Radiation-Grafted Polymers for Biomaterial Applications. I. 2-Hydroxyethyl Methacrylate: Ethyl Methacrylate Grafting onto Low Density Polyethylene Films

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Synopsis

Studies were conducted on the radiation grafting of 2-hydroxyethyl methacrylate (HEMA) and ethyl methacrylate (EMA) by the mutual irradiation technique onto low density polyethylene. Four different solution concentrations were used, and radiation doses ranged from 0.03 to 0.50 Mrad. Four copolymer compositions having different HEMA:EMA ratios were also studied using two total monomer concentrations. The kinetics of the grafting process demonstrated by the two monomers were basically different. While EMA showed a typical diffusion-controlled kinetic pattern, HEMA exhibited a more complex behavior, the main features of which were an induction period, a slight autoacceleration and a significant drop in graft level after a maximum is reached. The difference in behavior was interpreted in terms of partitioning of monomers into the polyethylene substrate. The surface topography of the grafted films was studied by means of scanning electron microscopy. A mechanism based on osmotic cell formation was suggested for the HEMA graft system. The copolymer systems investigated showed that the graft reaction is faster in the initial stages for higher percentages of EMA in the monomer mixtures; as grafting proceeds the trend is reversed.

INTRODUCTION

Water-swollen hydrophilic polymeric networks (hydrogels) have been the focus of much research directed towards the development of new materials for medical applications.[1-5] The inherently poor mechanical properties of hydrogels have encouraged the development of various techniques for reinforcing hydrogels, to make them suitable for use in biomedical devices. By radiation grafting monomers such as 2-hydroxyethyl methacrylate (HEMA), *N*-vinyl pyrrolidone (NVP), or acrylamide (AAm) onto strong inert polymeric supports, materials have been produced which combined the desirable surface properties of the hydrogel graft with the good mechanical properties of the substrate.[6-8]

By systematically varying the surface structure and composition of materials and observing the effects of this variation on biological interactions, one can explore fundamental aspects of such phenomena as protein adsorption, cell adhesion, and thrombogenesis on foreign surfaces. Several hypotheses have been formulated in relation to the biocompatibility of

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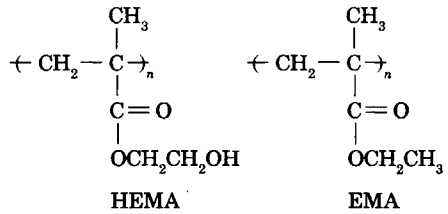
polymeric biomaterials.[9-11] Among them, it has been suggested that a particular ratio of hydrophilic to hydrophobic sites on a surface may be important for optimum blood compatibility.[12,13]

To test this hypothesis, a model system composed of radiation graft copolymers of 2-hydroxyethyl methacrylate (HEMA) and ethyl methacrylate (EMA) has been proposed.[14] The backbone structures of HEMA and EMA are identical, differing only in the hydroxyl group of HEMA. Thus, increasing fractions of HEMA in copolymers will result in higher hydroxyl group density and, therefore, increased wettability.



In an attempt to gain further insight into the nature of the HEMA–EMA model system, a number of variables affecting the radiation graft polymerization have been investigated. In this paper we focus on the synthesis and characterization of radiation-grafted homopolymers and copolymers of HEMA and EMA on low density polyethylene (PE). The grafted polymers have been characterized by scanning electron microscopy in order to explore their surface topography. Complementary studies on the structure and composition of the grafted systems will be reported in a second article.

EXPERIMENTAL

Highly purified 2-hydroxyethyl methacrylate (HEMA), supplied by Hydromed Sciences, Inc., was used as received. Gas chromatographic analysis indicated that this monomer contained 0.010–0.035% ethylene glycol dimethacrylate and 0.02–0.07% methacrylic acid. Ethyl methacrylate (EMA) was purchased from Polysciences, Inc., and used after distillation at 46°C and 50 mm Hg. Both monomers were stored at 4°C. All solvents were reagent grade.

Low density polyethylene sheets (Cadillac Plastics Corp.) were pressed against highly polished chrome plates at 130°C, 0.7 MPa, for 3 min, and rapidly quenched by immersion in an ice water bath. The 0.5-mm polyethylene substrate was cut into films 3.8 cm × 1.9 cm, washed in an ultrasonic cleaner for 5 min in 0.1% Ivory Soap solution, and rinsed three times in deionized water. Films were then dried for 18 h in a vacuum desiccator at 1 mm Hg, over anhydrous $Mg(ClO_4)_2$, and weighed immediately upon removal from the desiccator.

The radiation grafting procedure has been described previously.[14] Briefly, cleaned substrate polymer samples were immersed in a nitrogen-sparged monomer–ethanol–water mixture and irradiated in an ca. 10,000 Ci ^{60}Co radiation source, at ambient temperature. All experiments described in this paper utilized an ethanol–water (90.6:9.4) solvent mixture. After irradiation, the films were washed three times for 30 min in acetone:methanol (1:1)

mixtures, and placed in three changes of deionized water over a 24-h period with agitation. The samples were then weighed wet after blotting to remove surface water, and dried for 24 h in a vacuum desiccator at 1 mm Hg over anhydrous $Mg(ClO_4)_2$. The grafting solutions remained clear and colorless after irradiation, and exhibited relatively low viscosity. The following parameters were calculated for each film:

$$\text{graft level (mg graft/cm}^2) = \frac{W_d - W_i}{A} \times 1000$$

$$\text{water content (\%)} = \frac{W_w - W_d}{W_w - W_i} \times 100$$

where W_w = wet weight of the blotted, grafted polyethylene film (g), W_d = dry weight of the grafted polyethylene film (g), W_i = initial dry weight of the ungrafted polyethylene film (g), and A = the film area (cm^2).

Grafting experiments run on different days exhibited a significant coefficient of variation in the degree of grafting, even though the shape of graft curves was always reproduced. For any continuous curve presented in this paper, all experimental points were obtained from films grafted simultaneously. Where more than one curve is presented in a given plot, all points in the plot were obtained at the same time. Every point reported is the average of at least two determinations.

