Surface spectroscopic studies of polymer surfaces and interfaces:
2. Poly(tetramethyl-*P*-silphenylenesiloxane/poly(dimethylsiloxane) block copolymers

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The surface region of a series of poly(tetramethyl-*p*-silphenylenesiloxane)/poly(dimethylsiloxane) block copolymers was investigated using X-ray photoelectron spectroscopy and attenuated total reflectance Fourier transform infra-red spectroscopy. Analysis of the results shows the surface region to be equivalent to the bulk composition for all but one sample. This indicates that for all but the most crystalline samples the surface region comprises a relatively thick layer of non-crystalline amorphous domains.

(Keywords: e.s.c.a.; surface analysis; block copolymer; crystallinity)

INTRODUCTION

Characterization of structure–property relationships in polymeric materials is a necessary step in the development of property specificity in polymers. This requires a knowledge of the bulk properties of the polymer, as well as the surface properties, which often differ considerably from that of the bulk. Block copolymers of tetramethyl-*p*-silphenylenesiloxane (TMpS) and dimethylsiloxane (DMS) make an interesting system for this study since their structures can be changed morphologically (by their degrees of crystallinity) as well as chemically (by the ratio of the individual components). The structure and morphology of poly(TMpS) as a function of crystallinity has been extensively studied by Magill and coworkers[1-4] using a wide combination of techniques in order to establish a model for the sample structure. Results from differential scanning calorimetry and X-ray diffraction were employed to determine the degree of crystallinity as a function of sample preparation. Solution-grown single crystal mats showed the highest degree of crystallinity, followed by melt-cast and solution-cast samples. Hydrofluoric (HF) acid etching was used to ascertain that the crystalline regions were separated by less ordered regions, consistent with a lamellar texture.

Considerable controversy still surrounds the morphological structure for crystalline polymers, especially in the case of crystalline polyethylene[5]. For this reason surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS or e.s.c.a.) complemented by attenuated total reflectance (ATR) Fourier transform infra-red spectroscopy were used to investigate poly(TMpS)[6]. The results of this investigation showed the surfaces of single crystal mats were considerably less disordered than the melt-crystallized samples or polymer crystallized from relatively concentrated solutions where the textures were spherulitic.

Block copolymers of DMS and TMpS exhibit large changes in degree of crystallinity with composition. The melting temperature and the glass transition temperature also change substantially with changes in composition expressed as a wt% of DMS[7]. Magill and coworkers[1-3] also studied this system extensively so as to develop a morphological model that was reasonably consistent with the mechanical properties.

The model (*Figure 1*) consists of crystalline regions of TMpS interdispersed within disordered or amorphous regions of DMS and TMpS. This model is supported by chemical degradation studies, where the more vulnerable disordered amorphous regions were rapidly removed, leaving behind a crystalline core of well ordered TMpS. The degree of crystallinity was determined by X-ray[3] and thermal methods[4], which showed all the copolymer samples reached the same degree of crystallinity after etching, regardless of the concentration of DMS in the starting material. These results are consistent with the

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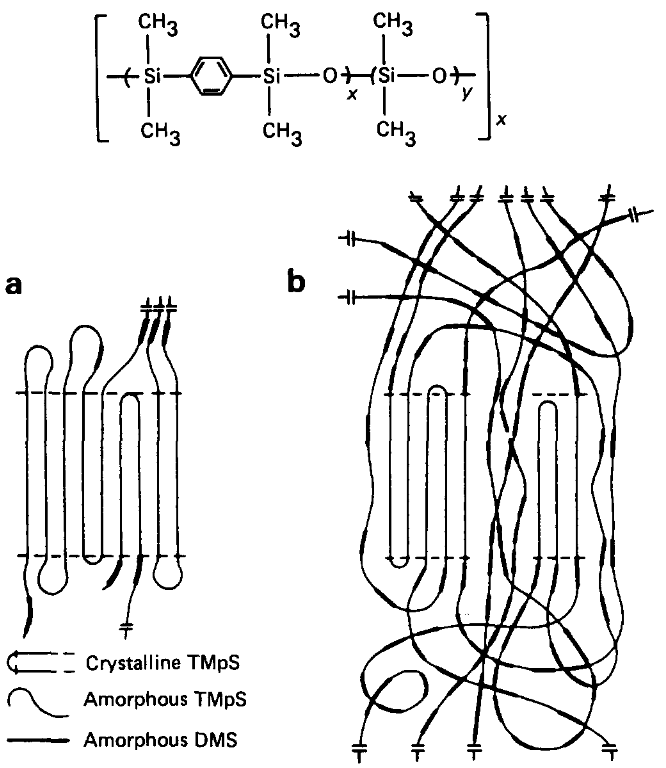

