Studies on the Radiation-Induced Graft Copolymerization of Mixtures of *n*-Butyl Acrylate and 2-Hydroxyethyl Methacrylate on Polyurethane. I. Synthesis and Characterization

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SYNOPSIS

Modification of polyurethane, by grafting two types of monomers, a hydrophilic and hydrophobic, with an aim to enrich the surface with both hydrophobic and hydrophilic moieties, is attempted. Grafting of 2-hydroxyethyl methacrylate and *n*-butyl acrylate from a mixture of these two onto polyurethane by γ-irradiation and subsequent characterization of the graft copolymer by infrared spectroscopic method, mechanical characterization, contact angle, and scanning electron microscopy is detailed.

INTRODUCTION

The possibility of creating an almost inexhaustible variety of molecular architecture having the required characteristics together with a comparatively good biocompatibility makes segmented polyurethanes one of the most extensively used materials in contemporary health care application.[1-3] Yet modification of polyurethanes by grafting various chemical entities with an aim to functionalize its specificity for favoring further biointeraction has been reported.[4-6] Often modification of polyurethane, even though improving several desirable biocompatible factors, fails to preserve some of the vital characteristics of polyurethane itself. This is particularly true in the case of 2-hydroxy(ethyl methacrylate) (HEMA)-grafted polyurethane. HEMA grafting is known to enhance the biocompatibility of polyurethane, but curtails considerably the mechanical properties.[4,7,8] To date, most of the studies of chemical modification of polyurethane by grafting have been restricted largely to single hydrophilic monomers.[9-13] Grafting from a binary mixture consisting of two types of monomers, hydrophobic and hydrophilic, could be more beneficial because of a very large spread in properties.

This communication reports the grafting of HEMA and *n*-butyl acrylate (BA) from a mixture onto polyurethane by γ-irradiation. The hydrophobic BA could enhance the hydrophobicity of polyurethane whereas incorporation of HEMA can enhance the hydrophilicity of the polymer. Optimization of these parameters may impart properties to the grafted polyurethane desirable for a better biomaterial.

EXPERIMENTAL

Materials

The polyurethane (PU) used in this study, based on methylene bis(*P*-cyclohexyl isocyanate) (Bayers), poly tetramethylene glycol 990 (QO Chemicals), and 1,4-butanediol (Merck) having 46% (wt %) hard segment content, was synthesized as reported elsewhere.[14] Polyurethane films were obtained by solution casting method using dimethyl acetamide (DMAC) as solvent and were solvent

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(ethanol and n-hexane) extracted for the removal of DMAC and other impurities, if any. 2-Hydroxyethyl methacrylate (HEMA) (Fuka) and n-butyl acrylate (BA) (Merck) were vacuum distilled prior to use. All other reagents were either chromatographic or spectroscopic grade and were used as received.

Instrumental

A Waters Associates gel permeation chromatographic system consisting of a Model 6000A solvent delivery pump, U6K injector, and 730 data module was used for determining the molecular weight parameters of the polymers. A set of 3 μ-styragel columns (Waters Assoc.) having a nominal pore size of 10^5, 10^4, and 10^3 Å was used in conjunction with THF or dichloromethane as mobile phase at a flow rate of 1 mL min^{-1} for getting the chromatographic profile of the polymers. The columns effluents were monitored by an R-401 differential refractometer. The columns were calibrated using polystyrene standards under the same chromatographic conditions.

Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer. Under water air bubble contact angles were measured using a Goniometer (Rame Hart, USA). SEM photographs were obtained using a Jeol 35C scanning electron microscope. Samples were coated with an evaporated gold layer prior to observation. A Model 1193 Instron universal testing machine was used for determining the ultimate stress and strain parameters as per ASTM D-882. The crosshead speed was 100 mm min^{-1}.