The surface topography of the grafted films was studied using a JEOL JSM-25 Scanning Electron Microscope. Prior to examination, the grafted hydrogels were dried and sputter-coated with gold and palladium.

RESULTS AND DISCUSSION

The present work is a detailed account of the effect of radiation dose on the grafting process of both monomers, HEMA and EMA, to low density polyethylene. Seven doses were selected, ranging from 0.03 Mrad to 0.50 Mrad. Due to the low total doses involved, it is assumed that negligible graft polymer degradation or crosslinking occurred. Four monomer concentrations were studied: 5%, 10%, 20%, and 30% (Table I).

It is apparent from Figures 1–3 that the kinetics of the grafting process are basically different for the two monomers investigated.

EMA. This monomer shows a kinetic pattern typical of a reaction which becomes monomer diffusion-controlled as the reaction progresses: a rapid rise in graft level during the first stages of the radiation is followed by a plateau (Fig. 1). As one would expect, the greater the monomer concentration, the higher the graft level will be, for any given dose. The absence of an induction period indicates there is no significant inhibitor level or diffusional barrier at the beginning of the grafting process. This can be attributed to favorable partitioning of the relatively hydrophobic monomer into the apolar polyethylene surface from the more polar surrounding aqueous alcohol solution. The simple linear relationship found between the graft level at low doses and the EMA concentration in the solution supports such an explanation (Fig. 4). Further evidence is provided by the fact that

TABLE I
Graft Level and Graft Water Content for EMA- and HEMA-Grafted PE Films[a]

	0.03 Mrad		0.06 Mrad		0.10 Mrad		0.15 Mrad		0.20 Mrad		0.25 Mrad		0.50 Mrad	
	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)
EMA														
5%	—	—	0.11	—	—	—	—	—	—	—	0.44	1.9	0.44	2.3
10%	0.18	—	0.26	—	0.37	—	0.54	10.6	0.65	9.0	0.59	10.0	0.55	10.7
20%	0.41	—	0.59	—	0.83	—	1.05	6.0	1.11	6.2	0.97	7.2	1.08	2.6
30%	0.61	—	1.07	—	1.48	—	1.39	5.6	1.50	6.8	1.40	3.8	1.48	7.4
HEMA														
5%	—	—	0.01	—	0.02	—	—	—	—	—	0.32	13.5	0.47	16.0
10%	0.02	—	0.03	—	0.16	—	0.43	14.7	0.83	13.6	1.35	18.6	1.13	30.1
20%	0.02	—	0.13	—	1.48	15.2	3.18	24.4	4.30	26.5	3.76	27.4	2.34	28.0
30%	0.09	—	1.26	10.2	4.06	20.3	5.60	30.6	4.69	30.9	4.63	32.6	3.13	28.2

[a] Reliable data could not be obtained for very low graft levels and/or water contents.

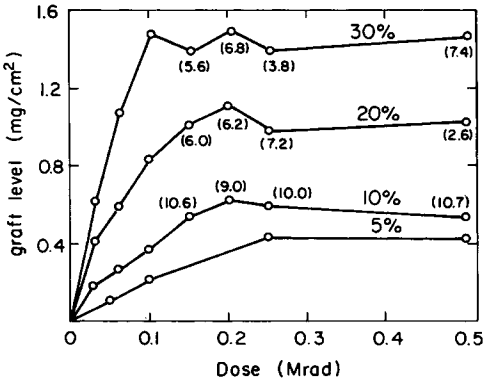


Fig. 1. Effect of radiation dose on the EMA graft level on polyethylene (the numbers in parentheses report the water content).

the initial slope shown by each of the graft level versus dose curves (the slope being directly related to the rate of grafting) is a linear function of EMA concentration.

The behavior observed at higher degrees of grafting can be attributed to the polar nature of the ethanol–water solution which would cause the growing poly(EMA) graft to adopt a closely packed conformation, resulting in tight coiling of the grafted chains. Thus, the diffusion of monomer to the active sites generated on the surface of the substrate is hindered. Moreover, an increase in the termination rate can be readily visualized in such a system. Under these conditions, the local concentration of the growing chains increases and hence termination by mutual interaction of two active ends (which is second order with respect to the concentration of growing chains) would be greatly favored. It should be stressed, however, that, due to lack of mobility, not all growing chains do terminate, and macroradicals of relatively long lifetime can be formed. Such trapped radicals can continue to propagate monomers, provided sufficient time is allowed for the diffusion of the monomer into the graft. The occluded radicals can cause the grafting

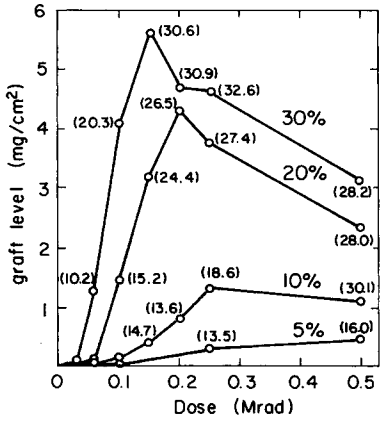


Fig. 2. Effect of radiation dose on the HEMA graft level on polyethylene (the numbers in parentheses report the water content).