Figure 1 Structure of copolymer and model of crystalline lamellae in TMpS/DMS copolymer samples (a) 90/10 and (b) 30/70

segregation of DMS from TMpS on thermodynamic grounds as well as the exclusion of DMS (with some TMpS inclusion) to the crystal surfaces.

In two previous papers[8a,b], it was demonstrated that surface analytical techniques could be used to determine the surface morphology of polymer samples containing a siloxane component. Results combined e.s.c.a. data with those obtained by low energy ion scattering spectroscopy in order to analyse the surface quantitatively. This work allowed us to construct a model for the surface morphology of block copolymers and blends of bisphenol-A-polycarbonate/poly(dimethylsiloxane). In addition, Gardella *et al.*[6] have shown that the surface region of TMpS homopolymer consists of predominantly amorphous (Si–C6H4–Si–O) linkages. This was in agreement with the model proposed by Magill, which demonstrates how an understanding of the surface morphology of a crystalline polymer can substantiate the model for bulk morphology. In this case the 'fold' segments were found to be present at the surface using e.s.c.a. analysis along with HF chemical etching. *FT*i.r./ATR was used to confirm that an amorphous structure was present at the surface or interfacial region of the poly TMpS.

With e.s.c.a. and *FT*i.r./ATR one can probe the surface or interfacial regions of the samples to two different depths. E.s.c.a. is capable of sampling to a depth of 10–50 Å (Ref. 9) and has proven its ability to determine the extent of surface segregation in copolymer samples[8a,10]. *FT*i.r./ATR, however, samples to a much greater depth (2500–10000 Å) (Ref. 9) than e.s.c.a. The infra-red technique has been shown[6] to be uniquely suited to studying changes in crystallinity in unoriented siloxane polymers. A better understanding of surface morphology can be obtained using both of these techniques in conjunction than from either technique alone.

In the present study e.s.c.a. and *FT*i.r./ATR were used to characterize the surface composition for a series of block copolymers of TMpS/DMS of different compositions and degrees of crystallinity. This study was undertaken in order to permit a more complete picture of the morphologies and surface chemistry of these materials. These results in combination with results obtained by Magill *et al.*[1–4] for these samples will provide a better insight into the morphology of these TMpS/DMS block copolymers.

EXPERIMENTAL

Materials and preparation

The single crystals were sedimented from dilute solution (approximately 0.03 wt%) onto platinum foil. Sample preparation has been described in detail previously[4a] and samples analysed in this study are listed in *Table 1*.

Spectroscopic analysis

*FT*i.r./ATR was used to analyse the copolymer crystal mats supported on platinum foils. Spectra were recorded with a Nicolet 7199A spectrometer with a Harrick (XBC-50N) beam condenser. A Harrick 60 degree KRS-5 Internal Reflection Element was used for all samples. An acceptable signal-to-noise ratio was obtained after 1000 scans at a resolution of 4 cm^{-1}.

