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Analysis of Polymer Surfaces by SIMS. 16. Investigation of Surface Cross-Linking in Polymer Gels of 2-Hydroxyethyl Methacrylate

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ABSTRACT: A series of poly(2-hydroxyethyl methacrylate) gels cross-linked with different concentrations of ethylene glycol dimethacrylate were examined by static secondary ion mass spectrometry (SIMS). Changes in the peak intensities of atomic versus molecular secondary ions were observed in negative ion SIMS as a function of cross-linker concentration. These changes in the distribution of secondary ions as a function of cross-linker concentration, and thus as a function of molecular weight between cross-links, are discussed with respect to the factors affecting secondary ion emission during the SIMS process. The sensitivity of static SIMS to the concentration of cross-links in the polymer chains on the surface of the polymer, demonstrated by this study, may advance the study of technologically relevant surface modifications involving surface cross-linking.

Introduction

Static secondary ion mass spectrometry (SIMS) has proven to be a valuable technique for the characterization of polymer surfaces. This is due to its surface sensitivity (outermost 20 Å),[1] its analytical sensitivity,[2,3] and the direct relationship between surface structure and the SIMS fragmentation pattern.[4,5] Static SIMS has been used to study different polymeric systems including homopolymers,[6–12] random copolymers,[13–15] block copolymers,[16,17] and polymer blends.[18] This study is part of an ongoing effort to systematically delineate the analytical potential of static SIMS for organic surface analysis (see refs 1, 7, 8, and 19–27 for a complete description of this research endeavor). Consistent with this overall goal, this study aims to answer the following questions: can surface cross-linking in a polymeric system be identified by static SIMS; furthermore, can spectroscopic parameters be defined that quantify the degree of cross-linking for this system, and finally, can these results be generalized to other polymer systems of interest?

Our interest in surface cross-linking stems from the technological importance of thin polymer films and surface-modified polymers.[28] In general, such surface modifications are created by wet chemical methods,[29–39] corona discharge treatment,[40–44] plasma treatment,[45,46] plasma deposition,[47,48] or radiation grafting.[49] These processes typically induce many chemical changes simultaneously. Circumstantial evidence from various studies suggests that in many instances one of the reactions that occurs is cross-linking of the surface.[50,51] There are a number of methods to measure the bulk or average degree of cross-linking in polymers. However, the lack of appropriate experimental techniques to evaluate the degree of surface cross-linking for these systems prevents an assessment of the role of cross-linking in the interfacial properties of these systems. For example, plasma treatment is frequently utilized as an adhesion promoter for polymer films.[42,52,53] While it is likely that plasma-treated polymers are cross-linked at the surface, the influence of cross-linking on the interfacial adhesion of the polymer surface remains unknown.

Core-level X-ray photoelectron spectroscopy (XPS), which to date has been the primary polymer surface analysis technique,[54] is relatively insensitive to the structural changes accompanying surface cross-linking, particularly when the process of cross-linking does not result in the introduction of chemically-distinct moieties. Static SIMS, on the other hand, is far more sensitive than XPS to polymer structure and is thus potentially of interest as a probe of surface cross-linking in polymers. While a large number of studies of model polymeric systems have provided a basis for the semiquantitative investigation of the complex organic surfaces created by surface modification procedures, the utility of static SIMS to assess the degree of surface cross-linking for surface-modified polymers has not been established, due in large part to the lack of studies on model systems.

Previous studies in our laboratories have influenced here both the choice of experimental technique and the model system used to investigate surface cross-linking. In previous studies, we observed a marked dependence of the absolute ion yields in negative static SIMS from plasma-deposited thin films created from 2-hydroxyethyl methacrylate (HEMA) as a function of deposition conditions.[60,61] Comparison of XPS results with the negative SIMS results for these films revealed that the absolute ion yields in negative SIMS were directly related to the degree of retention of precursor structure in the films; plasma-deposited films which showed a high degree of retention of precursor structure displayed absolute ion yields which were comparable to those from conventionally-polymerized HEMA, whereas plasma-deposited films with poor retention of precursor structure had much lower absolute ion yields. This effect was not observed in positive SIMS. Since loss of precursor structure and increased cross-linking in plasma-deposited films are likely to be related, we hypothesized that the absolute ion yields from these films is directly related to the cross-link density; increasing cross-link density decreases the absolute ion yields.

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Table I. XPS Results for the EGDMA-Cross-Linked Poly(HEMA) Gels

sample	vol of EGDMA (mL)	molar ratio EGDMA:HEMA (X)	wt % methanol in swollen gel	$\bar{M}_c$[a]
1	0.05	3.34×10^{-3}	59.4	868
2	0.1	6.68×10^{-3}	56.1	697
3	0.2	1.34×10^{-2}	51.3	524
4	0.4	2.67×10^{-2}	46.1	394
5	1.0	6.68×10^{-2}	36.2	247
6	2.0	2.01×10^{-1}	29.1	186
7	4.0	2.67×10^{-1}	29.7	190

[a] Number-average molecular weight between cross-links.