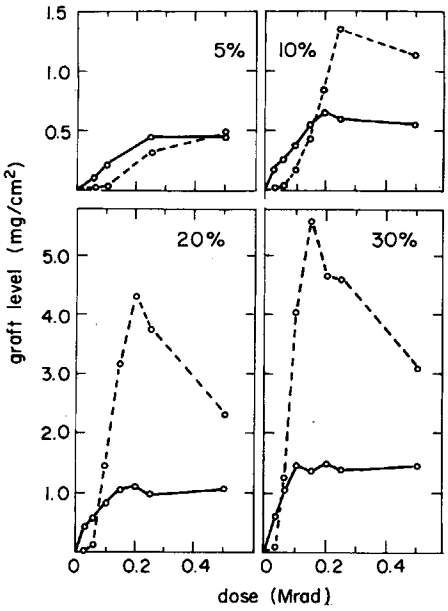


Fig. 3. Effect of radiation dose on EMA (— —) and HEMA (– – –) graft levels on polyethylene.

reaction to continue after removal of the sample from the radiation source. This effect was demonstrated with the following experiment. EMA solutions (10% and 20%) were grafted on polyethylene (0.20 Mrad at ambient temperature), and, while one half of the samples were taken out of the grafting solution and washed upon removal from the source, the second half were stored in the monomer solutions in the dark after removal from the radiation source. After 100 h these samples were washed. The change in the grafted films after long storage in the grafting solution was measured in terms of the relative increase in graft level. For samples stored for 100 h in the 10% EMA solution prior to washing, an average increase of 19% was measured; a 43% increase was exhibited by specimens stored in the 20% grafting solution. These findings clearly indicate the existence of a post-irradiation grafting effect, and support the observations previously described, namely, the existence of radicals trapped in the poly(EMA)–PE graft matrix.

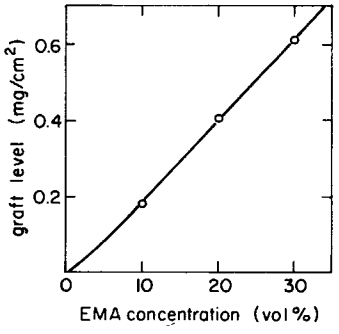


Fig. 4. Effect of EMA concentration on graft level (dose = 0.03 Mrad).

The numbers in brackets along the graft level vs. dose curves (Fig. 1) report the water content of the graft for that particular system. As expected, graft water content remains essentially constant during the radiation period in which the graft level reaches a plateau for any given monomer concentration. Sasaki et al. reported in an earlier study[14] that upon dehydration and subsequent rehydration, the percentage water found in the EMA grafts decreased substantially to almost zero. It was also found[15] that the water content returned to its initial level if the previously dehydrated samples were first exposed to a swelling solvent (e.g., acetone:methanol, 1:1) before reequilibration with water. These findings suggest that the water content for the rather hydrophobic graft is related more to water trapped within small pores in the graft than to true water of hydration. Due to the rather hydrophobic nature of poly(EMA) and the relatively low graft levels produced, no reliable water content data could be obtained for the early stages of the radiation process.

A scanning electron microscopy study of all grafted films was performed. From Figure 5, which shows micrographs of the EMA-grafted polyethylene surface as the extent of grafting increases, it is evident that a distinct surface texture develops as a consequence of the grafting process. The surface of the grafts appear as an array of small, relatively flat "globules," the size of which increases progressively as grafting proceeds and the largest having a diameter of approximately 6–8 μm. These are most likely related to the

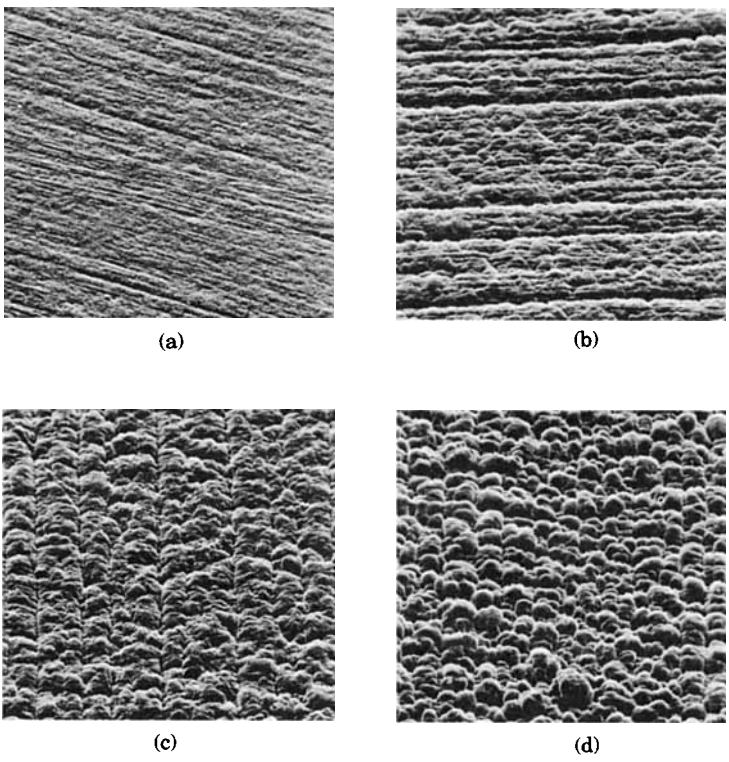


Fig. 5. SEM photographs (1000 × 45° tilt) of EMA grafts on polyethylene as a function of dose (Mrad) (EMA concentration—20%): (a) 0.10; (b) 0.15; (c) 0.20; (d) 0.50.

site of graft initiation, which would occur most frequently in the amorphous as opposed to crystalline surface regions.

HEMA. The rather unusual kinetics exhibited by the HEMA system (Fig. 2) can be characterized by the following elements: first, the existence of an induction period, the length of which is a function of the monomer concentration; second, a rapid rise in graft level to values much greater than those seen for EMA (especially at higher monomer concentrations) where a tendency towards an increasing slope of the grafting curve indicates a slight autoacceleration; third, a maximum followed by a very significant drop in the graft level. The existence of an induction period may be attributed to the unfavorable partitioning of the hydrophilic monomer between the polyethylene surface and the polar aqueous-alcohol solution; it may be also related to the presence of inhibitors in the polymerization system. Due to the higher affinity of the monomer solution for the poly(HEMA), the grafted polymer may be swollen and plasticized by the solvent and monomer molecules. This will enhance the mobility of the growing chains as well as increase the availability of their active sites to monomer molecules. This would also account for the slight upward curvatures of the grafting curves.