Grafting Procedure

Cleaned 6 × 1 cm strips of polymer, having a thickness of 0.4 mm, were immersed in monomers and monomers mixture (HEMA + BA, 1 : 1 v/v) for a specific period of time. The strips then immediately subjected to γ-irradiation from a Co^{60} source under nitrogen atmosphere to a total dose 0.5 Mrad. A varied percentages of grafting was achieved by increasing the exposure time to the monomers rather than changing the irradiation dose. The strips after irradiation were subjected to extensive extraction with water : alcohol mixture to remove unreacted HEMA and poly(HEMA).[4] For removing unreacted BA and poly(BA) the strips were extracted with carbontetrachloride and then with toluene. The strips were then vacuum-dried to constant weight. The grafting % was determined from $(w - w_0/w_0) \times 100$, where w is the final weight and w_0 is the initial weight of the strip.

Isolation of BA-Grafted Polyurethane

PU grafted with BA was kept in tetrahydrofuran overnight. Unreacted PU was dissolved and a swelled residue left. Poly(BA) was found to be insoluble in THF. The residue was extracted with methyl alcohol and vacuum-dried. The BA-grafted PU was found soluble in dichloromethane.

Isolation of HEMA-Grafted PU

HEMA-grafted PU kept in THF left a residue which was found to be insoluble in all solvents including dimethyl acetamide, indicating that the graft is crosslinked.

Isolation of (HEMA + BA)-Grafted PU

This material was first kept in THF for removing unreacted polyurethane. The swelled mass then kept in dichloromethane for removing any PU chains grafted only with BA. The insoluble residue was isolated dried and characterised.

IR Studies on the Graft Materials

Isolated BA-grafted PU (PU-B) was dissolved in dichloromethane. The solution dried over a KBr window, and the spectrum was scanned from 4000 to 600 cm^{-1}. However, HEMA-grafted PU (PU-H) and (HEMA + BA) grafted PU (PU-HB) swelled in dichloromethane, were spread over KBr window as a thin film, and were dried using an IR lamp; the spectra were then recorded.

RESULTS AND DISCUSSION

The extent of grafting of a single monomer and from the mixture, all exposed to the same time interval, is summarized in Table I. The extent of grafting of BA is less than HEMA. This could be due to the slower diffusion of the bigger BA molecules to the polymer matrix.

Table I Variation in the Extent of Grafting with Exposure Time to Monomers and Mixture

Contact Time with Monomer (min)	Extent of Grafting (%)		
	BA	HEMA	(BA : HEMA) Mixture
5	6.2	6.9	12.8
15	11.8	12.87	28

