

Block copolymers with low surface energy segments: siloxane- and perfluoroalkane-modified blocks

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(Received 13 June 1994; revised 14 October 1994)

In this paper we describe the preparation and preliminary characterization of diblock copolymers with a low surface energy block. These polymers were prepared by modifying the isoprene block in styrene-isoprene-based block copolymers with either short perfluoroalkyl or dimethyl siloxy 'fingers'. Specifically, the diene block of a styrene-isoprene block copolymer containing a large proportion of pendent vinyl groups (1,2- and 3,4-isoprene) was reacted with the appropriate hydrosilane in the presence of non-acidic Pt catalyst. The degree of attachment of hydrosilane was as high as 50% of the pendent unsaturations. Pendent vinyl groups were converted more efficiently than pendent methyl vinyl groups. These block copolymers, when mixed with the styrene homopolymer, exhibited surface segregation behaviour which depended on both polymer molecular weight and processing conditions. The surface segregation properties of the resulting block copolymers were studied by a variety of techniques which include contact angle measurements, and either X-ray photoelectron spectroscopy or Rutherford backscattering spectrometry. Contact angles as high as 110° were measured for both the siloxane- and perfluoroalkane-modified materials.

(Keywords: block copolymers; modification; characterization)

Introduction

Polymers that either in bulk or film form possess low energy surfaces offer a variety of interesting properties. Often such materials are fluorinated or siloxane-based polymers, since it is well known that both classes often have very low surface energies¹. Companion properties frequently include low coefficient of friction, chemical inertness and low dielectric constant². Such materials may also combine both biological inertness and resistance to attack by biological systems, since they offer surfaces that may minimize adhesion of biological entities³. Recently, marine coatings based on either fluoropolymers or silicones have been investigated as possible replacements for toxicant release coatings⁴.

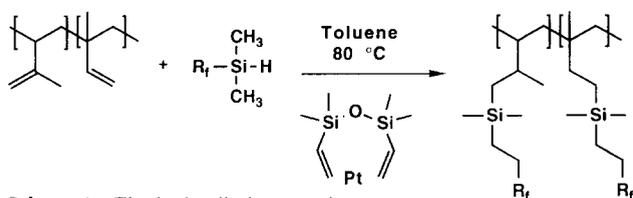
It has been observed that adding small amounts of a block copolymer, one of whose blocks has a low surface energy⁵ to a homopolymer can produce low energy surfaces by segregation of the block copolymer to the surface. Such an approach to creating polymer films with low surface energies may be both economical and provide novel process advantages. For example, the block copolymer may be added in excess and then act as a reservoir for renewal of the low energy surface after surface erosion has occurred. Low surface energy polymers based on either fluorocarbon or siloxane segments in the polymer backbone are often among the more difficult to synthesize with well controlled architectures. Several block copolymers with such components are known in the literature. Diblock copolymers of polystyrene and poly(dimethyl siloxane) are well known, but their synthesis usually produces some

broadening of the molecular weight distribution of the silicone block⁶. Several block copolymers containing fluorinated blocks are also known. Recently the synthesis of perfluoroalkyl-terminated polystyrene has been described⁷; however, the perfluoroalkane 'block' length of these polymers was limited to six carbons. Block copolymers based on methacrylate backbones that possess blocks with pendent fluorinated hydrocarbon groups have also been synthesized and examined for liquid crystalline behaviour, but have not been studied for their surface properties⁸.

In our studies we use polymer analogous chemistry to introduce low surface energy components to block copolymers prepared by anionic polymerization. The advantage of post-polymerization chemistry is that a source polymer with a very precise block copolymer architecture can be reliably prepared in large quantity and then through modification of one or both of the blocks, a new block copolymer can be produced. Such a procedure may make it possible to produce block copolymers that are impossible to produce directly using living techniques. An additional advantage of the modification approach is that one source block copolymer can be modified in several ways to enable direct comparison between different polymer designs. This latter aspect of modification chemistry has a distinct advantage for studies of the fundamental features of the segregation process. A potential disadvantage is that modified blocks will be reacted to unequal degrees. Great care must therefore be taken to react each modified block to the fullest extent possible, or at least to the same extent, so that valid comparisons may be made.