E.s.c.a. spectra were collected with a Perkin Elmer Physical Electronics Model 560 ESCA-SAM operated by a MACS data system (version 6 software). MgKα radiation (1253.6 eV) from the dual anode source was used for excitation at 300 watts (15 kV and 20 mA). The e.s.c.a. instrument has a cylindrical mirror analyser that is operated in the fixed analyser transmission mode. For these studies, data was collected at 25 eV pass energy and 0.1 eV sampling. These conditions produce a practical resolution of 1.1 eV measured at 1 000 000 cps on the Au $4f_{7/2}$ line. All data were processed utilizing standard software. Spectra were interpreted by plotting the e.s.c.a. peak area ratios in relation to a straight line corresponding to the linear interpolation between homopolymer data. This line is representative of the results which would be expected from a homogeneous bulk mixture of the homopolymers. Previous work[8a,b] has shown this to be a useful representation when studying surface segregation by e.s.c.a. analysis, since deviations from the 'ideal reference line' represent a deviation from

Table 1 Samples analysed in this study

Composition (%TMpS/%DMS)	Forms
100/0	Single crystal mat
90/10	Single crystal mat Melt-cast film Solution-cast film
80/20	Melt-cast film Solution-cast film
75/25	Single crystal mat
50/50	Melt-cast film
30/70	Single crystal mat Melt-cast film
0/100	Solution-cast film

Table 2 E.s.c.a. binding energy analysis of TMpS/DMS copolymer series (FWHM in parentheses)

Carbon 1s (eV)	Shakeup (Δ)	Oxygen 1s (eV)	Shakeup (Δ)
285.0 (1.9)	6.3	532.7 (1.9)	6.2

Sample	Wt% ratio	Silicon 2p (+0.2 eV)	Shakeup (Δ)
TMpS crystal	100/0	102.0 (2.1)	6.1
TMpS melt	100/0	101.9 (2.0)	6.2
TMpS/DMS crystal	90/10	102.1 (2.2)	6.3
TMpS/DMS melt	90/10	102.2 (2.1)	5.9
TMpS/DMS solution	90/10	102.1 (2.1)	6.0
TMpS/DMS crystal	75/25	102.2 (2.3)	6.0
TMpS/DMS melt	80/20	102.2 (2.2)	6.0
TMpS/DMS solution	80/20	102.1 (2.2)	6.1
TMpS/DMS crystal	50/50	102.3 (2.4)	6.3
TMpS/DMS melt	50/50	102.5 (2.2)	6.0
TMpS/DMS melt	30/70	102.6 (2.2)	5.8
DMS solution-cast	0/100	102.6 (2.0)	—

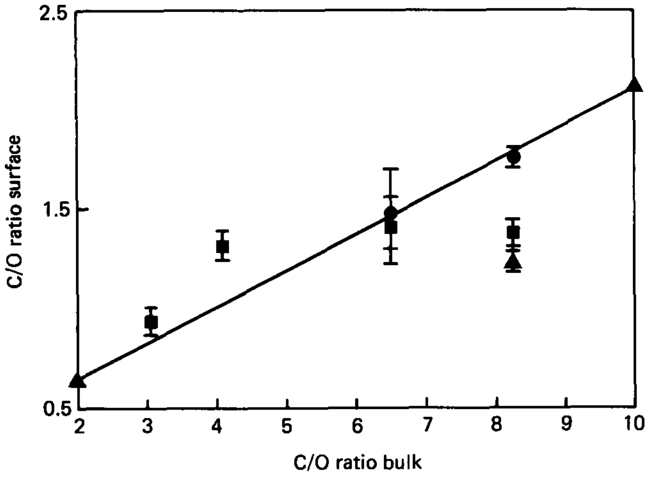

Figure 2 E.s.c.a. C/O peak area ratios vs. bulk composition: (■) melt-cast; (▲) crystal; (●) solution-cast

bulk sample concentration over the depth sampled by e.s.c.a.