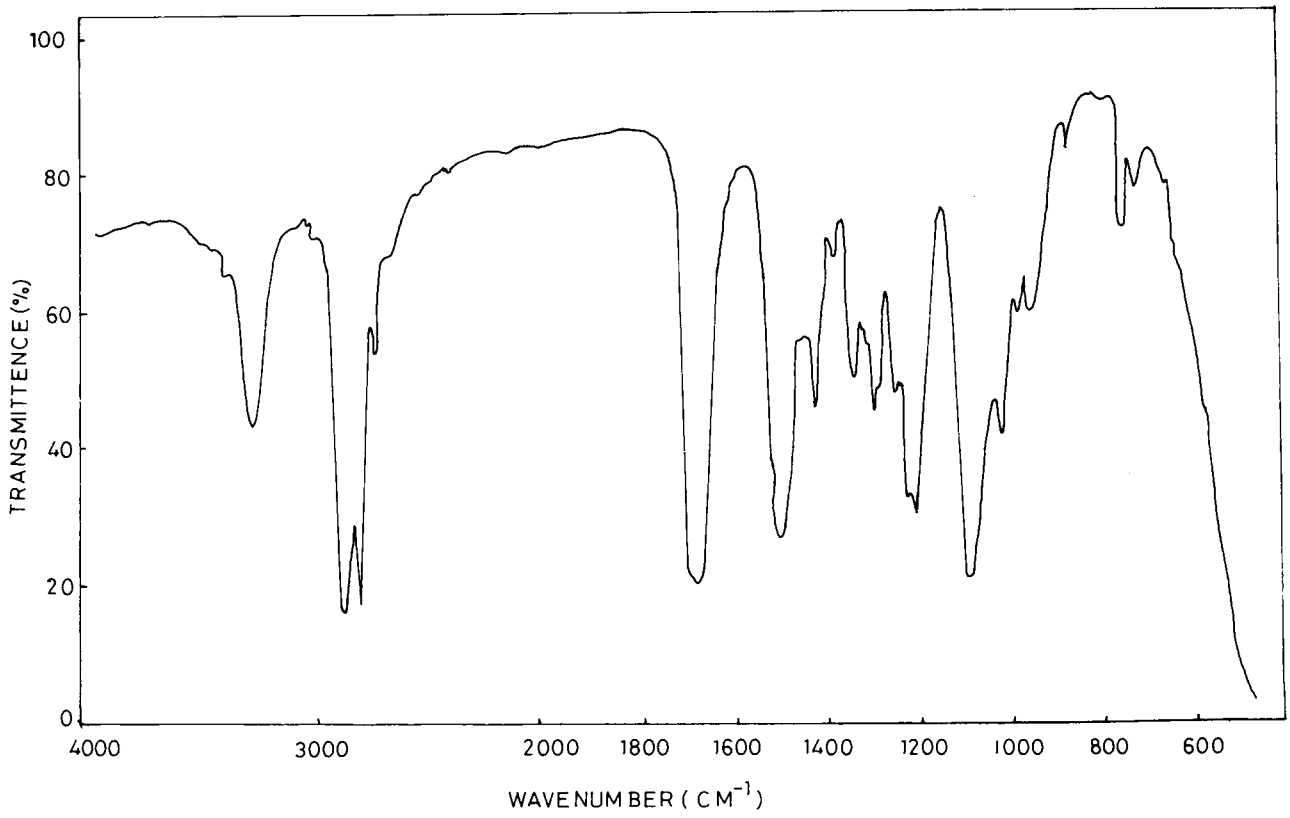

Figure 1 IR spectrum of polyurethane.

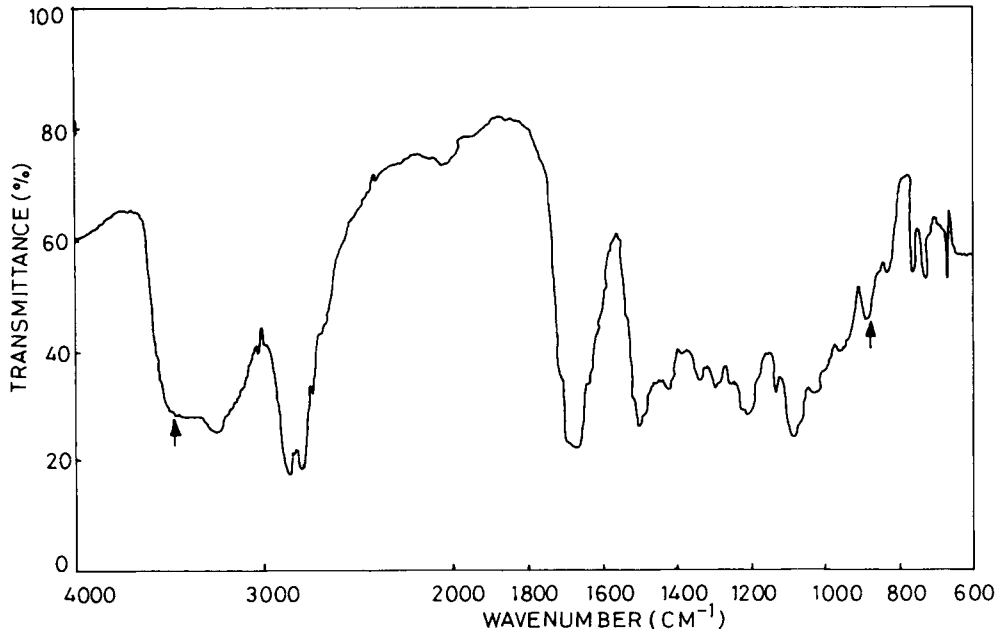

Figure 2 IR spectrum of poly(HEMA)-*g*-PU.