These studies suggested that poly(HEMA) cross-linked with ethylene glycol dimethacrylate (EGDMA) would be an appropriate model system to study surface cross-linking. Several other factors also influenced our choice of model system: first, the chemistry of EGDMA-cross-linked poly(HEMA) is well characterized, specifically with reference to its cross-linking mechanism.[55] Second, a theoretical framework based on the analysis of Flory and Rehner[56] has been developed[57,58] which allows the degree of cross-linking to be independently assessed by the equilibrium swelling of the polymer in an appropriate solvent. Third, the un-cross-linked polymer, i.e., poly(HEMA), and the cross-linking agent (EGDMA) are structurally similar. There are two reasons why we were specifically interested in studying a chemically cross-linked polymer where the cross-linking agent is structurally similar to the polymer itself. First, chemical speciation arising from dissimilarities in the chemical structure of cross-linker and polymer cannot be used to probe the surface cross-linking in such systems. These systems are in contrast to cross-linked polymers where the introduction of a unique elemental or molecular species in the cross-linking process provides a method to characterize the introduced cross-links. For example, disulfide bridges in vulcanized rubber allow the degree of cross-linking to be easily established by XPS or SIMS.[59] Second, we believe that the former situation more closely parallels the cross-linking that occurs during surface modification of polymers. The EGDMA-cross-linked poly(HEMA) gels may thus provide a suitable model system to clarify the ability to static SIMS to interrogate the surface cross-linking that occurs in other technologically-relevant surface modifications.

Experimental Section

Synthesis of Gels. 2-Hydroxyethyl methacrylate (HEMA) (99%, Aldrich Chemical Co., Milwaukee, WI) was simultaneously polymerized and cross-linked in solution with ethylene glycol dimethacrylate (EGDMA) (Scientific Polymer Products, Ontario, NY).[62] Typically, 10 mL of HEMA was mixed with 2 mL of deionized/reverse-osmosis-purified water, 3 mL of ethylene glycol (Mallinckrodt), and varying amounts of EGDMA (see Table I for molar ratio (X) of EGDMA:HEMA). To this mixture were added 1 mL each of a 400 mg/mL $(NH_4)_2S_2O_8$ and 150 mg/mL $Na_2S_2O_5$ solution in deionized/reverse-osmosis-purified water as initiators for the polymerization. The mixture was poured onto a glass plate primed with a thin glycerol film cast from ethanol solution. The mixture was then covered with another glass plate similarly primed with glycerol, which was separated from the bottom glass plate by stainless steel shims along the edges (cleaned by ultrasonication in reagent grade acetone and methanol). The polymerization and cross-linking were allowed to proceed overnight at ambient temperature. The cross-linked polymer film was extracted of low molecular weight material in doubly-distilled water over a 24-h period.

Swelling Measurements. The cross-linked polymer films (~0.5-mm thickness) were soaked in reagent grade methanol for 1 week. During this time, the solvent was changed every day.

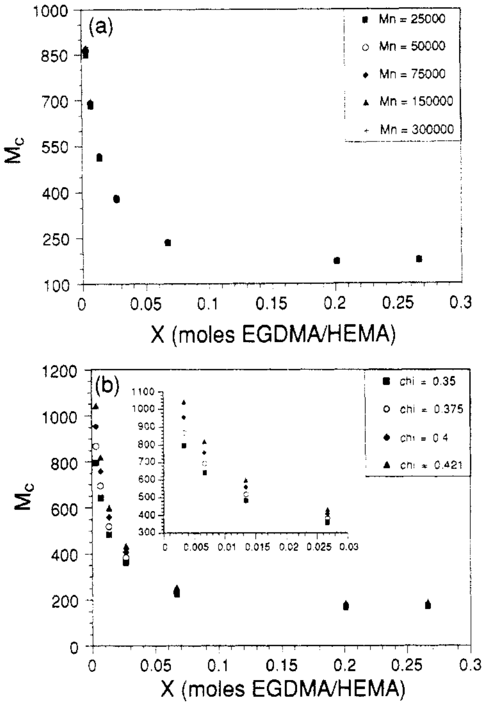


Figure 1. (a) $\bar{M}_c$ versus X: the effect of varying $\bar{M}_n$ at constant χ ($\chi = 0.375$). (b) $\bar{M}_c$ versus X: the effect of varying χ at constant $\bar{M}_n$ ($\bar{M}_n$ = 75000).

Polymer disks (12-mm diameter) were then punched out, the excess solvent was removed by swabbing gently with a #150 Whatman filter paper, and the swollen polymer disks were weighed to an accuracy of within 10^{-3} g to determine the wet weight. The polymers were then dried under vacuum for a week after which they were weighed to determine their dry weight. The molecular weight between cross-links for the gels was calculated by the method of Peppas et al.[58] as shown below:

$$\frac{1}{M_c} = \frac{2}{M_n} - \frac{(\bar{\nu}/V_1)[\ln(1-\nu_{2,s}) + \nu_{2,s} + \chi\nu_{2,s}{}^2]\left[1 - \frac{1}{N}\nu_{2,s}{}^{2/3}\right]^3}{\nu_{2,r}\left[\left(\frac{\nu_{2,s}}{\nu_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{\nu_{2,s}}{\nu_{2,r}}\right)\right]\left[1 + \frac{1}{N}\left(\frac{\nu_{2,s}}{\nu_{2,r}}\right)^{1/3}\right]^2}$$