RESULTS AND DISCUSSION

The e.s.c.a. binding energies for the homopolymer and copolymer samples are listed in *Table 2*. As expected all the samples showed carbon 1s, oxygen 1s, and silicon 2s and 2p features. The lack of any other peaks in the e.s.c.a. spectrum confirm the high degree of chemical purity in these samples. The binding energies of the TMpS carbon 1s and oxygen 1s peaks were insensitive to the sample composition, while the silicon 2p peak showed a slight shift to higher binding energy with increasing DMS concentration. This shift is due to the second oxygen bound to silicon in DMS which causes a shift of 0.6 eV in comparison with the TMpS homopolymer. All of the copolymer samples show shake-up satellites at approximately 6.3 eV above the main carbon 1s, oxygen 1s and silicon 2p peaks, due to the $\pi^* \leftarrow \pi$ transition in the TMpS phenyl ring[11,12]. This result indicates that there is TMpS present in the region sampled by e.s.c.a. for all of the copolymer samples studied. This observation is consistent with the model initially presented by Li and Magill[2] in which the sample was believed to be composed of crystalline regions of pure TMpS interdispersing the amorphous regions of DMS which are segregated to the crystal surfaces.

E.s.c.a. has been shown previously to be sensitive to surface speciation in block copolymer systems[8a,10], where the component with the lower surface free energy was limited to the surface of the copolymer. *Figures 2–4* show the C/O, Si/C, and Si/O peak area ratios for the copolymer samples plotted relative to a straight line representing the bulk concentration. The only samples to show surface concentrations significantly different from the bulk concentrations are the crystalline and melt-cast 90/10 TMpS/DMS samples, which show a consistent value for the Si/C peak area ratios along with a corresponding decrease in the C/O and Si/O peak area ratios. In a previous paper, Gardella *et al.*[6] demonstrated that the increase in oxygen content at the surface of homopolymers of TMpS, with decreasing crystallinity, was indicative of the presence of disordered or amorphous loops of the polymer chain at the surface of the less crystalline samples. For the TMpS/DMS copolymers there are two major effects capable of altering the e.s.c.a peak area ratios. First, as the DMS concentration is increased we would expect (for a homogeneous mixture at the surface) an increase in the Si/O and C/O peak area ratios to occur. This is

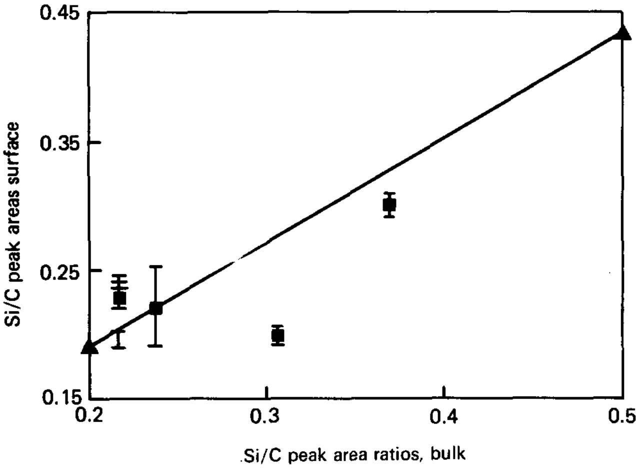

Figure 3 E.s.c.a. Si/C peak area ratios vs. bulk composition: (■) melt-cast; (▲) crystal; (●) solution-cast

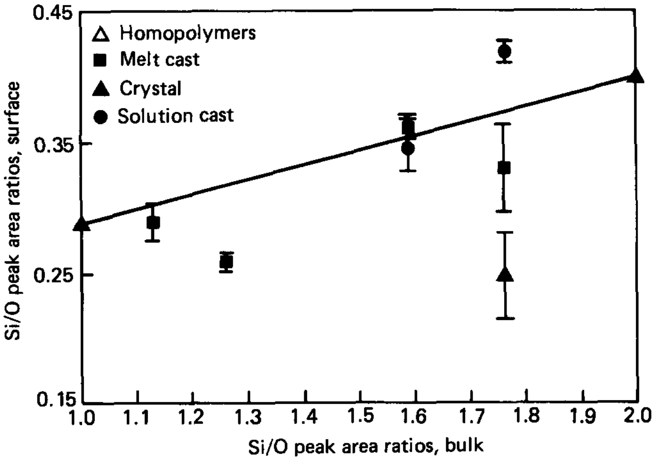

Figure 4 E.s.c.a. Si/O peak area ratios vs. bulk composition: (■) melt-cast; (▲) crystal; (●) solution-cast