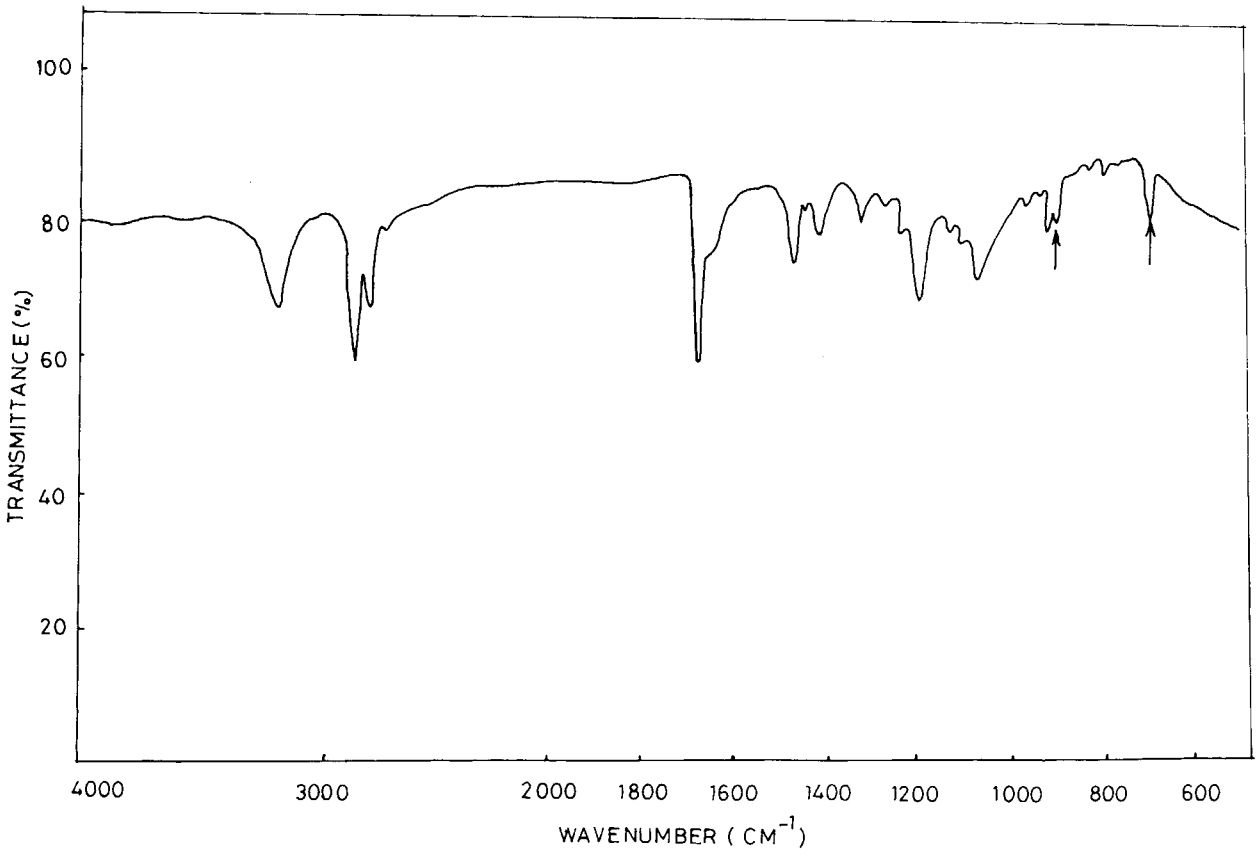

Figure 3 IR spectrum of poly(BA)-*g*-PU.