The sharp decrease in graft level after the maximum, especially at higher monomer concentrations, can be accounted for by considering that the nongrafted poly(HEMA) and the longer chains grafted onto the polyethylene surface readily dissolve in the solvent system. This could create pockets filled with viscous poly(HEMA) solution, which act as "osmotic cells" due to the lower activity of the monomer and solvent molecules in these regions compared to the bulk. The resulting activity or concentration gradient would accelerate monomer and solvent diffusion into these pockets. This, in turn, would lead to expansion of the osmotic cells which will eventually burst allowing the homopolymer to be washed out of the surface and more efficiently extracted from the bulk of the graft. The end result would be the observed "apparent" decrease in graft level at higher doses. This osmotic cell mechanism was first proposed by Hoffman et al.[16] for styrene grafted on polyethylene. Extraction studies to be presented in a later paper also support a model in which osmotic cells form. Graft polymer degradation is not a reasonable alternative explanation of the decrease in grafting level beyond the maximum, due to the low dose levels involved.

Even though an autoaccelerative behavior is not conclusively demonstrated by the data in Figure 2, it is important to realize that the graft levels measured, especially at the higher values, represent minimum upper limit graft levels since the increase in weight is, to some extent, counterbalanced by an increasingly severe drop in the weight of the grafted system due to the burst phenomena exhibited by the osmotic cells in the growing graft. One must consider, however, in describing such systems, whether a valid indication of the extent of reaction is the weight of the total system (i.e., including filled osmotic cells) or just the weight of the covalently grafted material.

Strong support for this bursting osmotic cell model is provided by the electron micrographs in Figures 6–8. Figure 6 shows the HEMA/polyethylene surface as the extent of grafting increases. It can be seen that large

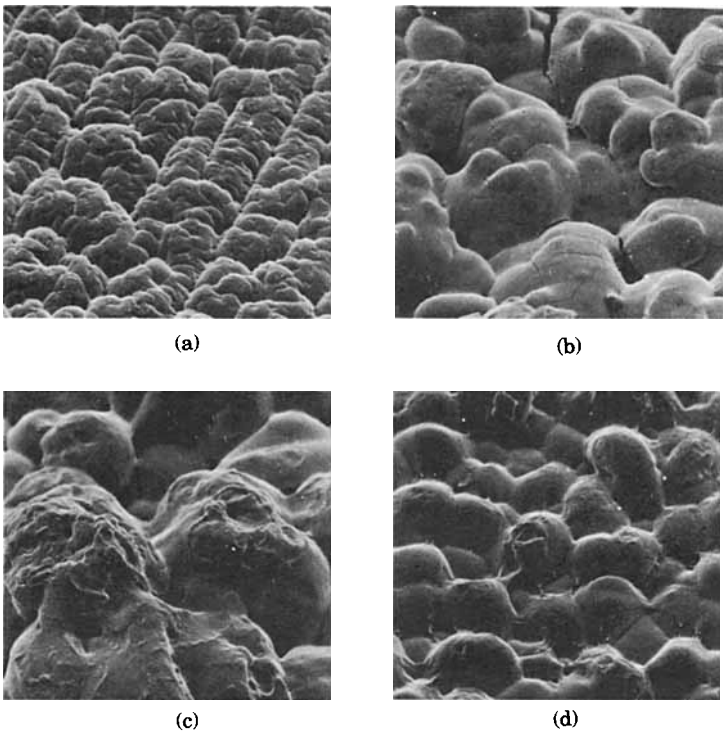


Fig. 6. SEM photographs (1000 ×, 45° tilt) of HEMA grafts on polyethylene as a function of dose (Mrad) (HEMA concentration—20%): (a) 0.10; (b) 0.15; (c) 0.20; (d) 0.50.

"bumps" develop in the surface as grafting proceeds. It is apparent that for the period where the graft level increases with radiation dose, the observed "bumps" gradually became larger. The dimensions of the "globules," in some cases, seem to be larger than 20 μm. The SEM photos show many of the "bumps" or "cells" have burst; a velvetlike appearance is observed for these systems, especially at the maximum graft levels. Figure 7 further illustrates this phenomenon. Stained sections prepared for transmission

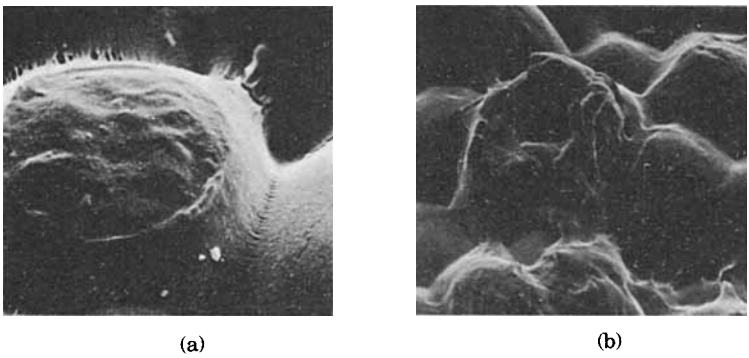
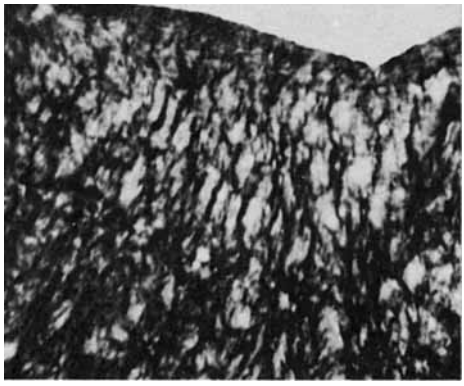
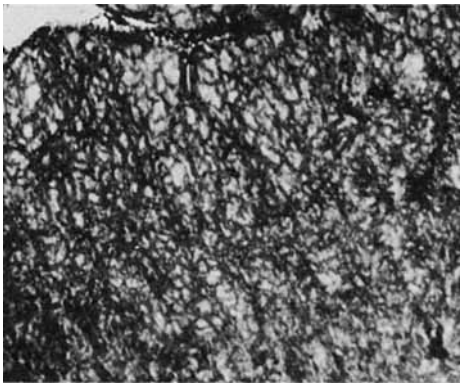


Fig. 7. SEM photographs of HEMA grafts on polyethylene showing burst osmotic cells (HEMA concentration in the monomer solution = 20%): (a) dose = 0.20 Mrad, 4500 ×, 45° tilt; (b) dose = 0.50 Mrad, 2000 ×, 45° tilt.