where $\bar{M}_c$ is the number-average molecular weight between cross-links, $\bar{M}_n$ is the number-average molecular weight of un-cross-linked polymer, $\bar{\nu}$ is the specific volume of un-cross-linked polymer, V_1 is the molar volume of solvent, $\nu_{2,s}$ is the polymer volume fraction of cross-linked gel after equilibrium swelling, $\nu_{2,r}$ is the polymer volume fraction of gel after cross-linking but before swelling (relaxed volume fraction), χ is the Flory polymer–solvent interaction parameter, $N = 2\bar{M}_c/\bar{M}_r$, and $\bar{M}_r$ is the molecular weight of polymer repeat unit. The above equation is valid for the equilibrium swelling of highly cross-linked, moderately swollen, polymer gels and is not constrained to a Gaussian chain length distribution between cross-links, a situation that describes the structure and equilibrium swelling behavior of these highly cross-linked poly(HEMA) gels. The following assumptions were made in the calculation of the polymer–solvent interaction parameter (χ): the calculation of χ requires an estimate of the coil expansion factor (α) and the molecular weight of the un-cross-linked polymer.[63] Since cross-linking and polymerization were carried out simultaneously, the value of $\bar{M}_n$ was not known *a priori*. Different values of χ were calculated assuming weight-average polymer molecular weights ranging from 4.7×10^4 to 5.12×10^5. We assumed these values of polymer molecular weights in the calculation of χ since values of α corresponding to these polymer molecular weights were available from Fort and Polyzoidis.[64] The value of χ in their calculations ranged from 0.37 to 0.461. We examined the variation in $\bar{M}_c$ as a function of varying χ and $\bar{M}_n$ (Figure 1). The values of χ and $\bar{M}_n$ used to calculate $\bar{M}_c$ in Figure 1 are consistent with those reported by Fort and Polyzoidis.[64] We observe that $\bar{M}_c$ does not show a strong dependence on $\bar{M}_n$ (Figure 1a) for χ = 0.375. This result is in accord with the observation of Peppas et al. that the calculated value of $\bar{M}_c$ is independent of $\bar{M}_n$ if a value of $\bar{M}_n \geq 75000$ is used;[58] in fact, we observe no significant effect of varying $\bar{M}_n$ on the calculated values of $\bar{M}_c$, even for $\bar{M}_n$ values as low as 25000. Figure 1b shows the effects of varying χ on $\bar{M}_c$ for $\bar{M}_n = 75000$ and clearly reveals that $\bar{M}_c$ is far more sensitive to χ than $\bar{M}_n$, particularly for the lightly cross-linked gels at the highest value of χ used in these calculations ($\chi = 0.461$). In view of these results, we used $\bar{M}_n = 75000$ and the average value of $\chi = 0.375$ in our final calculations in $\bar{M}_c$. Since the conclusions drawn in this study do not depend upon precise values of $\bar{M}_c$, these assumptions in the calculation of $\bar{M}_c$ are, we believe, justified.

Trifluoroacetic Anhydride Derivatization. Trifluoroacetic anhydride (TFAA) was acquired from Aldrich Chemical Co. Polymer gels were derivatized with TFAA vapor under ambient conditions for 15 min. Details of the experimental protocol and results for other hydroxyl-functionalized polymers have appeared previously.[15,48,65]

X-ray Photoelectron Spectroscopy. The gels were analyzed by XPS to verify their composition and purity. XPS analyses were performed on an S-Probe spectrometer (Surface Science Instruments, Mountain View, CA), which includes a monochromatized Al Kα X-ray source, a hemispherical analyzer, and a position-sensitive detector. All polymers were analyzed at a 35° take-off angle. The take-off angle is defined as the angle between the sample plane and the axis of the analyzer. Survey scans (0-1000 eV) were run at 150-eV analyzer pass energy and 1000-μm X-ray spot size to determine the elemental composition of each polymer. The experimental peak areas were numerically integrated and normalized to account for the number of scans, the number of channels per electronvolt, the Scofield photoionization cross section,[66] and the sampling depth. The S-Probe transmission function for a pass energy of 150 eV was assumed to be constant over the appropriate range of photoelectron kinetic energies.[67] The sampling depth was assumed to vary as $KE^{0.7}$, where KE is the kinetic energy of the photoelectrons.[67]

High-resolution C_{1s} spectra were obtained at a pass energy of 25 eV. The C_{1s} spectra were resolved into individual Gaussian peaks using a least squares fitting program. A combination of a low-energy electron flood gun, set at 5 eV, and a metal screen placed on the sample holder was used to minimize sample charging. All polymer binding energies (BEs) were referenced by setting the CH_x peak maximum in the resolved C_{1s} spectra to 285.0 eV.

Static Secondary Ion Mass Spectrometry. Quadrupole-based static SIMS analysis was performed on an XPS/SIMS instrument based on the ESCALAB Mk 1 UHV system (VG Scientific). Both the instrumentation and procedures for charge neutralization have been fully described elsewhere.[19] Xe^+ ions of 4 keV energy from a slightly defocused source (spot size $\sim$50 μm) were rastered over a 6 mm × 6 mm area with an average current density of $\leq$1 nA cm^{-2}. Total ion dose during spectral optimization and acquisition was $\leq 3 \times 10^{12}$ ions cm^{-2} for positive ion spectra (obtained first) and $\leq 5 \times 10^{12}$ ions cm^{-2} for negative ion spectra (obtained second using the same sample). Thus, the total ion dose for each sample analyzed was within the damage limit appropriate for static SIMS.[68] All positive ion spectra were optimized on the m/z 59 peak, while negative ion spectra were optimized on the m/z 85 peak. Charge neutralization was achieved by an electron beam with an accelerating potential of 700 V which covered an area of $\sim$1 cm^2. No evidence of electron-stimulated secondary ion emission was observed when the primary ion beam was switched off while irradiating the samples with the electron beam.

Results and Discussion

XPS. Figure 2a shows the XPS-measured O/C ratios for the EGDMA-cross-linked poly(HEMA) gels plotted versus the cross-linker to monomer bulk molar ratio (X = moles of EGDMA:moles of HEMA). The calculated values assuming stoichiometric incorporation of cross-linker and monomer are also reported in the figure. Since the stoichiometric O/C ratio of EGDMA is lower than that of HEMA, for high X, the stoichiometric O/C ratio decreases by $\sim$10%. This decrease in the stoichiometric O/C ratio is well within the analytical sensitivity of XPS. However, we note two problems in the XPS discrimination of polymer gels with different levels of cross-linking. First, high cross-linker concentrations are rarely used in polymer gel formulations, owing to the poor structural properties of the polymer gel. Second, in general, the XPS-determined O/C ratio increases with increasing X, whereas the calculated O/C ratio (assuming stoichiometric incorporation of EGDMA and HEMA in the cross-linked polymers) decreases with increasing X; this point is not evident for $X = 3.34 \times 10^{-3}$ given the magnitude of the error in the XPS-measured O:C for this sample.