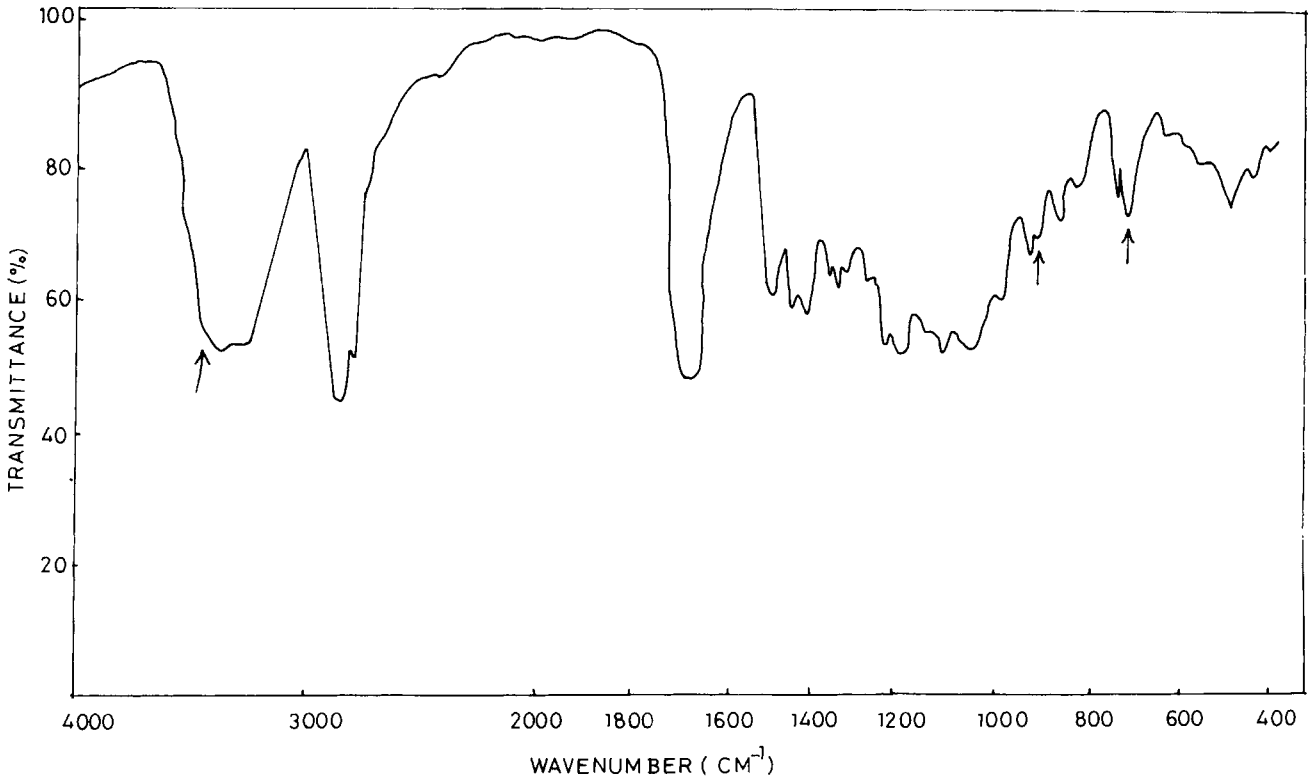

Figure 4 IR spectrum (HEMA + BA)-*g*-PU. The ↑ indicates the characteristic peaks of grafted species.

Table II Molecular Weight of the Polymers

Polymer	Weight Average Molecular Weight (M_w)	Number Average Molecular Weight (M_n)	D (M_w/M_n)
PU	230,000	100,000	2.30
BA-*g*-PU	450,000	180,000	2.50
HEMA-*g*-PU[a]	—	—	—
(HEMA + BA)-*g*-PU[a]	—	—	—

[a] Insoluble.