(a)



(b)

Fig. 8. Electron micrographs (7500 ×) of HEMA/PE graft (1.58 mg/cm²) after reaction of the poly(HEMA) graft with cinnamoyl chloride and then with OsO_4: (a) section perpendicular to surface, cut at −80°C; (b) section cut parallel to surface at room temperature.

electron microscopy reveal a very porous open structure (Fig. 8). The staining technique will be described in detail in a separate paper.[17]

The water content data (Fig. 2) show that, for a given HEMA concentration, the percentage of water in the graft increases with radiation dose until the maximum graft level is reached whereupon water content remains essentially constant. Since the affinity of the monomer for water is a fixed parameter of the system, and since the water content of crosslinked poly(HEMA) is almost independent of crosslink density,[18] the equilibrium water uptake will be determined by the void volume in the graft. These data suggest that the final structure of the grafted network becomes more porous as radiation proceeds. Such porosity is readily explained by the osmotic cell mechanism which has been previously alluded to, and to the voids created once the viscous solution entrapped in the grafted network is extracted out or precipitates in contact with nonsolvent (e.g., H_2O). It is also apparent that, for a given dose, the more concentrated the monomer solution, the higher the water content of the graft will be. This finding too, can be explained in terms of the "osmotic cell" mechanism set forth.

Figure 3 is a combined plot of the data presented in Figures 1 and 2, showing graft level vs. dose curves for both monomers, at the different

concentrations investigated. It is worth noting that EMA systems showed higher grafting rates than their hydrophilic homologs, in the early stages of the process. On the other hand, at longer radiation times, HEMA graft level increased rapidly, while EMA graft level tended to level off.

A preliminary study was conducted to determine whether the observed induction period is a consequence of favorable partitioning or is caused by the presence of inhibitors in the monomer solution. A dose study was performed on a series of polyethylene films which were first pregrafted to a very low level, washed and dried, and then regrafted. The results from the experiments suggested a significantly shortened induction period as evidenced by the substantially higher dose graft levels obtained for the regrafted system. The graft levels of plain polyethylene were, for 0.03 and 0.06 Mrad doses, 0.02 and 0.13 mg/cm^2, whereas the regraft reached 0.33 and 2.54 mg/cm^2 for the same doses, respectively. Therefore, it is concluded that the observed effect is probably due to a more favorable partitioning in the HEMA pregrafted system. In order to further test this swelling hypothesis, the equilibrium swelling level of polyethylene in grafting solutions was measured. As expected, the system containing the more hydrophobic EMA monomer exhibited much higher equilibrium swelling levels. For instance, in absorption experiments performed at room temperature for 160 h, a 20% HEMA solution reached an equilibrium absorption level of 0.13%, whereas the analog EMA solution reached a level of 1.23%. This finding clearly supports the hypothesis that the initial induction period with HEMA vs. the almost linear rate of grafting with EMA is due to the more favorable partitioning into polyethylene of EMA monomer as compared to HEMA monomer. Moreover, it also seems reasonable to assume that the EMA grafting reaction is not totally constrained to the surface of the polyethylene film and that bulk grafting takes place initially.

The effect of temperature (Fig. 9) and monomer concentration (Fig. 10) on grafting were also explored. EMA and HEMA solutions (20%) were grafted onto polyethylene films at temperatures ranging from 0°C to 65°C, and 0.25 Mrad radiation dose. While HEMA graft level gradually increased with temperature, EMA showed a very sharp increase at 65°C, the graft level increasing dramatically from 3.18 mg/cm^2 at 50°C to 19.20 mg/cm^2 at

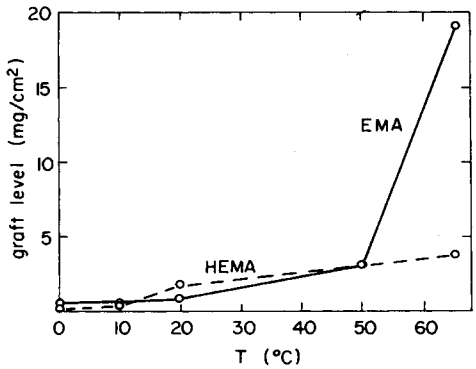


Fig. 9. The effect of temperature on the graft level (dose = 0.25 Mrad; monomer concentration = 20%).

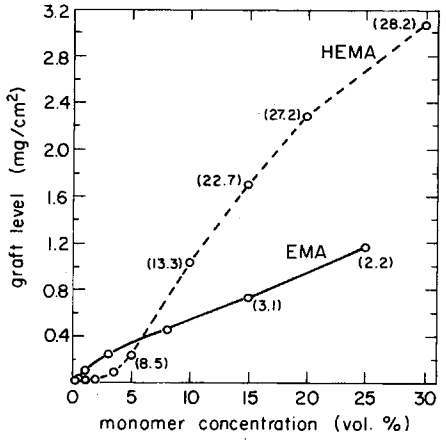


Fig. 10. The effect of monomer concentration on the graft level (dose = 0.25 Mrad; the numbers in parentheses report the water content).

65°C. It is hypothesized that this huge increase in graft level is due to the fact that the glass transition temperature of the grafted system was reached; this would result in a significantly higher diffusion of the monomer into the graft. Preliminary DSC studies support this hypothesis. Although the monomer solution might be expected to plasticize the poly(EMA) reducing its T_g below 50°C, this process can be slow and would be accelerated by the elevated temperature. It is also possible that the accelerated rate of grafting at elevated temperature could be related to differences in the activation energy of polymerization of HEMA and EMA.

Previous experiments[19] have shown the EMA graft to be only lightly crosslinked, where HEMA produced a network with a significantly higher crosslink density. This also supports our findings, since only a slightly crosslinked graft, having a sharp T_g, could show the pronounced temperature dependent grafting behavior exhibited by poly(EMA). Furthermore, since poly(HEMA) graft has been found to be highly crosslinked, a broad T_g range, shifted to higher temperatures, would be obtained; this could explain the absence of a sharp transition in the graft level as a function of temperature in the temperature range investigated.

