



## UV LIGHT INDUCED GRAFTING OF 2-HYDROXYETHYL METHACRYLATE ONTO POLYURETHANE STIMULATED BY N,N-DIETHYL DITHIO CARBAMATO GROUP

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### ABSTRACT

The dithiocarbamate groups are known to act as photoinitiators in the free radical polymerization of vinyl monomers. The photolability of this group is due to the breaking of the C – S bond by UV irradiation. A photoinitiator, N,N-Diethyldithiocarbamate-(1,2)-propanediol (DCPD) was synthesized from sodium N,N-Diethyldithiocarbamate (SDDC) and 3-chloro-1,2-propanediol(CPD). A polyurethane macrophotoinitiator (PUCS) was then synthesized by a two step process where N,N-Diethyldithiocarbamate-(1,2)-propanediol was used as the chain extender. Other compounds used included 4, 4'- diphenyl methane diisocyanate (MDI), polypropylene glycol(PPG), M.W 1000. This polyurethane macrophotoinitiator having this pendent N,N-Diethyldithiocarbamate group was then used to polymerize 2-Hydroxyethyl methacrylate(HEMA) in a photochemical reactor (Compact- LP-MP 88) at 254 nm. The resultant graft copolymer, polyurethane-g-poly2-Hydroxyethyl methacrylate was freed from the homopolymer by a standard procedure. The graft copolymer was characterized by Fourier transform infrared spectroscopy, <sup>1</sup>H- NMR spectroscopy, thermogravimetric analysis and scanning electron microscopy.

**Keywords :** graft copolymer; macrophotoinitiator; photopolymerization; polyurethane; thermogravimetric analysis(TGA); scanning electron microscopy(SEM).

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## INTRODUCTION

Polyurethanes are a broad class of polymers having only one aspect in common – the presence of urethane linkage. But the urethane linkage may constitute only a portion of the total number of linkages in the polymer chain. The structure has some resemblance to polyamides because both of them contain – CONH – groups. The presence of additional oxygen in the chain increases its flexibility and thus, the melting point of polyurethane is much less than that of the corresponding polyamide. The alteration of the physical properties and morphology of the polyurethanes can be achieved by changing the nature of diisocyanate, diols, vinyl monomers etc. It is this potential for tailoring the properties of polyurethanes to suit a specific purpose, has made it a highly versatile class of polymer. These compounds are widely used to control the stability of disperse system, as compatibilizers for improving the compatibility of polymer mixtures, thickeners, film-forming coatings, protective coatings, and so on<sup>1</sup>. Polyurethane-g-polyvinyl copolymers constitute an important class of copolymers that is both academically and commercially important. The commercial importance arises from its wide-ranging applications in coating materials, adhesives and sealing compounds.

The scope of utility of polyurethanes can be widened by its modifications. One way of modification may be its graft copolymerization<sup>2-3</sup> with vinyl monomers. For controlled incorporation of vinyl blocks into polyurethane blocks, iniferter concept developed by Otsu<sup>4-6</sup> can be employed. The N, N-diethyl dithiocarbamate<sup>7-8</sup> group is known as an important photoinitiator and the graft copolymerization of polyurethane through this group has not been studied so far.

Photoiniferter was investigated for graft copolymerisation<sup>9-12</sup>. A photoinitiator diol with pendent N,N-diethyl dithiocarbamate group was synthesised from sodium N,N-diethyl dithiocarbamate (DDC) and 3-chloro-1,2-propane diol (CPD). In this paper, we report the incorporation of pendent photolabile N, N-diethyl dithiocarbamate groups into a polyurethane macromonomer. This polyurethane

macrophotoinitiator was then UV- irradiated in presence of 2-Hydroxyethyl methacrylate (HEMA) to synthesize polyurethane-graft-poly2-Hydroxyethyl methacrylate copolymer (PUCS-g-PHEMA).