Figure 1 shows the IR spectrum of PU. Figure 2 illustrates the IR spectra of PU–H. The characteristics absorption peaks of HEMA are centered around 3500 and 900 m^{-1}. IR spectra shown in Figure 3 is that of PU–B. Characteristic absorption bands of grafted BA are around 940 and 740 cm^{-1}, respectively. Figure 4 (IR spectrum of PU–HB) shows the characteristic peak of poly(HEMA) at 3500 cm^{-1} and poly(BA) at 940 and 740 cm^{-1} indicating the grafting of both species.

The molecular weight parameters commutted from GPC traces are shown in Table II. The data are, however, partially due to the insolubility of HEMA-*g*-PU and the binary graft in the common solvents. Table III summarizes the contact angle data. BA-grafted PU produces a larger contact angle than the bare PU indicating more hydrophobic nature. The PU–H and PU–HB distinctly show the hydrophilic nature (smaller angle than the bare PU). Interestingly, PU–HB shows an angle close to that of PU–H rather than PU–B, indicating more HEMA concentration on the surface. ATR–IR analysis (figures are not shown) also favored the same trend.

SEM photographs of PU, PU–B, PU–H, and PU–HB are shown in Figures 5(A), 5(B), 5(C), and 5(D), respectively. Evenly distributed spots are seen on the surface of BA-grafted PU. In PU–H the grafted species are densely concentrated unevenly. Apparently the difference of the two surfaces can easily be observed. The mixed graft appears as thick bunches, again showing distinct morphology.

The stress–strain characteristics of the materials modified with HEMA, BA, and both are summarized in Table IV. For the sake of comparison, the materials used consist of nearly the same grafting yield. Both stress and strain decreases considerably in PU–H. The same behavior has been reported by Jansen and Ellinghorst.[4] The hard segment domains have been shown to be impermeable to all monomers including HEMA.[15] The grafting is, therefore, confined to the soft segment domains. In PU, the ultimate stress–strain parameters, to a large extent, are also dependent on the soft segment orientation along the stress, and strain induced soft segment crystallization.[16] The interference of these aspects by HEMA grafting can certainly lessen the mechanical properties.

The mechanical properties of BA-grafted PU, on the other hand, is almost identical to that of PU (Table IV). The more flexible poly(BA) chains can presumably mix up with the soft segment of PU and adverse interference of the grafted chain could be rather low. More flexibility is evident from the higher strain of PU–B than PU itself. The stress–strain values of PU–HB are less than PU, but it is much higher than the HEMA-grafted PU. The strength of mixed graft material is certainly adequate to most of the intented applications.

Table III Under Water Air Bubble Contact Angle—Variation with the Nature of Monomer

Material	Grafting	Contact Angle (deg)
Polyurethane	—	53 ± 0.5
BA-*g*-PU	12	56 ± 0.6
HEMA-*g*-PU	12.87	42 ± 0.3
(BA + HEMA)-*g*-PU	12.8	45 ± 0.7

Table IV Variation in Mechanical Properties: Effect of Modification

Material	Extent of Grafting (%)	Stress (kg/cm^2)	Strain (%)
PU	—	445 ± 12	498 ± 13
BA-*g*-PU	12	398 ± 6	625 ± 11
(HEMA)-*g*-PU	12.87	243 ± 8	413 ± 16
(HEMA + BA)-*g*-PU	12.8	340 ± 12	520 ± 14

