence of free radical initiator using a medium pressure mercury vapor lamp. A probable free radical mechanism for the crosslinked polymers has been suggested. Double bond conversion studies of the monomers have been carried out by FT-IR technique by monitoring the decrease in the intensity of IR absorption of acrylate and methacrylate double bond during photocrosslinking; this study reveals that the conversion increases with increasing the irradiation time as well as by increasing the initiator concentration and it was observed that polymers from methacrylated monomer have higher double bond conversion than acrylated. Hardness and density of the polymers increases with increasing the irradiation time and initiator concentration; polymers from methacrylated monomer have higher value of hardness and density. The swelling study shows that the crosslink density and percent gel content increases with increasing the irradiation time and initiator concentration, whereas swelling coefficient and molecular weight between crosslinks decreases. Thermogravimetric analysis and DSC studies were made for a few polymers and it is revealed there was no marked difference in T_g values.

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