## EXPERIMENTAL

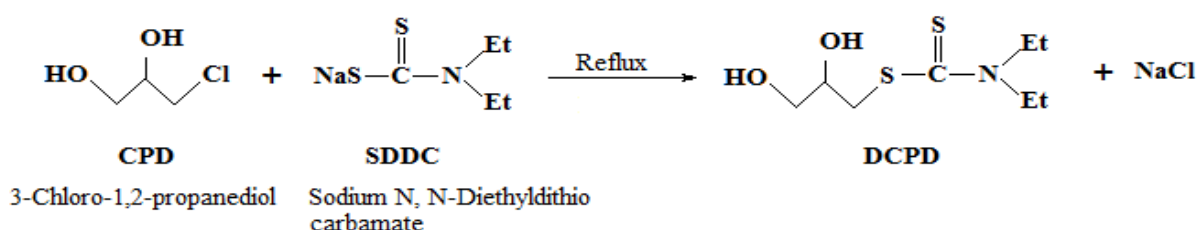
### Materials and methods

4,4'-diphenylmethanediisocyanate(MDI; Aldrich), 2-hydroxyethylmethacrylate (HEMA; E.Merck), 1,4-butanediol(BD; E.Merck), polypropylene glycol,M.W.1000 (PPG; Aldrich), were distilled under reduced pressure before their use. Dibutyltindilaurate (DBTDL; E.Merck) was used as received. Dimethylsulphoxide(DMSO; E.Merck), N,N-dimethylformamide (DMF; E.Merck) were dried over barium oxide, distilled under reduced pressure and stored at 0 – 4°C. Ethylmethylketone(MEK; E.Merck) was also distilled before its use. Other analytical grade reagents were used as received.

The Fourier transform infrared (FTIR) spectra were recorded in Perkin Elmer spectrum RX1 FTIR spectrophotometer (Norwalk, CT). The <sup>1</sup>H-NMR spectra were recorded in a Varian FT NMR AS 400-MHz spectrometer (Netherlands). Scanning electron microscopic (SEM) studies were done with a Leo 1430 VP electron microscope (Cambridge,UK). The thermogravimetric analysis(TGA) was carried out with a TA instruments series STD 2960 (Switzerland).

### Synthesis of N,N-Diethyldithiocarbamate-( 1,2 )-propanediol ( DCPD )

N,N-Diethyldithiocarbamate-( 1,2 )-propanediol ( DCPD ) was synthesized from equimolar mixture of 3-chloro-1,2-propanediol (CPD) and sodium N,N-Diethyldithiocarbamate(SDDC). The mixture was refluxed for 7 hours in a solvent mixture of acetone and absolute ethahol (Scheme 1). At the end of the reaction, the solvents were removed in a Bucci rotavapor. The crude product was purified with column chromatography and finally distilled under pressure. DCPD was characterized by elemental analysis and UV-vis , FTIR and <sup>1</sup>H- NMR spectroscopy, details of which were reported elsewhere<sup>13</sup>.



**Scheme 1:** General reaction scheme for the synthesis of DCPD

### Synthesis of polyurethane macrophotoinitiator(PUCS)

Polyurethane macrophotoinitiator was synthesized from MDI, PPG, and DCPD by a two-step procedure. MDI(2.0006 g) and PPG(2.6608 g) were reacted at 70°C for 1½ hours under nitrogen atmosphere. Then the temperature of the reaction mixture was lowered to 50°C. The chain extender diol DCPD (1.1878 g) was dissolved in 25 ml DMSO and slowly added from a pressure equalising funnel to the reaction mixture. This was followed by the addition of catalyst dibutyl tin dilaurate and then the reaction mixture was again heated at 90°C. At the end of five hours the reaction mixture was poured into water to precipitate the resultant polymer. It was then dried in a vacuum oven for several days.

### Photograft copolymerization

The photograft copolymerization reactions were carried out in a Heber multilamp photochemical reactor (COMPACT- LP- MP 88) at 254 nm. The polyurethane macrophotoinitiators (PUCS) with pendent N,N-Diethyldithiocarbamate groups were then used to initiate polymerization of HEMA to synthesize polyurethane-graft-poly-2-Hydroxyethylmethacrylate copolymers [(PUCS)-g-PHEMA]. A mixture of PUCS (0.2050 g) and HEMA in various amount (from 0.4411 to 2.6424 g) in DMSO(10 ml each) was first purged with dry nitrogen. The reaction tubes were then sealed and photoirradiated in a Heber multilamp photochemical reactor at 254 nm for 8 hours. The resultant polymers were isolated by precipitation in water and filtered. The graft copolymers were freed from the PHEMA homopolymers by soxhlet extraction with methanol-water system.

