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Notes

On the Surface Morphology of Block Copolymers

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Block copolymers composed of segments having different surface energies are useful additives for the surface modification of bulk polymers.[1,2] The surfaces of samples of the block polymers themselves, as well as mixtures containing them, are substantially enriched in the component of lower surface energy.[1-3] Recently, X-ray photoelectron spectroscopy has provided direct confirmation of such surface enrichment.[4-6] These studies have demonstrated, however, that quite different surface morphologies may exist. With dimethylsiloxane-containing copolymers, a substantially complete siloxane surface layer is found, confirming the earlier inference from wettability and surface tension measurement.[1,2,7] Ethylene oxide–styrene block copolymers, on the other hand, have surfaces composed of separate styrene and ethylene oxide domains, although the former are in higher concentration and seem to protrude.[6]

The thermodynamic criterion for liquid spreading provides a rationale for these observations. In order for liquid b to spread over the surface of liquid a, it is necessary that the spreading coefficient,[8] $S_{b/a} = \gamma_b - (\gamma_a + \gamma_{ab})$ (the γ's being the surface tensions and γ_{ab} the interfacial tension between the liquids), be positive. If $|\gamma_a - \gamma_b| < \gamma_{ab}$, neither liquid can spread on the other. If this condition applies at the block copolymer surface during its formation, the isolated domain morphology is to be expected.

The low surface tension of poly(dimethylsiloxanes) (PDMS), relative to other polymers, favors spreading. Available data[9] indicate that in all cases where all three tensions have been measured, PDMS will spread. With few exceptions, the surface tension of PDMS is at least 10 dyn/cm lower than that of other polymers, while very few polymer interfacial tensions measured to date exceed this magnitude. The most likely candidates for the existence of the nonspreading condition with PDMS are the fluorinated polymers (the only polymers whose surface tensions are close to that of PDMS; a substantial interfacial tension between perfluoroalkanes and PDMS also exists[10]), and possibly poly(butylene oxide), for which $(\gamma_a - \gamma_b) =$ 4.7 dyn/cm at 150 °C.

Similarly, in the case of ethylene oxide–propylene oxide (PEO–PPO) block copolymers, for which surface tension measurements imply a substantially complete PPO surface,[3] the difference in surface tension of the homopolymers is ~12 dyn/cm, while measured interfacial tensions range from 1.3 to 2.8 dyn/cm;[11] thus PPO is expected to spread over PEO.

For styrene–ethylene oxide copolymers (PS–PEO), on the other hand, the homopolymer surface tensions differ by only ~2 dyn/cm. No direct measurement of interfacial tension between PEO and PS has apparently been reported; however, I have measured[12] γ_{ab} between ethylene glycol and ethylbenzene as 10.6 dyn/cm at 23 °C. Clearly, this large interfacial tension between the monomer analogues is entirely consistent with the nonspreading behavior implied by the observed isolated domain morphology.[13]

When values of all three tensions are available, the surface morphology may be predicted. Thus, literature data[9] yield a value of $S^{150\ ^\circ\mathrm{C}} = +5.9$ dyn/cm for the spreading of poly(*n*-butyl methacrylate) on poly(methyl methacrylate), suggesting that a block copolymer would exhibit a substantially complete poly(butyl methacrylate) surface layer. On the other hand, $S^{150\ ^\circ\mathrm{C}} = -4.6$ dyn/cm for poly(isobutylene)–poly(vinyl acetate), leading to the expectation of an isolated domain morphology for such a block copolymer.

Of course, surface and interfacial tensions vary with both temperature and molecular weight, and it is not obvious how much such variations will alter the values which are relevant to the actual process of surface formation for a particular block copolymer sample. It would also appear that geometrical limitations (e.g., for a short block of the surface-active component, especially in a repeating block or ABA copolymer where it is constrained at both ends by attached matrix blocks) might preclude effective spreading. In the cases cited above, the relatively large magnitude of the spreading coefficients (positive or negative) lend confidence to their predictive value. Further study is clearly needed for cases where the relative surface and interfacial tensions are more closely matched.

References and Notes

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Radiation-Induced Oligomerization of α-Methylstyrene

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It has been established that the radiation-induced polymerization of α-methylstyrene which occurs only when