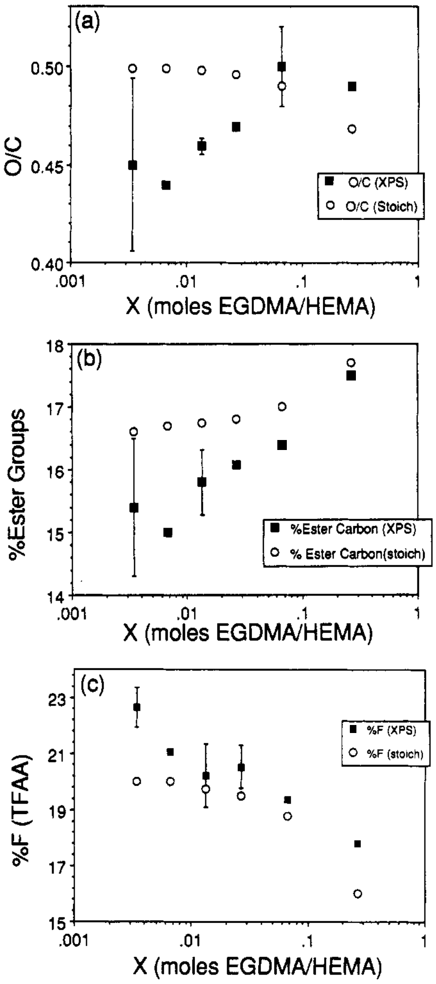
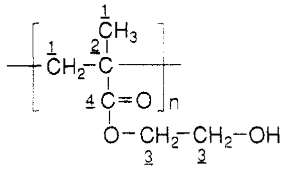


Figure 2. (a) XPS-measured O/C ratios for the EGDMA-cross-linked poly(HEMA) gels plotted versus X (filled squares). (b) Least squares curve fitting results of the high-resolution C_{1s} photoelectron spectra of the cross-linked poly(HEMA) gels. The percent area of the ester group in the resolved C_{1s} spectra plotted versus X is shown by the filled squares. (c) XPS-measured percent fluorine for the cross-linked poly(HEMA) gels derivatized with TFAA vapor plotted versus X (filled squares). The calculated values in all three parts of the figure are shown by the open circles and assume in (a) and (b) complete and stoichiometric incorporation of EGDMA and HEMA in the cross-linked polymer; additionally, in (c) that reaction of TFAA with the hydroxyl groups in the cross-linked polymers is stoichiometric and complete.

The possible orientation of oxygen-containing moieties in the gels may explain this trend. One of the processing steps involves swelling the cross-linked gels in methanol before cutting into disks for analysis. The polymer disks are then dried under vacuum before further spectroscopic analysis. The swelling process may orient the polymer chains such that the hydroxyl-functionalized side chain is preferentially oriented outward. Upon drying under vacuum, the polymer gels that are lightly cross-linked reorient to present the alkyl backbone to the vacuum. The polymer chains of the gels prepared at higher cross-linker concentration, however, are less mobile and may not effectively restructure upon drying. Their polymer chains may thus preferentially retain a hydrophilic orientation under vacuum. The ability of the highly cross-linked gels to restructure upon swelling but not upon drying may by influenced by steric effects, namely, the increased intermolecular volume available to the polymer molecules in the swollen state. An alternative explanation for the increase in XPS-determined oxygen concentration as a function of cross-linker concentration may be due to increased retention of absorbed water and/or methanol for the highly cross-linked gels, a possibility suggested by the 1–2 orders of magnitude pressure rise upon introduction of the gels into the spectrometer.

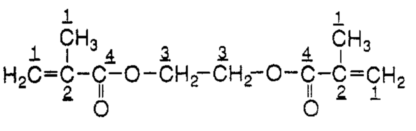
The C_{1s} photoelectron spectrum often allows carbon atoms in different bonding environments to be distinguished on the basis of their binding energy (BE) shifts. The C_{1s} spectra were curve fit with four peaks; the structure of poly(HEMA) and the various carbon species are labeled below.

Poly(HEMA)



A four-peak fit distinguishes between carbon atoms labeled 1 (primary carbon atoms referenced to 285.0 eV) and the β-shifted carbon atom 2, whose C_{1s} BE has been shown to be 0.8 eV higher than that of the primary carbon by high-resolution XPS of poly(methyl methacrylate)[69] and its gas-phase analogs.[70] EGDMA, which has the structure shown below, would be expected on the basis of its molecular structure to have C_{1s} peak area ratios for species 1, 2, 3, and 4 of 2:1:1:1, which are different from the peak area ratios of the equivalent carbon species for poly(HEMA) (2:1:2:1).

EGDMA



Note that cross-linking occurs across the double bond in EGDMA, leading to a CH_2 species labeled 1, the BE of which is expected to be indistinguishable from that of the primary carbon atoms (also labeled 1) in poly(HEMA). In principle, then, the EGDMA-cross-linked poly(HEMA) gels should be distinguished from each other on the basis of the different concentration of carbon atoms in the polymer and cross-linker. The concentration of the ester carbon atoms relative to the hydrocarbon species, determined by least squares fitting of the XPS C_{1s} spectral envelope, are shown in Figure 2b. The XPS-determined concentration of the ester carbon species follows the stoichiometric values for the polymer gels. However, the XPS-determined values are, in all cases, lower than the stoichiometric values. This may be caused by incomplete consumption of EGDMA during polymerization and cross-linking of the polymer gels.