The graft copolymers were characterized<sup>14</sup> by monomer conversion (M%), grafting (G%) and grafting efficiency (GE%) as follows.

$$M(\%) = [F_1(g) - PUCS(g)] / F_3(g) \times 100$$

$$G(\%) = [F_2(g) - PUCS(g)] / F_2(g) \times 100$$

$$GE(\%) = [F_2(g) - PUCS(g)] / [F_1(g) - PUCS(g)] \times 100$$

Where  $F_1$  is the weight of dry graft copolymer product,  $F_2$  is the weight of dry graft copolymer after removal of the homopolymer and  $F_3$  is the weight of monomer (HEMA) added.

The effects of reaction conditions on the conversion percentage of HEMA (M%), grafting percentage (G%) and grafting efficiency (GE%) on PUCS were investigated.

### RESULTS AND DISCUSSION

Polyurethane macrophotoinitiator (PUCS) and polyurethane-graft-poly-2-Hydroxyethyl methacrylate copolymers [(PUCS)-g-PHEMA] were characterized by FTIR, 1H-NMR spectroscopy. The polymers were further investigated by thermogravimetry and SEM.

#### Effect of monomer concentration

The effect of the change in monomer concentration on M%, G% and GE% were investigated by varying the monomer (HEMA) concentration. The percentage conversion of monomer (M%), grafting percentage (G%) and grafting efficiency (GE%) on PUCS are shown by Figure 1 and Figure 2 respectively. The conversion percentage of HEMA (M%) and the grafting (G%) increased with rise in monomer concentration. The grafting efficiency (GE%) also increased and finally attained a maximum value at which it changes to a small extent or remained almost unchanged.

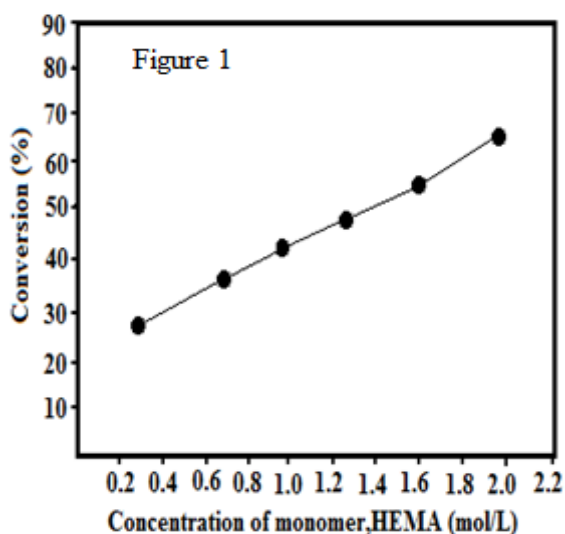


Figure 1: M% of HEMA as a function of the HEMA monomer concentration

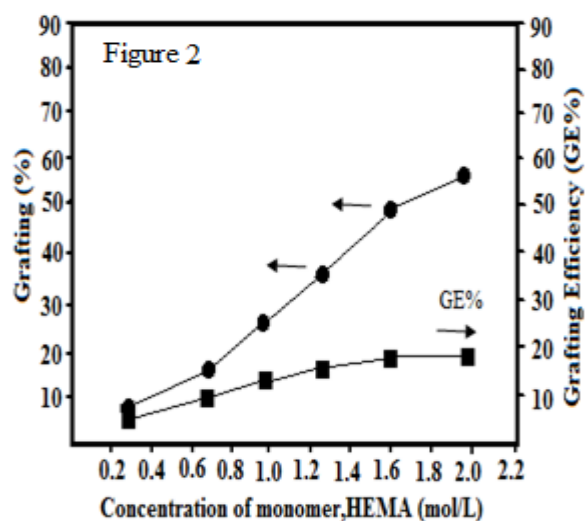


Figure 2 : Effect of G% and GE% of HEMA on PUCS as a function of the HEMA monomer concentration