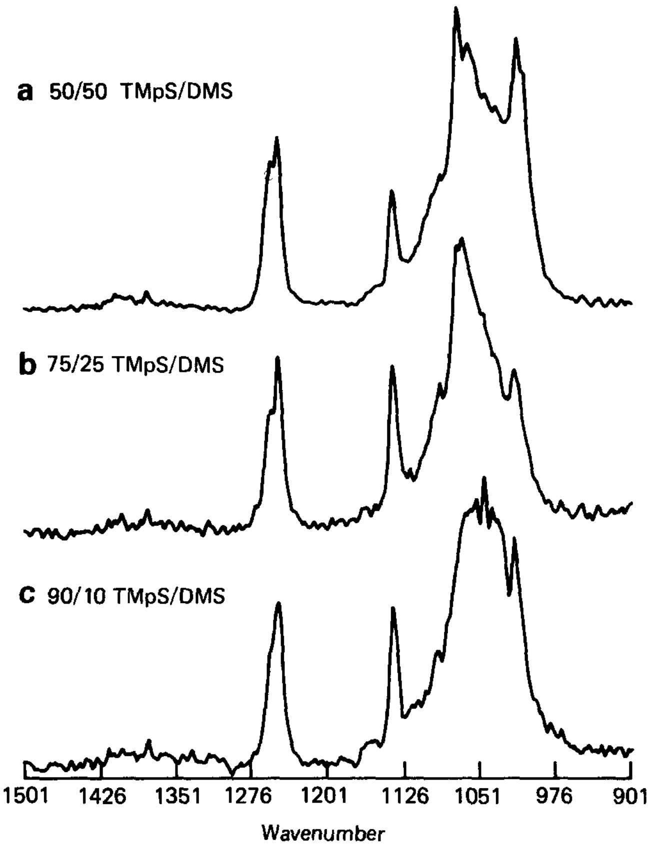

Figure 5 *FT*i.r./ATR results for single crystal copolymer samples: (a) 50/50; (b) 75/25; (c) 90/10

represented by the straight lines in *Figures 2–4*. Second, as the crystallinity increases the Si/O and C/O ratios will increase (1) if more DMS is excluded to the surface and (2) if the amorphous layer is sufficiently thin to enable sampling by e.s.c.a. The only samples to show surface concentrations different from the bulk concentrations are the crystalline and melt-cast 90/10 TMpS/DMS samples, which show a consistent value for the Si/C peak area ratios along with a corresponding decrease in the C/O and Si/O peak aeea ratios. Since the copolymers with low DMS concentrations obtain the highest degree of crystallinity[4], DMS is excluded from the core region and is present at higher than bulk concentration in the amorphous surface region in these samples. This picture of surface composition and crystallinity (*Figure 1*) is also consistent with crystal thickness from long spacing measurements[3]. The single crystal copolymers increase in thickness drastically from 60 Å for the TMpS to 250 Å for the 50/50 copolymer. This suggests that the disordered surface region in the 90/10 copolymer is thin (*Figure 1a*), and thickens as the DMS concentration increases. This would 'force' disordered TMpS into the surface region sampled by e.s.c.a., because of the short DMS block length (12 units). In the higher DMS concentration copolymers, this effect, taken with the drastic increase in crystal thickness, yields a surface region which has a homogeneous composition. However, the surface TMpS in these higher concentrations would all be disordered, in this view (*Figure 1b*). It will be demonstrated from the discussion below that *FT*i.r./ATR analysis can be used to provide further support to this picture, as to results obtained from HF etching experiments on these copolymer samples[4].