Graft level vs. monomer concentration curves (Fig. 10) follow, for each monomer, an overall pattern similar to the graft level versus radiation dose curves shown in Figures 1–3. Since varying the initial concentration of the monomer may simultaneously affect the partitioning behavior of the system as well as a number of factors involved in the reaction such as the viscosity of the reacting medium, the extent of the competing homopolymerization reaction, and the length of the grafted chains, an in depth study of this issue is underway. Nevertheless, it is worth noting that the water content in the graft increases with HEMA concentration, this being in full agreement with the data presented in Figure 2, where, for a given dose, larger monomer concentrations result in higher degrees of water uptake.

HEMA/EMA Copolymers. The kinetics of the grafting process at room temperature were also studied for monomer mixtures having HEMA/EMA ratios ranging from 4:1 to 1:4 at total monomer concentrations of 10% and 20% (Table II). Figure 11 presents a plot of the graft level as a function of

TABLE II
Graft Level and Graft Water Content for EMA/HEMA Copolymers Grafted on PE Films

HEMA/EMA ratio	0.03 Mrad		0.06 Mrad		0.10 Mrad		0.15 Mrad		0.20 Mrad		0.25 Mrad		0.50 Mrad	
	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)	Graft level (mg/cm²)	Water content (%)
10% Total monomer concentration														
4:1	0.05	—	0.19	—	0.31	3.4	0.85	5.9	1.15	10.0	1.25	14.2	0.90	33.6
3:2	0.08	—	0.24	—	0.38	5.2	0.80	2.5	1.12	6.8	1.19	7.2	0.96	19.5
2:3	0.11	—	0.26	—	0.39	3.0	0.53	1.0	0.75	3.3	0.74	9.0	0.79	6.7
1:4	0.13	—	0.24	—	0.39	6.6	1.14	2.7	0.68	4.5	0.65	6.1	0.59	7.0
20% Total monomer concentration														
4:1	0.11	—	0.36	7.4	1.12	8.9	2.79	13.6	2.85	20.3	2.27	22.1	1.73	23.6
3:2	0.15	—	0.69	—	1.06	5.1	2.92	6.8	2.23	11.6	2.11	16.4	1.61	18.8
2:3	0.21	—	0.74	—	0.84	—	2.74	4.3	1.46	7.1	1.39	10.3	1.20	10.7
1:4	0.25	—	0.71	4.1	0.81	—	1.81	2.9	0.97	6.0	1.03	5.6	0.99	5.7

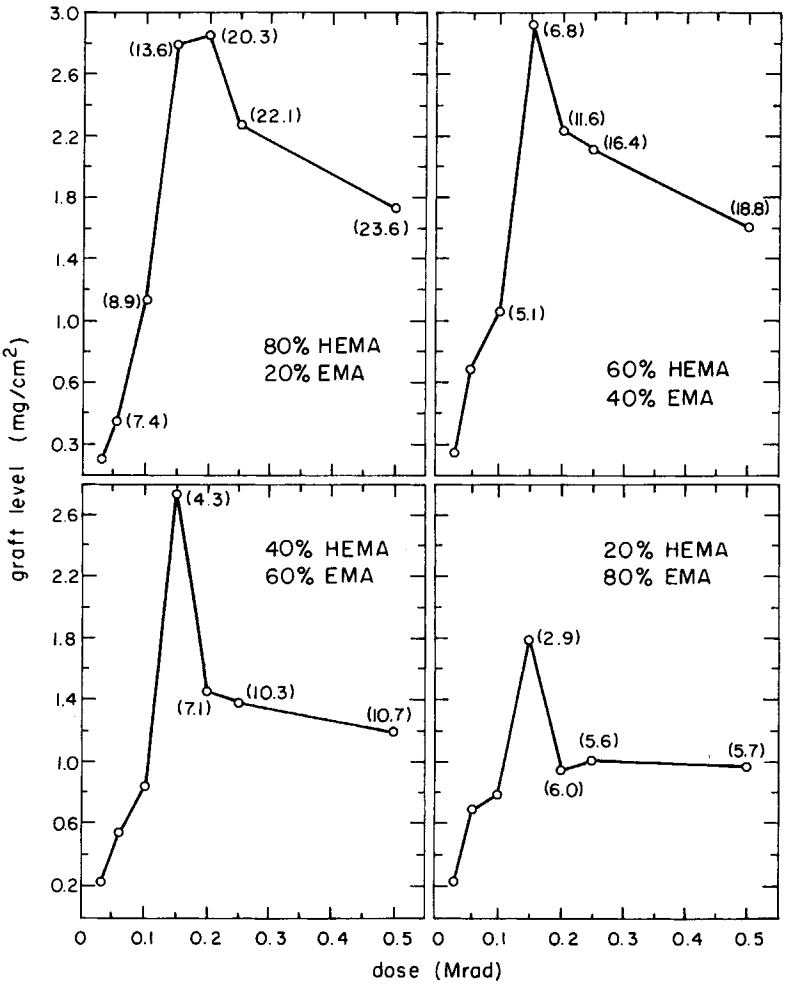


Fig. 11. Effect of radiation dose on EMA/HEMA graft copolymerization on polyethylene (total monomer concentration = 20%).

dose, for the different monomer compositions studied. The water content of these grafts are parameters of interest since they are believed to influence biological interactions with these materials.[20-22] As illustrated in Figure 12, for the highest dose used (0.50 Mrad), the water content of the grafted films is seen to decrease with increasing fractions of EMA in the monomer mixture.