### Spectroscopic analysis

The formation of (PUCS)-graft-PHEMA copolymers was observed from the FTIR spectrum <sup>1</sup>H-NMR spectrum and <sup>13</sup>C-NMR spectrum. The FTIR spectra of PUCS and (PUCS)-g-PHEMA are shown in Figure 3 and Figure 4 respectively. A broad and intense peak at 1734.50 cm<sup>-1</sup> arises due to overlapping of C = O stretching of both PHEMA<sup>15</sup> and polyurethane macrophotoinitiator units. The nature of the peaks due to C = O groups were different from that in the polyurethane macrophotoinitiator. This is because of additional hydrogen bonding with the hydroxyl group of PHEMA block. As a result, there was an increase in the intensity of the peak. The peak at 1165.35 cm<sup>-1</sup> ( C – O – C ) is also observed. The peak appeared at 3400 cm<sup>-1</sup> is due to urethane N-H stretching and all other peaks are appeared in their respective regions. Further, the presence of broad peak at around 3462.62 cm<sup>-1</sup> was due to overlapping bands arising from urethane N – H stretching and -OH group in PHEMA in the graft copolymer. Further, the peak at around 1261.88 cm<sup>-1</sup> corresponded to –SC(S) N group<sup>16</sup> in the (PUCS)-g-PHEMA copolymer.

The <sup>1</sup>H-NMR spectrum of (PUCS)-g-PHEMA copolymers is shown by Figure 5 and it also indicated the expected resonance for the – CH<sub>3</sub> protons ( δ 0.73 ppm and δ 0.92 ppm ), the – CH<sub>2</sub> protons ( around δ 1.02 ppm ) of the PHEMA unit. The peak appeared at about 9.5 – 8.5 ppm reveals the urethane –NH of polyurethane backbone. The NMR peaks of aromatic ring protons are resonated at around 7.0 – 7.3 ppm. The Figure 5 also shows a characteristic peak of methoxy protons ( δ 3.53 ppm ) of PHEMA unit in the resultant graft copolymer. The resonance peak at around 3.74-3.85 ppm is due to –COOCH<sub>2</sub>-CH<sub>2</sub>- protons from PHEMA. The other peaks in (PUCS)-g-PHEMA are same as in PUCS.

Figure 6 showed the <sup>13</sup>C-NMR spectrum of (PUCS)-g-PHEMA copolymer. The peak appeared at 151.4 ppm was due to the carbon from C= O unit of the urethane in the polymer chain<sup>17</sup>. The peak at 17.7 ppm was due to the methyl carbon from the PPG unit. The peaks at around 40.4 ppm and 66.7 ppm were due to CH<sub>2</sub> and CH group of the PPG unit respectively. The peaks appeared in the range 75 – 80 ppm were probably due to the presence of carbon atoms attached to benzene rings of the polyurethane. The peaks at around 129 – 140 ppm were due to aromatic carbon atoms present in the polymer chain. The peaks at around 177.6 ppm<sup>18</sup> indicated the presence of ester C = O group from PHEMA unit in the polymer chain. The peaks appeared at 51.28

ppm and 59.02 ppm were due to the presence of – OCH<sub>2</sub> and CH<sub>2</sub>–OH from the PHEMA unit in the (PUCS)-g-PHEMA copolymer respectively. The peaks appeared at around 129 – 140 ppm also indicated the presence of aromatic carbon atoms present in the polymer chain.

### Scanning electron micrographs ( SEM )

SEM investigations were carried out to study the surface morphology of the polymers. Scanning electron microscopic investigations<sup>19-20</sup> carried out on different types of polyurethanes revealed a two- phase morphology with a spherulitic or granular surface originating from a hard aromatic urethane microphase dispersed in the soft elastomeric phase of the polyester or polyether segment.

The Figure 7 and Figure 8 are scanning electron micrographs ( SEM ) of the PUCS and (PUCS)-g-PHEMA copolymer respectively. The scanning electron micrographs of the (PUCS)-g-PHEMA copolymer (Figure 8) showed a different morphology from that of the macrophotoinitiator(PUCS). The nucleation process of the hard segment spherulites in the polyurethane segment was influenced by the growing PHEMA chain. This indicates the different surface morphology of the two polymers. This is due to incorporation of some growing chains of PHEMA into polyurethane backbone.

### Thermogravimetry analysis (TGA)

The TGA- thermograms of PUCS and (PUCS)-g-PHEMA copolymer are shown in Figure 9 and Figure 10 respectively. The difference in the nature of the thermograms indicated differences in their chemical composition which was the result of graft copolymerization of PHEMA on polyurethane backbone. The macrophotoinitiator showed the one stage degradation at 375 °C. On the other hand the graft showed degradation at 398.88 °C. Apparently the thermal stability was marginally increased as a result of graft copolymerization.