In this paper we discuss a new route to the preparation of block copolymers containing low surface energy

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Scheme 1 The hydrosilation reaction

fluorinated blocks, that involves the use of hydrosilation chemistry to modify styrene–diene block copolymers. Specifically, the diene block of a styrene–isoprene block copolymer containing pendent vinyl groups (1,2- and 3,4-isoprene) was reacted with a perfluorohydrosilane in the presence of a non-acidic Pt catalyst. The reaction is shown schematically in *Scheme 1*. It was reasoned that the addition of pendent fluorinated ‘fingers’ would provide a more effective low surface energy block than the attachment of a block consisting of a relatively stiff, perfluorinated main chain. The degree of attachment of hydrosilane was as high as 50% of the pendent unsaturations. Pendent vinyl groups were converted more efficiently than pendent methyl vinyl groups.

Fluorinated polyhydrocarbons (e.g. polytetrafluoroethylene (PTFE), $\gamma = 24 \text{ mJ m}^{-2}$) and siloxane polymers (e.g. polydimethylsiloxane (PDMS), $\gamma = 21 \text{ mJ m}^{-2}$) have similarly low surface energies at 20°C ¹. An additional family of siloxane-modified diblocks has therefore been prepared for comparison with the fluorinated block copolymers using the same polymer analogous (or polymer modification) chemistry⁹. Either material would be expected to make an excellent candidate for low surface energy formation.

The resulting block copolymers were studied by a variety of techniques for their surface segregation properties in mixtures with homopolystyrene. These techniques include contact angle measurements, and either X-ray photoelectron spectroscopy (XPS) or Rutherford backscattering spectrometry (RBS). Contact angles with water as high as 110° were measured for both the siloxane- and perfluoroalkane-modified materials. The molecular weight of the matrix polystyrene was shown to influence the nature of the surface segregation behaviour during processing.

Experimental

Synthesis of the perfluorohydrosilane, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyldimethylhydrosilane (TFHS).

The 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyldimethylchlorosilane (TODCIS, **1**) was obtained from Hüls and used as received. All other reagents were from Aldrich. The conversion to the hydrosilane is shown in *Scheme 2*. To a 100 ml, three-necked round-bottomed flask fitted with a condenser, stopper and dropping funnel were added 3 g (0.075 mol) LiAlH_4 under dry N_2 atmosphere. A quantity of 40 ml of dioxane, which had been dried over Na, was then added and heated to reflux. To the heated mixture was added 25 g (0.0568 mol) of TODCIS over 0.5 h from the dropping funnel. The mixture was then refluxed for 2 h. After this time, the dioxane was distilled off, and vacuum distillation was used to recover the hydrosilane product (yield = 58% theoretical). ^1H n.m.r.: 0.15 (S), 0.85 (M), 2.05 (M), 3.9 (M).

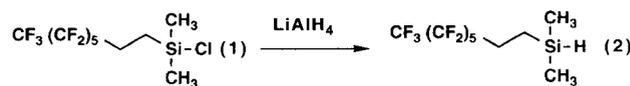
*Synthesis of poly(styrene-*b*-isoprene).* The synthesis of a block copolymer with styrene and 1,2-*co*-3,4-isoprene

blocks was carried out as follows. Distilled styrene monomer was transferred by vacuum distillation to the monomer port of the vacuum reactor. Initiator (0.8 ml 1.6 M sec-BuLi in tetrahydrofuran (THF)) was added to the reactor after evacuating for at least 2 h. After cooling to -78°C using dry ice/acetone, the reactor was evacuated for a further 2 h. Dry THF (250 ml) was added to the reactor via vacuum distillation. The monomer port of the reactor was opened and styrene monomer (11 ml) was added. The polymerization was allowed to proceed at -78°C for 2 h. Isoprene monomer (16 ml) was added to the reactor by vacuum distillation from n-BuLi solution. Formation of the isoprene was allowed to proceed at -78°C for up to 4 days, depending on the desired molecular weight. To terminate the reaction, 1.5 ml MeOH was added. The resulting polymer was precipitated in MeOH, filtered and dried. ^1H n.m.r.: multiplet centred around 1.5, 4.6(D), 4.8(S), 5.7(S), 6.5(D), 7.05(S).

