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Segment Length Distributions from Thick Polymer Films: ToF-SIMS of Polymer Surface Structure

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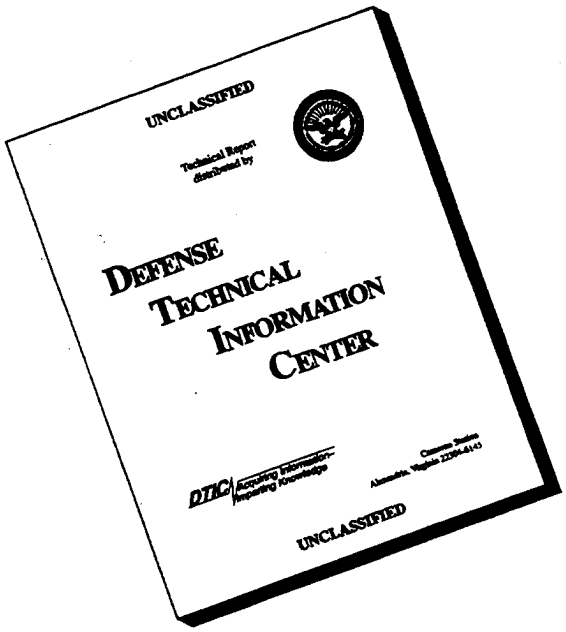

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Over the past fifteen years, the use of ESCA and infrared techniques have made great strides in relating the differences between polymer surface composition and structure and the bulk composition and structure. Much has been learned about the role of synthetic structural design and the role of processing variations and the resulting surface structure and composition of polymers. Yet, a quantitative description of segment length distribution at the surface of a multicomponent polymer remains elusive. Since, fundamentally, polymers involve a distribution of chain lengths which yield the particular properties, it would be desirable to know whether, at the surface, the distribution of segment or chain lengths is different than in the bulk. Therefore, like composition, the surface structure can lead to properties different than that predicted by the simple knowledge of the bulk structure, in this case representing the segment length distribution.

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Segment Length Distributions from Thick Polymer Films: ToF-SIMS of Polymer Surface Structure

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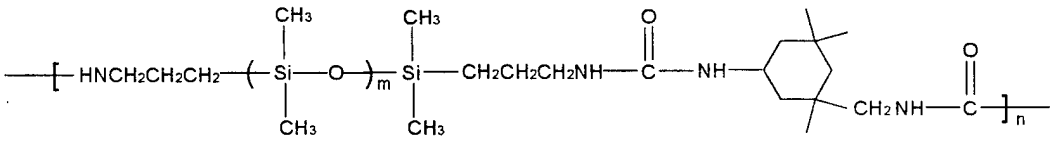
Over the past fifteen years, the use of ESCA and infrared techniques have made great strides in relating the differences between polymer surface composition and structure and the bulk composition and structure. Much has been learned about the role of synthetic structural design and the role of processing variations and the resulting surface structure and composition of polymers. Yet, a quantitative description of segment length distribution at the surface of a multicomponent polymer remains elusive. Since, fundamentally, polymers involve a distribution of chain lengths which yield the particular properties, it would be desirable to know whether, at the surface, the distribution of segment or chain lengths is different than in the bulk. Therefore, like composition, the surface structure can lead to properties different than that predicted by the simple knowledge of the bulk structure, in this case representing the segment length distribution.

The present work will report results from the surface chemistry of a new class of poly dimethyl siloxane-urethane segmented copolymers [1], having the following molecular structure.

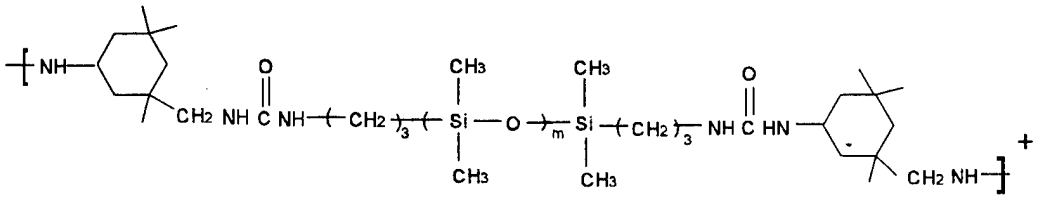


The ESCA analysis of the surface chemistry of these materials has been reported in the earlier work [2]. The ToF-SIMS results yielded some important fundamental new information.

We first analyzed, as references, submonolayer preparations of the difunctional prepolymer PDMS, using silver as a substrate. In Figure 1(a), the

spectrum of PDMS (MW=1000) on Ag, four repeating ion series are detected, the last is a Ag cationized oligmer. The latter series yields the molecular weight distribution, as shown in Figure 2(a).