### CONCLUSIONS

The study reveals the successful synthesis of polyurethane macrophotoinitiator (PUCS) with pendent N,N-diethyldithiocarbamate groups and (PUCS)-g-PHEMA copolymer. The characterizations of polymeric materials synthesized were done by the different spectroscopic analysis, SEM and thermogravimetric analysis. Thermal behaviours of the copolymers and SEM investigations together also indicated a successful graft

copolymerization process. The effects of reaction conditions on the conversion percentage of HEMA (M%), grafting percentage (G%) and grafting efficiency (GE%) on PUCS were investigated. The conversion percentage of HEMA (M%) and the grafting (G%) increased with rise in monomer concentration. The grafting efficiency (GE%) also increased and finally attained a maximum value at which it changes to a small extent or remained almost unchanged. This indicates the living radical fashion through the terminal  $[-S-C(=S)-N Et_2]$  group.

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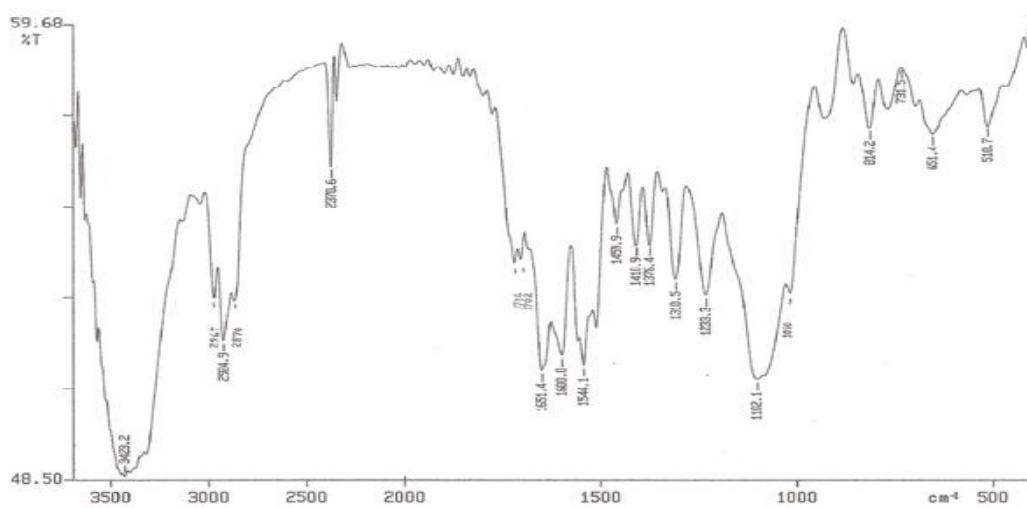


Figure 3: FTIR Spectrum of polyurethane macrophotoinitiator ( PUCS).