*Hydrosilation of poly(styrene-*b*-isoprene).* Generally, the procedure was similar to that reported previously⁹ and is shown in *Scheme 1*. The styrene–isoprene (S–I) block copolymer that was chemically modified had a molecular weight of 170 000 with $M_w/M_n = 1.15$. The relative block size was 2 S: 1 I. The polymer (2 g) was dissolved in 100 ml anhydrous toluene in a 250 ml three-necked round-bottomed flask fitted with a rubber septum, stopper and condenser. The solution was purged with N_2 for 5 min, and under N_2 atmosphere, the solution was heated to 78°C . The catalyst (Hüls) (20 μl , 6.7×10^{-4} mmol Pt) was injected into the solution using a syringe. After 30 min, 2.4 ml of pentamethyl disiloxane (PMDS) (12 mmol, 0.85 for vinyl content) was added over 15 min at a temperature of 81°C . The reaction was maintained at 82.5°C for 72 h. Longer reaction times were required for the hydrosilation reaction using the perfluorohydrosilane (TFHS, **2**), see Results and Discussion. ^1H n.m.r.: -0.1 (S), 0.35(S), 0.8(T), multiplet centred around 1.5, 4.6(S), 4.8(S), 5.0(S), 6.5(D), 7.05(S). The 5.7 ppm peak characteristic of the 1,2-double bond completely disappears, suggesting its quantitative reaction within the limits of detection of ^1H n.m.r.

Molecular weights were determined by gel permeation chromatography using THF as solvent at 35°C , a 254 nm u.v. detector, and Ultrastaygel columns of 500, 10^3 and 10^4 Å pore sizes and a linear column with mixed pore sizes. Calibration was made with monodisperse polystyrene standards.

Analysis of thin films. RBS was used to determine the segregation of the siloxane-modified block copolymer to the surface by determining the Si content of a polymer film as a function of depth. A silicon wafer coated with a film of poly(2-vinylpyridine) (PVP), which formed an immiscible buffer layer about $0.5 \mu\text{m}$ thick, was used as a substrate to spin cast a film of the block copolymer in homopolystyrene, about $0.35 \mu\text{m}$ thick, from a solution in toluene. The PVP was used to separate the segregation sample from the silicon wafer so that the Si peak of the



Scheme 2 Formation of perfluorohydrosilane

block copolymer and the Si peak associated with the silicon wafer were distinct in the RBS spectra, thus enabling easier analysis of the segregation results. RBS spectra were measured using a $^4\text{He}^{2+}$ ion beam with an energy of 2.0 MeV, and these were analysed using standard software¹⁰⁻¹² to determine the atomic fraction of Si and thus the volume fraction $\varphi(z)$ of the block copolymer as a function of depth z . By measuring the integral excess

$$z^* = \int (\varphi(z) - \varphi_\infty) dz$$

where φ_∞ is the volume fraction of copolymer in the bulk, we can determine the areal chain density Σ of copolymer at the surface⁵.

Contact angle measurements were made using a Ramé-Hart NRL contact angle goniometer. Both advancing and receding contact angles were measured in three different spots per sample and two measurements were taken at each spot.

XPS was used to determine the ratios of C bonded to F and C bonded to H in the near-surface regions of films of the block copolymer. The XPS instrument was an SSL-100-3 photoelectron spectrometer using monochromated Al K_α X-rays (1486.6 eV) with a depth resolution of 10 Å. The angle of measurement of the Cornell-built XPS instrument was 45° and the maximum sampling depth was 100 Å based on the established electron escape depth for the device. The relative composition ratio of C, F and Si was determined through calibration.

Results and discussion

The synthesis of the starting block copolymer was carried out using conventional vacuum line techniques. Reaction conditions were chosen so as to maximize the content of pendent vinyl groups in the isoprene block. Towards this end, THF was used as reaction solvent and the reaction was carried out at -78°C . The two poly(styrene-*b*-isoprene) copolymers used in this study had a total molecular weight of $\sim 175\,000$ ($M_w/M_n \leq 1.15$) and composition of $\sim 66\%$ styrene. The isoprene block was determined by ^1H n.m.r. to consist of $\sim 40\text{ mol}\%$ 1,2-isoprene with the remainder being 3,4-isoprene. Thermal analysis of the block copolymers showed the expected glass transition temperature (T_g) for both blocks.