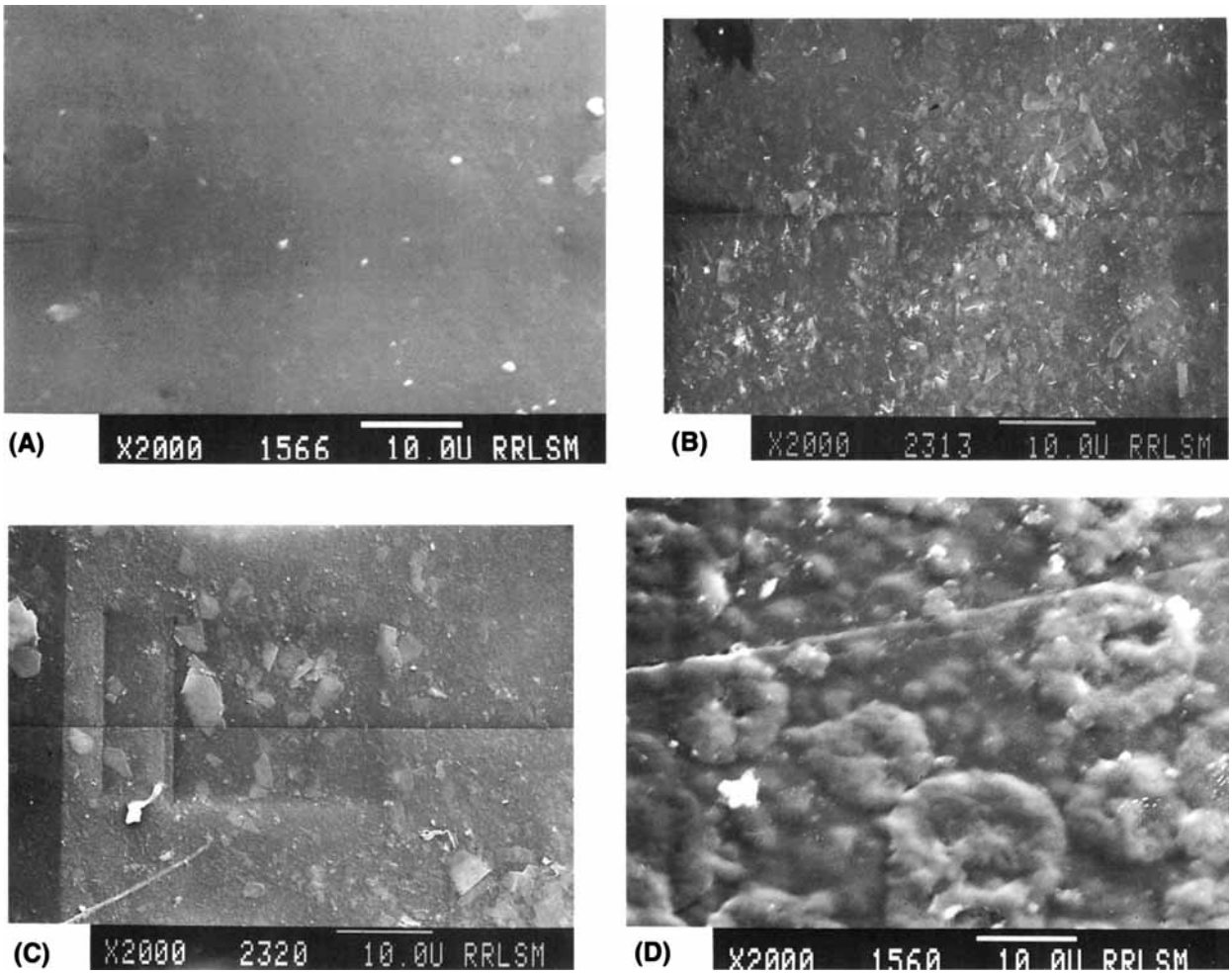

Figure 5 (A) SEM photograph of bare PU—magnification 2000×. (B) SEM photograph of BA-*g*-PU % of grafting 6.2. (C) SEM photograph of HEMA-*g*-PU % of grafting 6.9. (D) SEM photograph of (HEMA + BA)-*g*-PU % of grafting 12.8.

The surface-mediated biocompatibility of material is often traced to hydrophilic/hydrophobic balance.[17,18] When both hydrophilic and hydrophobic chains are grafted to PU, to a certain extent, it could be possible to functionalize the surface to a specific need. By choosing the monomers in such a way, it is even possible to create a hydrophilic-rich or hydrophobic-rich surface. The study points out the possibility of tailoring the surface or both the surface and bulk of polyurethane to the specification demanded for a particular application by choosing various monomers and optimizing the experimental parameters.

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