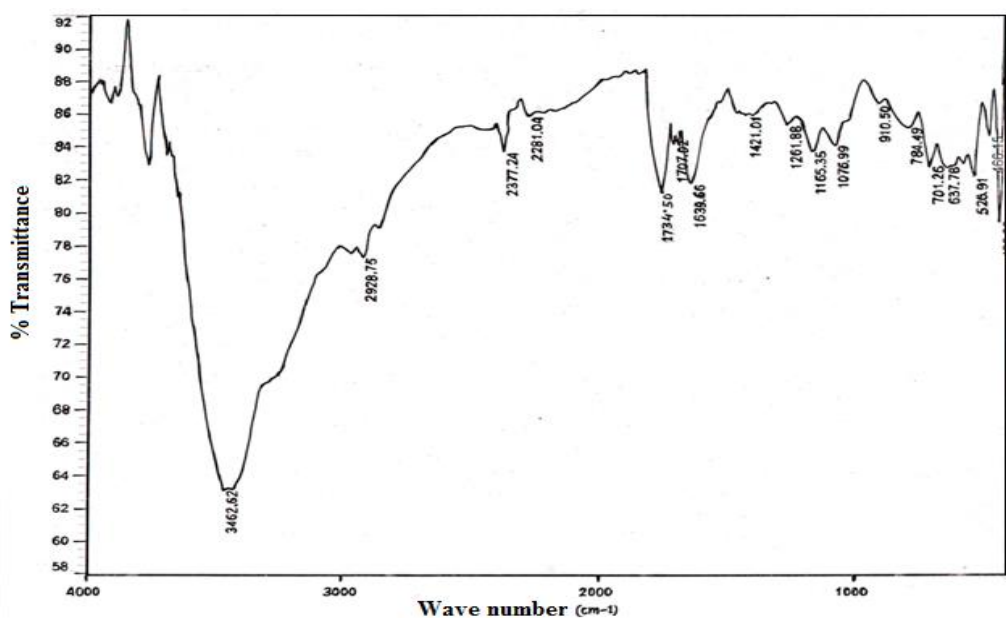


Figure 4: FTIR Spectrum of ( PUCS)-g- PHEMA copolymer.

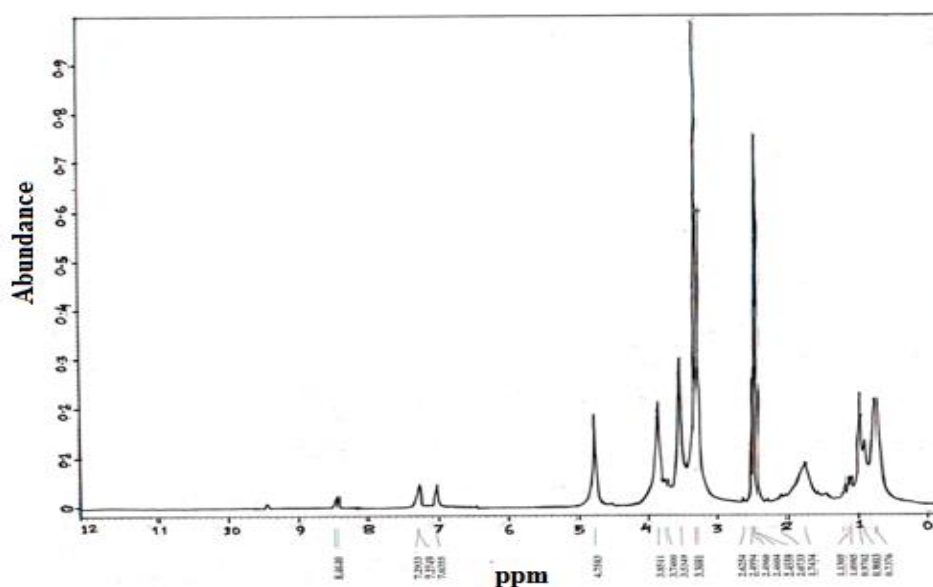
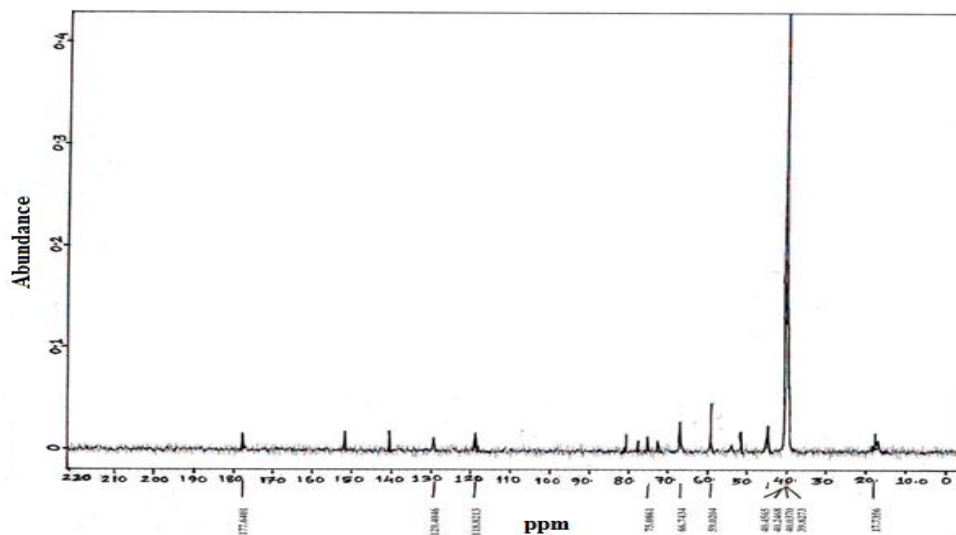
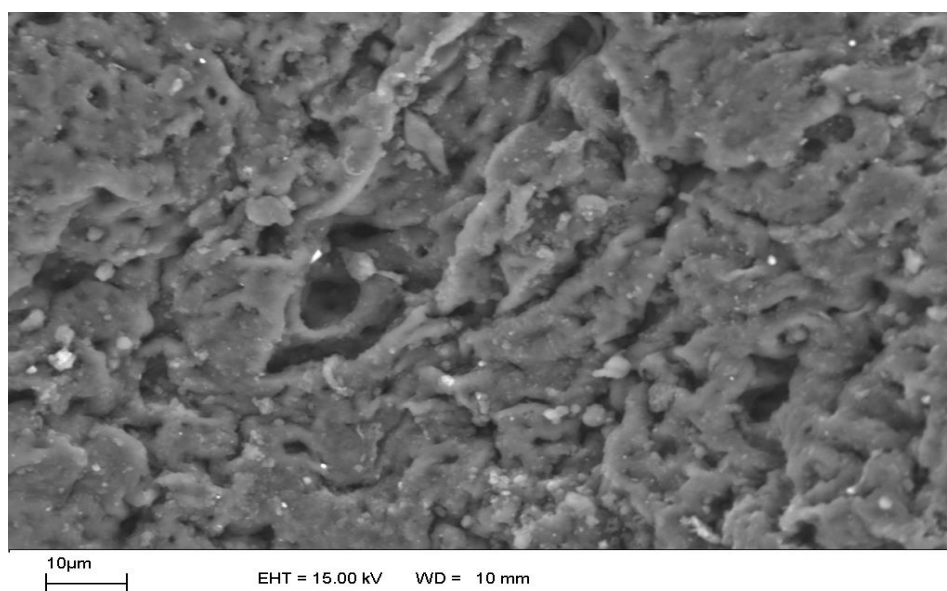