The effects of the monomer ratio on the graft level for different radiation doses is shown in Figure 13. It is apparent from Figure 11 and, even more clearly, from Figure 13, that the grafting reaction is faster in its early stages (at lower doses) for higher percentages of EMA in the grafting solution. Moreover, a linear relationship between the percentage of EMA in the monomer mixture and the graft level at very low doses (0.03 Mrad) was found (Fig. 14). The more favorable partitioning of the relatively hydrophobic EMA into the apolar polymeric substrate from the more polar so-

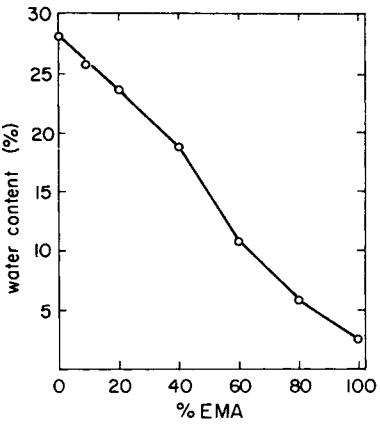


Fig. 12. Effect of monomer composition on the graft water content (dose = 0.50 Mrad; total monomer concentration = 20%).

lution, which will result in a higher local concentration around the active sites created in the polyethylene, can account for this behavior. As grafting proceeds (at higher doses) and partitioning considerations become less determinant, the trend is reversed, and, since HEMA exhibits higher overall grafting rates than EMA, mixtures with the higher HEMA content are those with higher degrees of graft. It is also worth noting that the sharp decrease in graft level after the maximum is larger where the fraction of HEMA in the grafting solution is larger.

A scanning electron microscopy study of all grafted films was performed. Micrographs of two copolymers, 80% HEMA–20% EMA and 20% HEMA–80% EMA, are presented in Figures 15 and 16, respectively, as a function

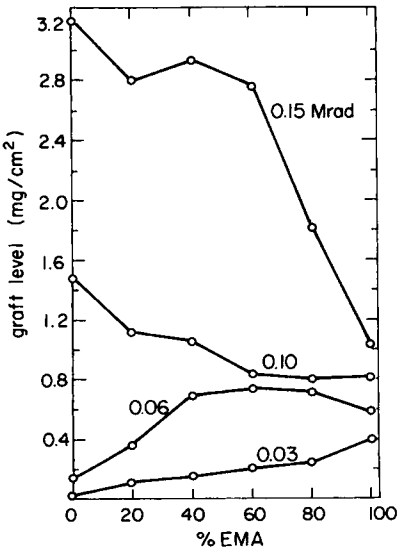


Fig. 13. Effect of monomer composition on EMA/HEMA graft copolymerization on polyethylene (total monomer concentration = 20%).

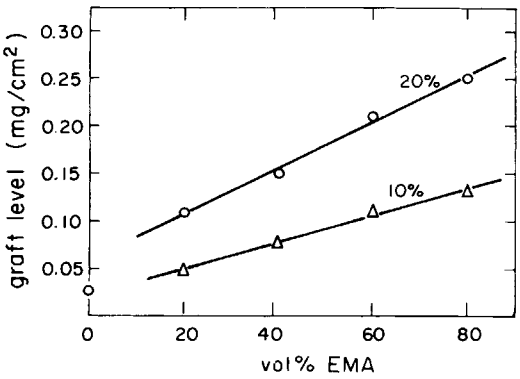


Fig. 14. Effect of monomer composition on graft level (dose = 0.03 Mrad; total monomer concentration: Δ = 10%; O = 20%).

of radiation dose. There is a direct correlation between the clearly different surface topography of the two systems, as shown by the micrographs in Figures 15 and 16, and the significantly different growth pattern they follow, as shown in Figure 11. It is also apparent that the surface roughness is more extreme for the HEMA-rich grafts and becomes more finely textured at higher fractions of EMA.

These results are in full agreement with our previous findings for the homopolymers systems (see above) and clearly show that the two monomers studied have different grafting rates, such that EMA shows a relatively fast reaction at the beginning of the grafting process, and the HEMA graft rate, which starts slowly, increases rapidly as grafting proceeds.

Since our findings strongly suggest a preferential incorporation of one particular monomer at different stages of the grafting process, important questions may be raised relative to the composition of the graft through its depth. This could be important, since the surface of the graft is the most relevant issue in terms of the biointeraction of the grafted system. Furthermore, it can be speculated that the significant difference in grafting rates and in the thermodynamic compatibilities exhibited by both monomers could result in a domain structure for the cograft, consisting of discrete microregions of HEMA and EMA. In order to answer these questions, further studies are underway.

CONCLUSIONS

HEMA and EMA monomer can be readily grafted to polyethylene using the mutual irradiation method. The resulting materials have unique properties compared to the starting polyethylene. Specifically the following conclusions can be drawn about these radiation grafting systems:

(1) The kinetics of the grafting process on low density polyethylene are essentially different for EMA and HEMA:

(i) EMA exhibits a diffusion-controlled kinetic behavior, where an early rise in graft level is followed by a plateau value for the graft level.