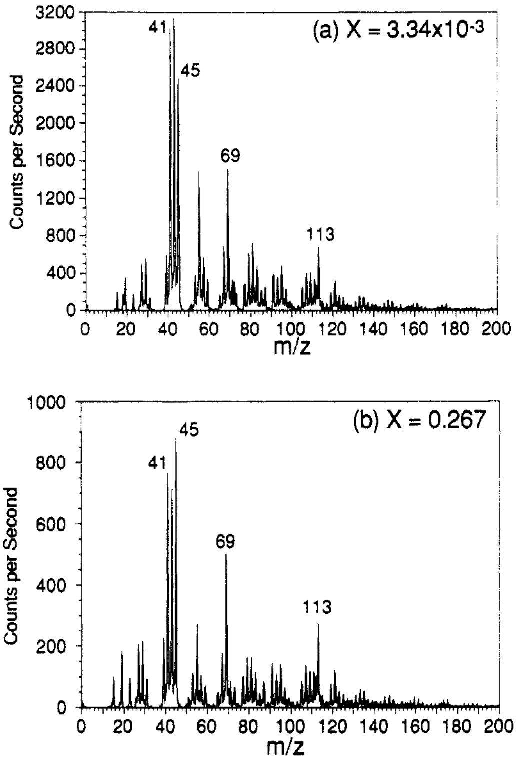
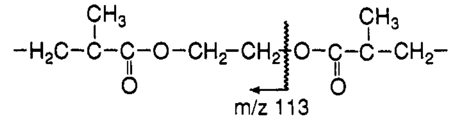


Figure 3. Positive static SIMS (m/z 0–200) of EGDMA-cross-linked, poly(HEMA) gels: (a) $X = 3.34 \times 10^{-3}$; (b) $X = 0.267$.

Derivatization with TFAA vapor has been shown to be a precise and sensitive label for surface hydroxyl species.[15,48,65,71] Derivatization with TFAA results in the conversion of the hydroxyl groups present in the poly(HEMA) component of the gel to a trifluoro ester species. The percent fluorine incorporation for the polymer gels after derivatization with TFAA is shown in Figure 2c. While the decrease in the fluorine incorporation as a function of EGDMA concentration parallels that predicted from gel stoichiometry, excess F is observed in all cases. There are two likely explanations for this observation: first, the polymer gels retain some fraction of the solvent, either methanol or water, used in their swelling measurements. Derivatization of the hydroxyl groups in the solvent and retention of the derivatized product would result in excess fluorine reported by XPS compared to that predicted by the stoichiometry of the polymer gels. The second possibility is related to the assumption of polymer gel stoichiometry. We note that the assumption that the gel surface composition is stoichiometric may be untenable, based on the relative concentration of ester species measured by XPS. Less than stoichiometric incorporation of EGDMA, suggested by XPS, would result in excess fluorine reported by XPS.

In summary, the XPS results clearly show that the deviation in the XPS results for the gels are small, *i.e.*, ≤10% from stoichiometric composition. They are, however, significant in terms of the analytical accuracy and sensitivity of XPS. The incorporation of EGDMA appears to be less than stoichiometric, suggested by direct XPS of the gels and corroborated by derivatization–XPS. We conclude that discrimination between gels by XPS is complicated by their inherently slight compositional differences, exacerbated by less than stoichiometric incorporation of cross-linker, possible orientation effects in the polymers, and the effects of absorbed solvent that may be retained even in the ultrahigh vacuum of the spectrometer. We note that the compositional changes measured by XPS are much smaller than the structural changes that accompany cross-linking. The effects of cross-linking on bulk polymer structure are dramatic even at low crosslinker concentration, as illustrated by the equilibrium swelling results in Table I (percent methanol incorporation in swollen gels).

Static SIMS. Positive Ions. The positive ion spectra of a lightly cross-linked gel ($X = 3.34 \times 10^{-4}$) is shown in Figure 3a; that of a highly cross-linked gel ($X = 0.267$) is shown in Figure 3b. The positive ion spectra of methacrylate homopolymers have been systematically investigated previously.[6-8] These studies allow the secondary ions in the SIMS fragmentation patterns of methacrylate polymers to be identified with some confidence. Comparison of the positive ion spectrum of poly(HEMA)[8] with that of the EGDMA-cross-linked poly(HEMA) gels reveals the spectra to be qualitatively similar. Peaks unique to EGDMA are not observed in the spectrum of the cross-linked polymers as compared to poly(HEMA). Comparing the chemical structure of EGDMA with that of poly(HEMA), that is not surprising. Poly(HEMA) can be distinguished from other methacrylate polymers based on peaks at $m/z = 41$ (C_2HO^+) and $m/z = 113$ ($[M-OH]^+$), both of which are more intense in the positive ion spectra of hydroxyl-functionalized methacrylate homopolymers.[8] For the cross-linked polymer gels, the peaks at m/z 41 and m/z 113 have similar intensities compared to poly(HEMA),[8] even at high cross-linker ratios. This suggests that these ions can be created from pure cross-linker; cleavage of EGDMA as shown below could account for the m/z 113 ion from the EGDMA component of the cross-linked gel.