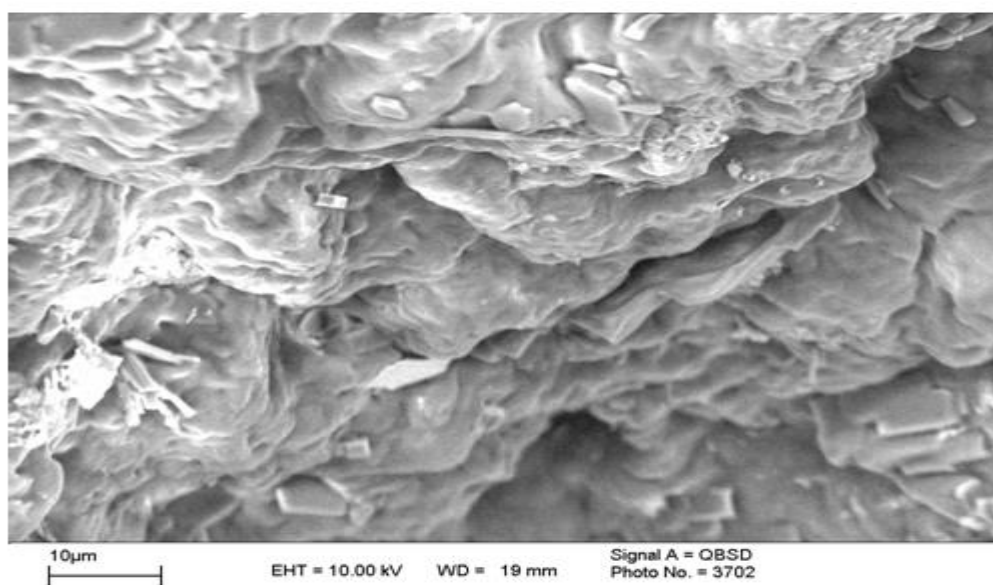
Figure 5: <sup>1</sup>H-NMR Spectrum of ( PUCS)-g- PHEMA copolymer.