(ii) HEMA shows a complex kinetic behavior which is characterized

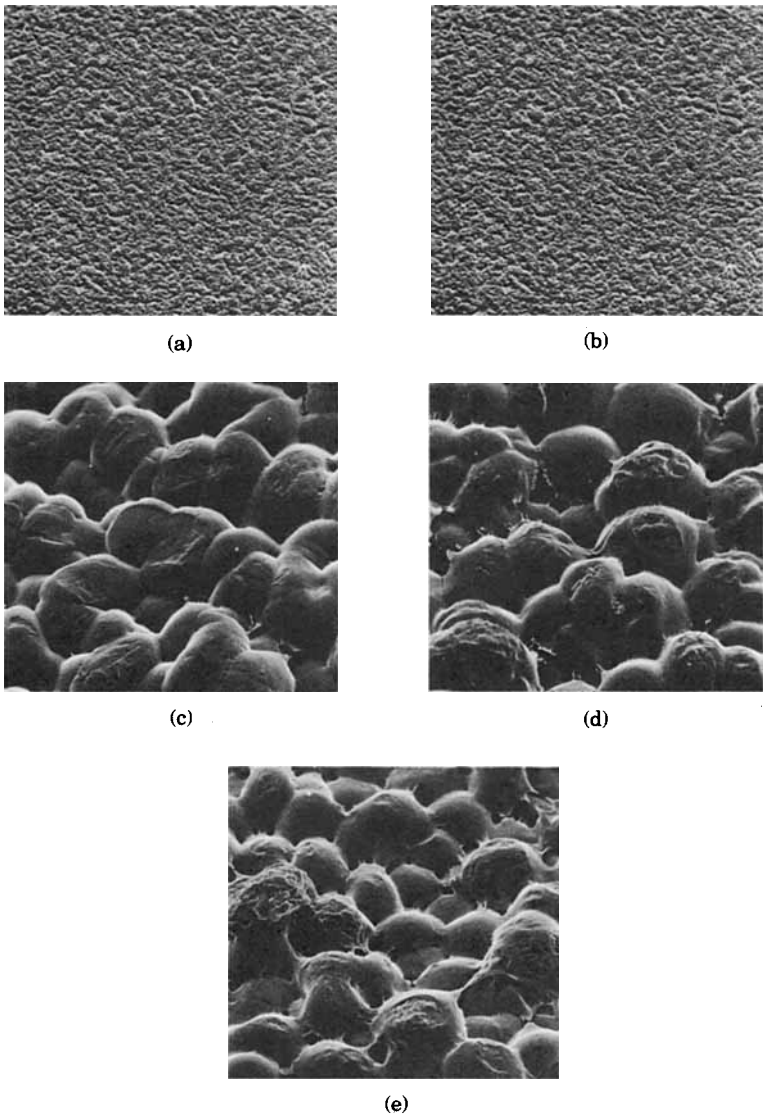


Fig. 15. SEM photographs (1000 ×, 45° tilt) of an 80% HEMA–20% EMA copolymer graft on polyethylene as a function of radiation dose (Mrad) (total monomer concentration = 20%): (a) 0.06; (b) 0.10; (c) 0.15; (d) 0.20; (e) 0.50.

by an induction period, a slight autoacceleration, and a substantial drop in the graft level, after a maximum is reached.

(2) The different degrees of partitioning of both monomers between the apolar polyethylene surface and the polar solvents mixtures is viewed as a factor of primary importance in determining the different kinetic behaviors observed.

(3) It is suggested that, due to the fact that polymerized HEMA chains readily dissolve in the solvent system, "osmotic cells" could be created. It is surmised that preferential diffusion into these pockets, and their eventual

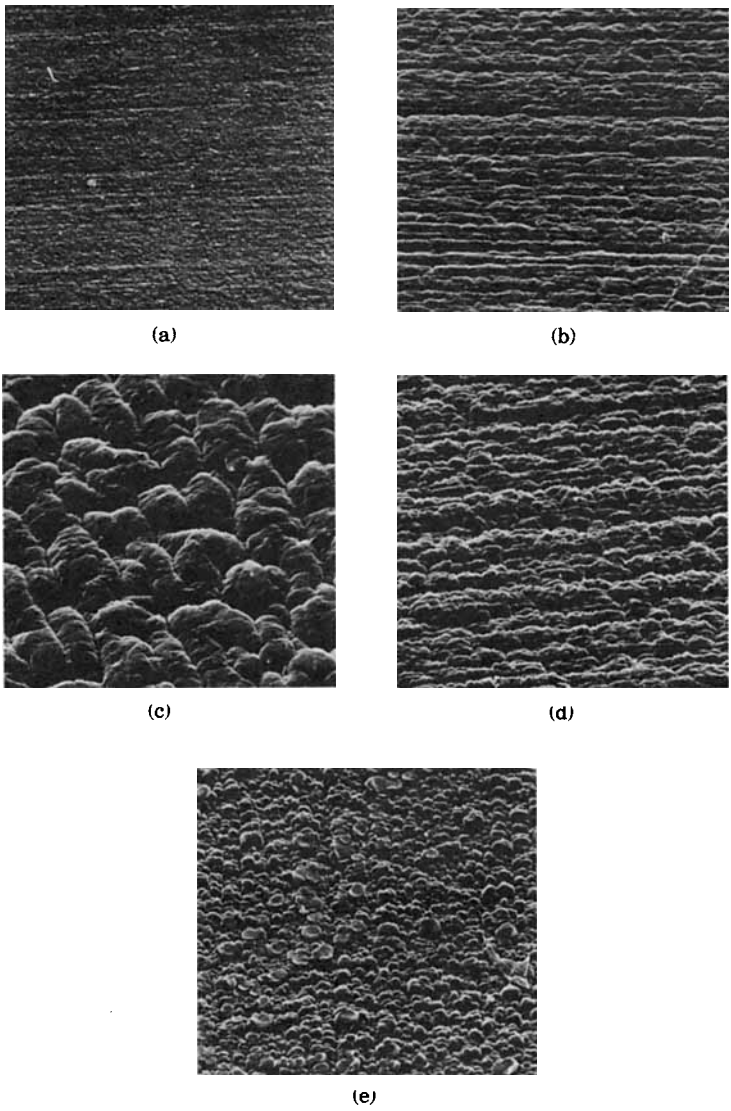


Fig. 16. SEM photographs (1000 × 45° tilt) of a 20% HEMA–80% EMA copolymer graft on polyethylene as a function of radiation dose (Mrad) (total monomer concentration = 20%): (a) 0.06; (b) 0.10; (c) 0.15; (d) 0.20; (e) 0.50.

bursting, could account for the significant drop in graft level, seen at higher doses.

(4) The water uptake of the HEMA grafts increases with radiation dose, up to a maximum water content of approximately 30%.

(5) A distinct surface texture is developed in the grafted systems, and this roughness is more extreme for HEMA grafts and becomes finer at higher fractions of EMA.

(6) Since the two monomers studied have inversly different grafting rates, important questions relative to variations in the composition of the graft as the reaction proceeds can be raised.

(7) The HEMA/EMA graft copolymer system has been found to be a useful model for studying biological interactions and has been extensively studied in this regard.[12,23,24]

A number of interesting questions concerning the structure of these radiation grafts and the mechanism of their formation have been raised in this work. These questions will be specifically addressed in manuscripts now in preparation on the HEMA/EMA graft system where the questions of extraction, graft morphology, graft microstructure, and HEMA/EMA copolymerization behavior will be addressed.

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