*FT*i.r./ATR can be used in conjunction with e.s.c.a. in order to probe the surface region at different depths (e.s.c.a. between 50–100 Å and *FT*i.r./ATR to about one micron)[13]. In this case, because of the thickness of crystals and lamellae, the ATR experiment effectively samples into the bulk. In this work and our previous study[6], the ATR sampling was used because transmission was made impossible by the scattering of these samples. *Figure 5* shows the *FT*i.r./ATR results for samples with 50, 25, and 10% DMS concentrations, respectively. It is apparent that the copolymers comprise TMpS and DMS because of the presence of the peak at 1138 cm^{-1}, which is present in the TMpS spectrum only. This observation is also consistent with the e.s.c.a. results, which indicate that a pure DMS overlayer is not present in these samples. It is possible to remove the TMpS contribution to the copolymer spectrum by subtraction. This is accomplished using the standard Nicolet subtraction routine where the TMpS (crystalline sample) contribution is subtracted in order to leave a pure DMS spectrum. This is accomplished by subtracting the TMpS contribution until the 1138 cm^{-1} peak (which is present in the TMpS only) is indistinguishable from the background. *Figure 6* shows the spectra for the copolymer samples after subtraction of the TMpS contribution. Ideally, the remaining spectrum would be anticipated to be that of pure DMS. The more crystalline (90/10 and 80/20 TMpS/DMS) samples have a strong negative going feature at 1075 cm^{-1}, while all other samples show only a weak feature in this region. Gardella *et al.*[6] have shown that this feature is indicative of changes in the degree of crystallinity for TMpS homopolymers. For example, when a TMpS spectrum with higher crystallinity is subtracted from a sample of

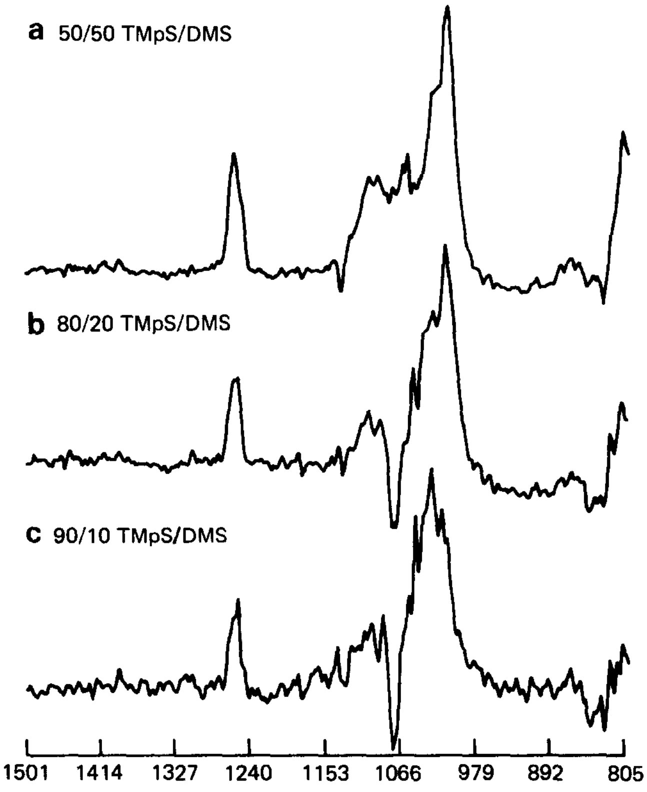

Figure 6 *FT*i.r./ATR subtraction results, single crystal TMpS subtracted from single crystal (a) 50/50; (b) 75/25; (c) 90/10