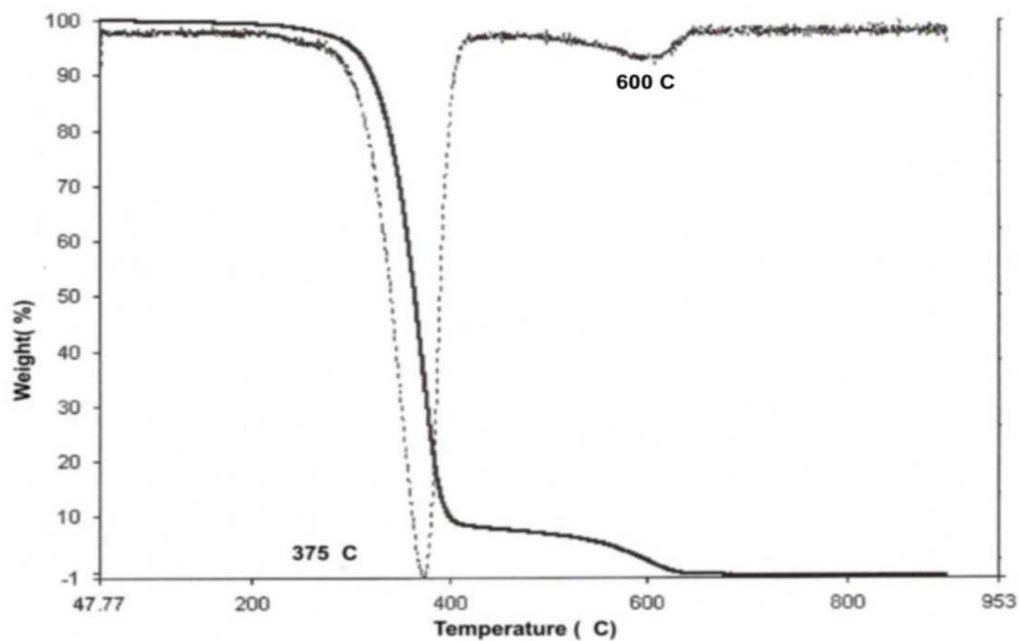
**Figure 6:** <sup>13</sup>C- NMR Spectrum of ( PUCS )-g- PHEMA copolymer.



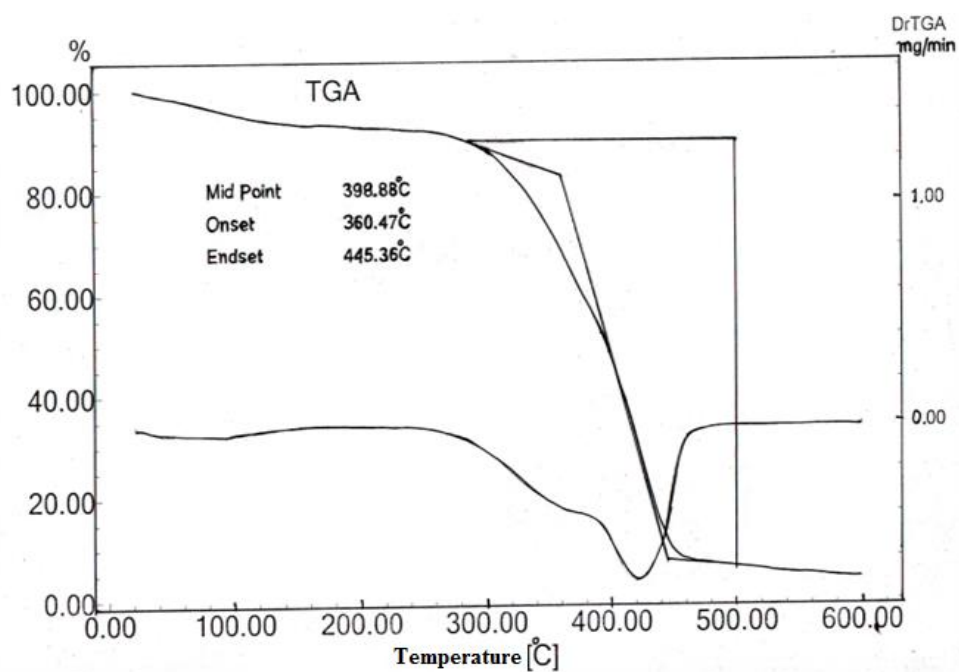
**Figure 7:** Scanning electron micrograph of PUCS



**Figure 8:** Scanning electron micrograph of (PUCS)-g-PHEMA copolymer.



**Figure 9:** TGA-Thermogram of polyurethane macrophotoinitiator (PUCS).



**Figure 10:** TGA-Thermogram of (PUCS)-g-PHEMA copolymer.