$$-H_2C-\overset{CH_3}{\overset{|}{C}}-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2\wr O-\underset{\underset{O}{\|}}{C}-\overset{CH_3}{\overset{|}{C}}-CH_2-$$

m/z 113

While the spectra in Figure 3 are qualitatively similar, it appears that there are variations in peak relative intensities between samples with high and low cross-link densities, particularly for the m/z 69 ion. However, as has been illustrated elsewhere,[72] such effects can easily be caused by very small changes in surface potential in quadrupole SIMS. A first test for systematic peak intensity variation is to normalize the peak intensity of interest to that of the total ion yield ($\sum I$). This is done in Figure 4a for the m/z 69 peak of all the samples, from which it is clear that there is no systematic variation in the $m/z\ 69/\sum I$ ratio. Note, however, the marked changes in $\sum I$ across the sample set (Figure 4b). Nearly half of the data points represent measurements made on repeat samples, and inspection of individual points shows the variation in $\sum I$ to be random. For polymer films attached to a metal stub using double-sided sticky tape, changes in the system capacitance due to variations in interfacial contact make it virtually impossible to reproduce absolute intensities, when control of surface potential depends on variation of the bias applied to the metal stub. Normalization of the peak intensity to total ion yield allows this problem to be largely circumvented, and its use allows the analytical significance of the variation in intensity of a particular peak to be assessed across a sample set. For the m/z 69 ion, we see that the $m/z\ 69/\sum I$ ratio is essentially constant, suggesting that the variation in its intensity across the gel series is not significant. However, as demonstrated elsewhere in this study, systematic variations in the peak intensity of a secondary ion normalized to total ion yield ($m/\sum I$) can be analytically significant.

Negative Ion Spectra. The negative ion spectra of a lightly cross-linked poly(HEMA) gel ($X = 3.34 \times 10^{-4}$) is shown in Figure 5a; that of a highly cross-linked poly(HEMA) gel ($X = 0.267$) is shown in Figure 5b. Two salient facts emerge upon examination of the spectra. First, the same peaks are observed in the negative ion spectra of the cross-linked poly(HEMA) gels as in the un-cross-linked polymer, i.e., poly(HEMA).[7,37] Prominent molecular secondary anions are observed at m/z = 59, 85, 127, and 139 for the cross-linked gels. For poly(HEMA), these ions have been rationalized on the basis of the repeat unit structure of the polymer.[8]

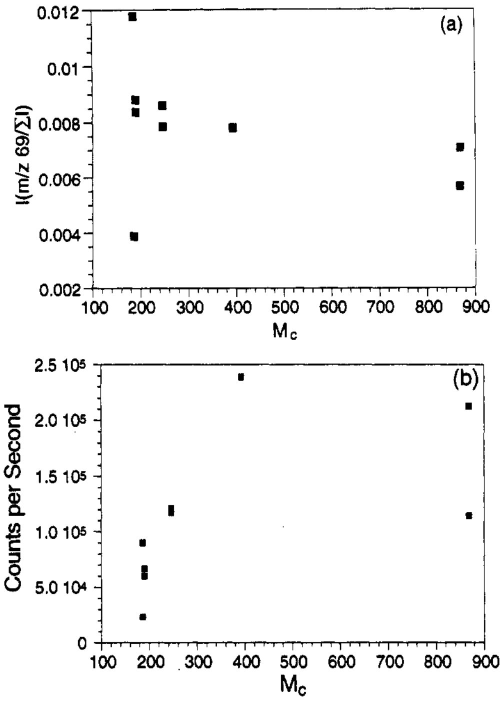


Figure 4. (a) Peak intensity of m/z 69 in positive ion spectra of EGDMA-cross-linked poly(HEMA) gels normalized to absolute ion yield ($m/z\ 69/\sum I$) plotted versus $\bar{M}_c$. (b) Summed peak intensities of positive ions, m/z 0–200, plotted versus $\bar{M}_c$.

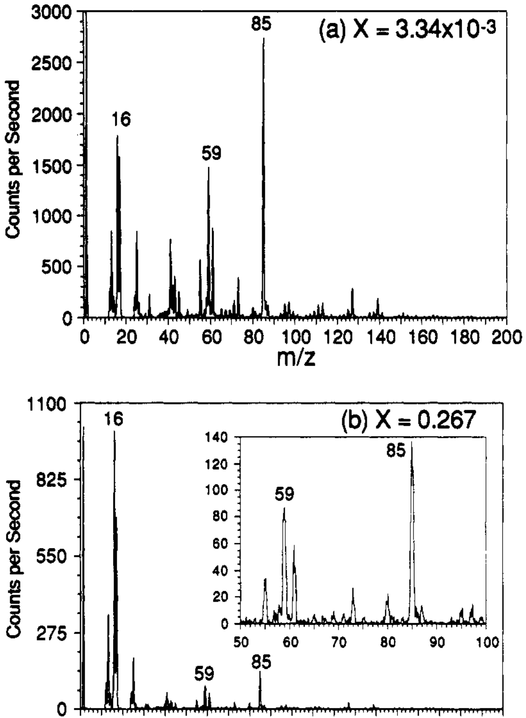
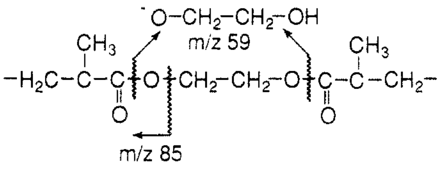


Figure 5. Negative static SIMS (m/z 0–200) of EGDMA-cross-linked poly(HEMA) gels: (a) $X = 3.34 \times 10^{-3}$; (b) $X = 0.267$.