lower crystallinity, a negative peak appears at 1075 cm^{-1}. Therefore, the 90/10 and 80/20 samples appear to have a more disordered TMpS component in the region sampled when compared to the TMpS homopolymer, than do the samples with higher DMS concentrations. This result coincides with the increased DMS segregation found in the highly crystalline samples in the e.s.c.a. analysis and it can be interpreted as follows: In samples with a high degree of crystallinity and a low DMS concentration, a highly crystalline core is formed which forces an amorphous region consisting of greater than bulk DMS concentration to the surface. However, for samples of lower crystallinity and relatively higher DMS concentration, the degree of crystalline and amorphous regions is consistent throughout the sample, and when sampled by e.s.c.a or *FT*i.r./ATR gives an average composition which is equivalent to that of the bulk material. It is interesting to contrast these results with the results on BPAC/DMS copolymers published previously[8a], where the DMS, being surface segregated exclusively for reasons of thermodynamic incompatibility, is present in greater than bulk concentrations in the surface region for all concentrations studied. While both of these systems contain DMS, the BPAC/DMS samples are comprised of a non-crystalline material with a DMS block length of 20 units, while the TMpS/DMS samples are comprised of a semicrystalline material with a DMS block length of only 12 units. Clearly, these differences lead to different surface morphologies, with the BPAC/DMS copolymers showing a much greater degree of surface segregation than the TMpS/DMS copolymers. This is to be associated in part with the longer block length found in the BPAC/DMS samples and to the lack of crystallinity in the BPAC/DMS copolymers. This work indicates that the TMpS/DMS samples provide a good system for the study of the effects of crystallinity on the surface structure of block copolymers. Therefore, as suggested in our previous work[8a], the individual effects that are responsible for surface sensitive properties in polymers can be studied independently through the careful choice of the polymer systems.

CONCLUSIONS

By combining e.s.c.a. and *FT*i.r./ATR, the surface region of TMpS/DMS is characterized. From the e.s.c.a. results it is seen that no surface segregation of the DMS segments is present, except for the crystalline 90/10 sample. This result implies that the amorphous regions of the polymer are perpendicular to the surface normal and that the surrface region is consistent with the bulk. The 90/10 sample is unique in that the crystalline sample has an increase of DMS in the surface region.

It is also shown that *FT*i.r./ATR results can provide information on the degree of crystallinity for copolymers as well as homopolymers. In this case, the samples which attain the highest degree of crystallinity (90/10 and 80/20) are shown to have a more amorphous region over the outer micrometre than do the less crystalline samples. In combination with the e.s.c.a. data, one sees that these samples have a surface which differs from the bulk in both composition and morphology.

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REFERENCES

1 Okui, N. and Magill, J. H. *Polymer* 1977, **18**, 1152
2 Li, H. M. and Magill, J. H. *Polymer* 1978, **19**, 416
3 Okui, N. and Magill, J. H. *Polymer* 1977, **18**, 845
4a Okui, N., Magill, J. H. and Gardner, K. H. *J. Appl. Phys.* 1977, **48**(10), 4116
4b Kojima, M. and Magill, J. H. *J. Macromol. Sci.-Phys.* 1974, **B10**(3), 419
5 'Conformation of Macromolecules in the Condensed State', *Dis. Faraday Soc.* 1979, 68
6 Gardella, J. A., Jr., Chen, J. H., Magill, J. H. and Hercules, D. M. *J. Am. Chem. Soc.* 1983, **105**, 4536
7 Magill, J. H. *Makromol. Chem.* 1986, **187**, 455
8a Schmitt, R. L., Gardella, J. A. Jr., Chin, R. L., Magill, J. H. and Salvati, L. Jr. *Macromolecules* 1985, **18**, 2675
8b Schmitt, R. L., Gardella, J. A., Jr. and Salvati, L., Jr. *Macromolecules* 1986, **19**, 648
9 Clark, D. T., 'Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy', Ed. D. Briggs, Heyden, London, 1972, pp. 211–247
10 Thomas, H. R. and O.Malley, J. J. *Macromolecules* 1979, **12**, 323
11 Gardella, J. A., Jr., Chin, R. L., Ferguson, S. A. and Farrow, M. M. *J. Electron Spectr. Rel. Phenom.* 1984, **34**, 97
12 Gardella, J. A., Jr., Ferguson, S. A. and Chin, R. L. *Appl. Spectrosc.* 1986, **40**(2), 224
13 Harrick, N. J., 'Internal Reflectance Spectroscopy', Wiley-Interscience, New York, 1967