Normally, the analysis of polymer films which are thick, and therefore representative of coatings involves sufficient chain entanglement and intrachain interactions so as to mediate against high mass ions being generated [3]. In this case, however, the volatility of the siloxane segment makes it a prime candidate for generation of fragment ions from the surface, despite solid state effects. We successfully measured such high mass distributions from two different copolymers, where the segment length distribution of the siloxanes was varied by using different PDMS prepolymers [1]. In particular, polymers with average PDMS molecular weights of 1000 and 2400 were subjected to analysis, in the form of a solvent cast thick (ca. 50 um) films. High mass ToF-SIMS results are shown in Figures 1(b) and (c). These ions were assigned to the structure series given below, with masses ranging from 1156 to 2118 Dalton.



The resulting PDMS segment length distribution can be obtained because these fragments contain the intact DMS block. Figures 2(a), (b) and (c) shows a comparison of the MW distribution obtained from the PDMS oligomer (MW=1000) to the segment length distributions obtained from analysis of data in Figures 1(b) and (c). It is evident that the change in molecular weight of the DMS does not change the distribution of PDMS segment lengths at the surface of the material. This means that the surface of the polymer synthesized with nominal molecular weight 2400 should not have different properties expected from the longer PDMS segments.

References:

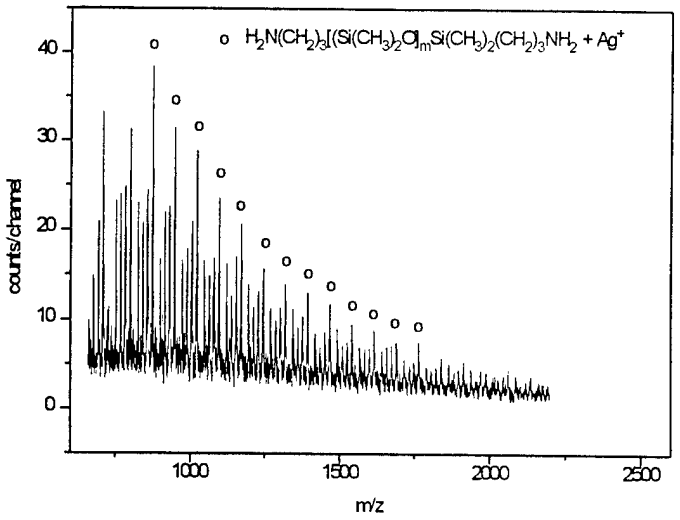
[1] T. Ho, K. J. Wynne and R. A. Nissan, Macromolecules, **1993,** 26, 7029-7036.

[2] X. Chen, J. A. Gardella, Jr. T. Ho and K. J. Wynne, Macromolecules, **1995**, 28, 1635-1642.

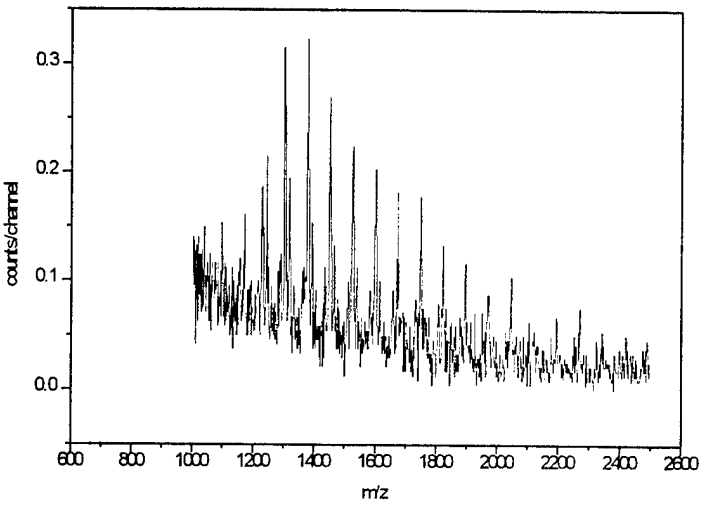
[3] I. V. Bletsos, D. M. Hercules, J. H. Magil, D. van Leyen, E. Niehuis and A. Benninghoven, Anal. Chem. **1988**, 60, 938.

Figure 1

(a) ToF-SIMS spectrum for the submonolayer film of PDMS 1000 on Ag.



(b) ToF-SIMS spectrum for the thick film of PU-DMS No.1 on Al in the range of 1000-2500 m/z.



(c) ToF-SIMS spectrum for the thick film of PU-DMS No.3 on Al in the range of 900-2500 m/z.