We note that the m/z 85 ion is characteristic of all methacrylate polymers.[6,8] It is thus likely that it is not created solely from the poly(HEMA) component of the polymer gel. In particular, bond scission adjacent to the ether carbon in backbone ester polymers is responsible for the dominant molecular anions in their negative ion spectra[12] and can be invoked to account for the *m/z* 85 ion from the EGDMA component of the cross-linked poly(HEMA) gel as shown below:



The *m/z* 59 ion for poly(HEMA) has been shown to be created by loss of H_2 from the hydroxyethanolate ion (*m/z* 61).[38] Creation of this ion from the EGDMA component of the cross-linked gel would require the bond scission shown above, along with hydrogen transfer from the methyl substituent.

The second observation of interest that emerges upon comparing the spectra in Figure 5 is that the absolute intensities of molecular secondary ions in the negative ion spectrum of the heavily cross-linked poly(HEMA) gel (Figure 5b) are substantially diminished compared to those of the lightly cross-linked poly(HEMA) gel (Figure 5a). The intensities of the *m/z* 59 and *m/z* 85 peaks relative to the total ion intensity ($\sum I$) plotted versus $\bar{M}_c$ are shown in Figure 6a. Two intriguing observations are apparent in this and related figures (Figure 6b,c). First, the relative intensity of the molecular ions (i.e., *m/z* 59 and *m/z* 85) dramatically decreases with decreasing $\bar{M}_c$ (Figure 6a). Conversely, the peak intensity of *m/z* 16 (O^-) normalized to $\sum I$ increases threefold over the same range (Figure 6b). The net effect of the depression in the yield of molecular secondary anions (*m/z* 59 and *m/z* 85) compared to that of atomic secondary ions such as *m/z* 16 (O^-) is shown in Figure 6c. The peak intensity of the *m/z* 85 anion normalized to the *m/z* 16 peak intensity drops by approximately 1 order of magnitude as $\bar{M}_c$ decreases from ~400 to ~200. These results are in accord with the results of a previous study of plasma-deposited HEMA; large decreases in total negative molecular ion yield from the plasma-deposited films were noted when reaction conditions expected to produce high cross-link densities were used.[60] On the other hand, and analogously to the results in this study, much less variation in the intensity of molecular ions in positive SIMS as a function of cross-linking density was noted.

Three factors need to be considered in an explanation of this intriguing experimental observation. Conceptually, these factors may be classified in terms of three broadly defined variables: the effect of surface compositional changes across the polymer gel series and its effect on the formation of the secondary ions of interest (i.e., *m/z* = 16, 59, and 85); the effects on ion formation probabilities of other (i.e., not related to compositional) properties of the polymer gels; and the detection efficiency of these ions due to their energy distribution in the quadrupole mass spectrometer.

The first variable addresses the effect of surface composition on the yield of secondary ions of interest, independent of their ion formation probabilities. We note that the surface oxygen concentration changes by less than 10% across the entire series of gels. A number of previous studies have shown that secondary ion yields have an almost linear relationship with the surface concentration of species capable of producing these ions.[7,14,15,38] This applies to both atomic and molecular secondary ions. Thus, the order of magnitude change in the relative peak intensities of the molecular ions with respect to atomic secondary ions in the present case cannot, we believe, be rationalized on the basis of the slight compositional variation in these gels.

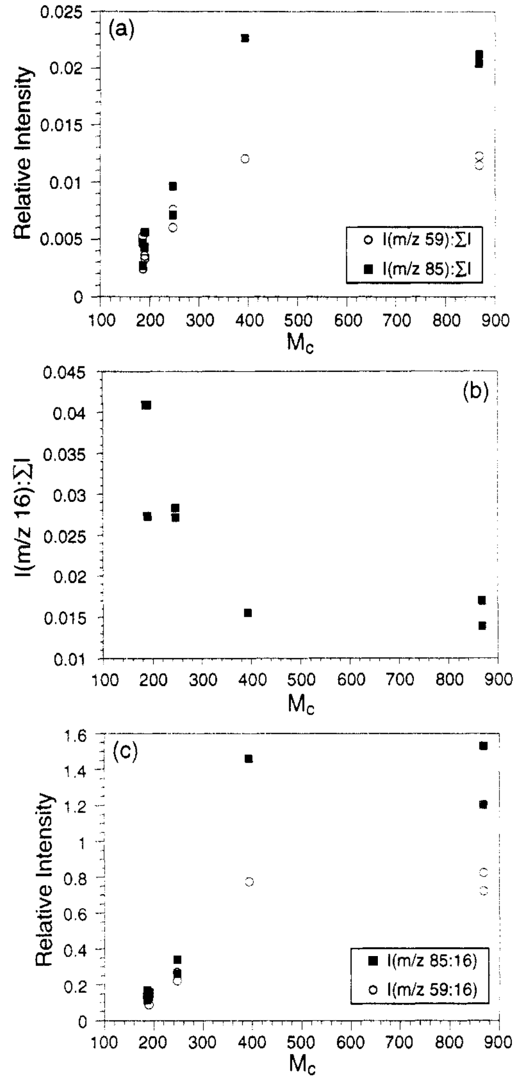


Figure 6. Relative intensities of secondary ions in the negative static SIMS of the EGDMA-cross-linked poly(HEMA) gels plotted versus $\bar{M}_c$: (a) peak intensities of *m/z* 59 and *m/z* 85 normalized to total secondary ion yield ($\sum I$); (b) peak intensity of *m/z* 16 normalized to $\sum I$; (c) relative intensities of *m/z* 59 and *m/z* 85 normalized to the peak intensity of *m/z* 16 (O^-).

A key structural property that varies across this system is cross-link density. We believe that the steep drop in the peak intensities of the molecular secondary ions and the increase in the peak intensity of the atomic secondary ions as a function of $\bar{M}_c$ are related to structural effects in the polymer system under study: specifically, the presence of surface cross-links. We postulate that the increased bonding of polymer chains that accompanies chemical cross-linking is implicated in the dramatic changes observed in the yields of the secondary anions of interest. However, this effect could arise from either changes in ion formation probabilities of the secondary ions of interest or changes in their detection efficiency as a function of cross-linking.

Surface cross-linking could account for the variation in the intensities of negative secondary ions by altering the relative ion formation probabilities of the atomic and molecular secondary anions. We hypothesize that the increased bonding between polymer chains that accompanies cross-linking decreases the formation probability of molecular ions relative to atomic ions. This is consistent with the soft emission nature of molecular secondary ions in static SIMS, wherein it is believed that molecular ions are created at the end of the collision cascade initiated by the incoming primary particle.[73] Atomic secondary ions, can, however, be created by other mechanisms such as direct emission processes,[74-76] which we suspect are insensitive to the interchain bonding in the cross-linked polymers.

Fowler et al. have demonstrated[77] by time-of-flight SIMS (TOF-SIMS) studies of a perfluorinated polyether homopolymer that the intensity of "interior fragments" containing a number of monomer units (i.e., fragments not involving either end group) increases with $\bar{M}_n$. This is in accord with simple statistical arguments assuming that only two bonds are broken to liberate the interior fragments and two end groups (although such arguments cannot be justified within the context of our present understanding of secondary ion formation processes). For instance, the normalized intensity of an ion containing six repeat units was shown to increase linearly across a series from $\bar{M}_n$ = 9.0 to 43.3 (monomer units). Interruptions to the polymer chain, such as cross-links, would effectively introduce new end groups and reduce the probability that a given "interior fragment" could be formed. We note that $\bar{M}_c$ = 868 corresponds to 6.6 repeat units of poly(HEMA) while $\bar{M}_c$ = 190 corresponds to <2 repeat units. The molecular ions whose yields are sensitive to $\bar{M}_c$ (m/z 59 and m/z 85) are smaller than the interior fragments corresponding to these values of $\bar{M}_c$. However, accumulating evidence from triple quadrupole SIMS studies suggests that many smaller fragments result from decomposition of larger fragments by stepwise processes.[78] Therefore, the intensity of these smaller fragments will carry the "memory" of larger units. In view of the above, the behavior of the m/z 59 and m/z 85 secondary anions is consistent with the results of Fowler et al.

Increased cross-linking leads to an increase in the O^- yield. Though this result is consistent with the increase in the XPS-measured O/C ratio for these polymers with increased cross-linking, we note that the variation in oxygen concentration measured by XPS is not significant enough by itself to account for the much larger variation in the O^- yield. We have shown previously that the O^-/CH^- peak intensity ratio correlates linearly with the XPS-measured O/C ratio but that the slope of this plot is different for different oxygen-containing moieties.[12] These results indicate that the O^- yield can vary with chemical composition at constant oxygen concentration. As cross-linking increases, the concentration of alcohol groups in the gel decreases, resulting in a change in the functional group distribution. The increase in oxygen concentration with increasing cross-link density combined with changes in the distribution of functional groups for the polymer gels provides an additional reason for the increase in the relative yield of O^- with increasing cross-linking.

The third, and complementary, possibility is related to the detection efficiency of the secondary ions. Throughout these experiments, the energy filter setting of the quadrupole mass spectrometer remained unchanged. The spectral intensity for each sample in negative SIMS was optimized by adjusting the target bias only so as to maximize the m/z 85 signal on a rate meter. In fact, very little variation in this parameter was necessary provided the sample mounting was consistent, which suggests that the m/z 85 anion, at least, suffered little change in energy distribution maximum. This does not rule out a change in the shape of the energy distribution, which could lead to a change in detected signal. The O^- signal, on the other hand, is much broader and has a different maximum, so that only a small fraction of the O^- ions are detected. Again, changes in the energy distribution of this ion resulting from increased cross-linking could lead to a change in the detected signal. Such a possibility could be checked by direct measurement of the secondary ion energy distributions and also by TOF-SIMS studies, where the much wider energy window (several hundred electrovolts for a TOF-SIMS spectrometer compared to several electrovolts for a quadrupole mass spectrometer) would almost eliminate energy distribution effects.

Conclusions

The results from this study suggest that static SIMS fragmentation patterns of polymers, particularly in the negative ion mode, are sensitive to the degree of cross-linking. This suggestion is based upon consistent and corroborative evidence from swelling measurements, XPS studies, derivatization experiments, and static SIMS spectra. The results from this study are also consistent with static SIMS observations made on rf plasma-deposited poly(HEMA) thin films.[60,61] This is the first study in the literature to systematically illustrate that cross-linking might be probed by static SIMS. Also, this may be the only method that can practically interrogate the cross-linking in the outermost 15–20 Å in situations where the cross-linking group is chemically similar to the main polymer chain. However, many questions remain. The generality of the phenomena observed here will be explored in planned experiments with well-characterized cross-linked poly(dimethylsiloxanes) and dextrans. Also, the argument might be made that molecular mobility rather than cross-linking is being measured. This will be investigated in chemical systems where chemistry is not varied, but mobility is systematically perturbed by temperature and packing effects. Studies with isotopically labeled cross-linking groups can provide new insights into the fragmentation mechanisms. Finally, the importance of the energy distribution of the secondary ions will be explored by directly comparing quadrupole and TOF-SIMS results.

The influence of surface cross-linking and surface mobility on adhesion and biological interaction has often been suggested.[79-82] However, these aspects of surface structure have largely been intractable to analysis. The possibility that static SIMS might offer heretofore unrealized insights into the cross-linking or mobility of the surfaces of complex materials is attractive and provides the impetus for future studies of this type.

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