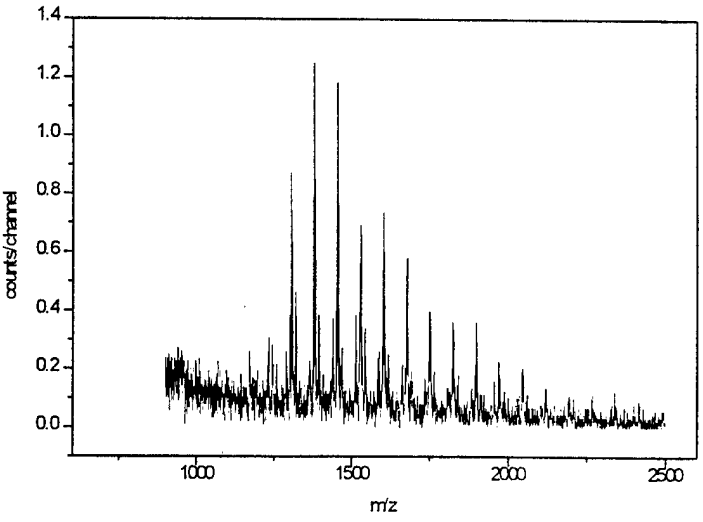
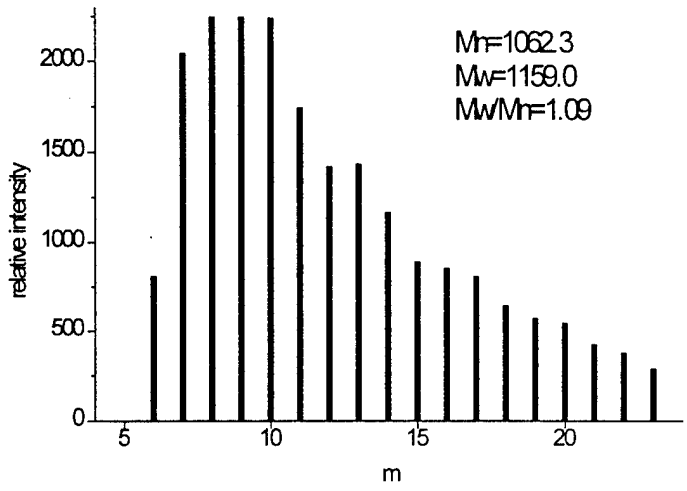
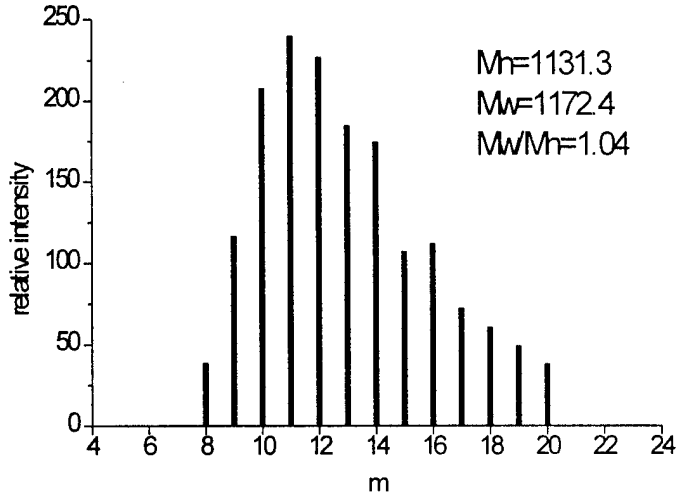


Figure 2

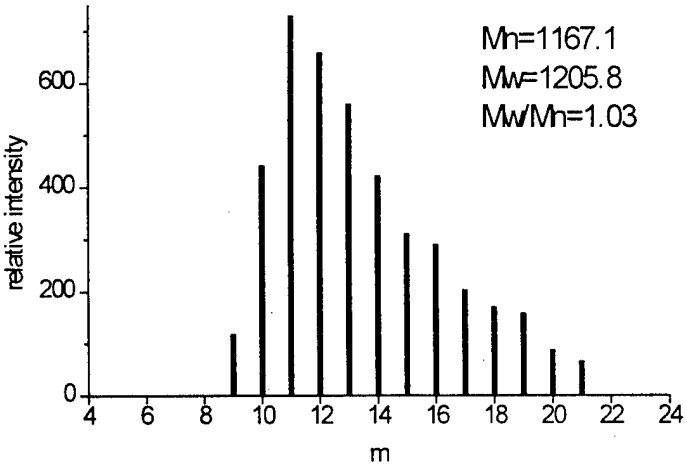
(a) Molecular weight distribution of PDMS 1000 (submonolayer film on Ag).



(b) Molecular weight distribution of PDMS segments segregated at the surface of the thick film of PU-DMS No.1.



(c) Molecular weight distribution of PDMS segments segregated at the surface of the thick film of PU-DMS No.3.



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