The hydrosilation reaction was performed using anhydrous conditions under N_2 atmosphere. Both PMDS and tridecafluorodimethyl hydrosilane (TFHS) were used to modify the isoprene blocks of the copolymers. The general scheme for the preparation of

the modified blocks is given in *Scheme 1*. The extent of modification was measured by ^1H n.m.r. and is listed in *Table 1*. Reactivity of the PMDS to the polymer was greater than that of the TFHS, but it was not clear from our studies what the source of this difference was. Generally, $\sim 70\%$ of the vinyl groups reacted, whereas 20% of the methyl vinyl groups were converted in the case of the PMDS. Reaction times for PMDS attachment were 72 h. Attachment of the TFHS proceeded at a lower rate, requiring much longer reaction times of up to 10 days. More efficient attachment of the hydrosilane to the unsubstituted vinyl group was observed in both cases⁹. The perfluoroalkyl-modified polymer, listed in *Table 1*, was therefore reacted for a much longer time to achieve the same level of modification as the siloxane-modified polymer.

The siloxane-modified polymer possessed molecular weight distributions that were nearly identical to the starting blocks, indicating that virtually all chains were modified to approximately the same extent. The perfluoroalkyl-modified block copolymer possessed a broader distribution ($M_w/M_n = 1.43$) as measured *versus* polystyrene standards, in part due to the lower reactivity of the TFHS. The T_g of the modified block was shown by thermal measurements to be -35°C in the case of the PMDS-modified block and -2°C in the case of the TFHS-modified segment. These values are higher than PDMS but lower than the usual processing temperature of PTFE. Such T_g values provide the amorphous, low surface energy block with significant mobility.

In order to investigate the surface segregation behaviour of the modified block copolymers, a series of blends were prepared and studied by measuring the contact angle of water droplets on the surface of films made from the blends. Both advancing and receding contact angle values were measured and are listed in *Table 2*. The blends

Table 2 Results of contact angle measurements (in degrees)

Sample	Unannealed		Annealed	
	Advancing	Receding	Advancing	Receding
<i>PMDS siloxane-modified P(S-b-I)</i>				
Block only	112	70	112	71
10 wt% in PS ^a	109	73	105	75
25 wt% in PS ^a	111	74	110	70
<i>TFHS perfluoroalkyl-modified P(S-b-I)</i>				
Block only	110	63	113	54
10 wt% in PS ^a	111	74	109	69
25 wt% in PS ^a	113	72	103	66

^a Molecular weight of polystyrene was 125 000

Table 1 Characteristics of modified block copolymers

Initial				Modified				
Mol. wt	M_w/M_n	PS (%)	1,2-PI (%)	3,4-PI (%)	Mol. wt	M_w/M_n	1,2 converted (%)	3,4 converted (%)
<i>PMDS siloxane-modified P(S-b-I)</i>								
170 000	1.15	45.2	22.5	32.3	183 000	1.18	>95	<5
<i>TFHS perfluoroalkyl-modified P(S-b-I)</i>								
174 000	1.11	47	21.7	31.3	371 100	1.43	>95	~25

consisted of either 10 or 25 wt% block copolymer in a matrix of homopolystyrene with $M_n = 125\,000$. Both the fluorinated and siloxane-modified block copolymers were investigated and were found to exhibit notably similar values of $\sim 110^\circ$ advancing and $\sim 75^\circ$ receding contact angles. The observed values are somewhat larger than those usually reported for fluorinated polymers such as PTFE, indicating an extremely non-polar surface. They are also considerably larger than the 90° value of advancing water contact angles for the homopolystyrene. The hysteresis observed between the advancing and the receding contact angle in all samples is very often observed with polymers and even self-assembled organic monolayers on Si. The hysteresis may be due to surface roughness or lateral inhomogeneity in surface composition.

Of the two modified block copolymers, the polymer modified with PMDS has a composition suited for analysis with RBS owing to the presence of silicon in the low surface energy block. (While in principle the F on the fluorinated block copolymer can be determined by RBS, in practice the backscattering cross-section for the alpha particles from F is so low, scaling like the atomic number squared, that the method is rather insensitive. Loss of surface F by radiation damage is also a potential problem.) RBS enables a determination of composition *versus* depth in thin film samples with a depth resolution of tens of nanometres. A series of blends of homopolystyrene with the siloxane-modified block copolymer was therefore prepared and investigated in thin film form for surface segregation using RBS. Films were about $0.35\ \mu\text{m}$ in thickness and were coated on silicon wafers. Factors studied included both M_n of the polystyrene homopolymer, amount of block copolymer and the effect of annealing on the extent of segregation. The annealing temperature chosen was 160°C . Homopolymer molecular weights ranged between 9000 and 575 000.

The RBS data clearly indicate the presence of significant segregation in the samples. *Figure 1* shows RBS spectra illustrating the effect of annealing observed when an intermediate homopolystyrene molecular weight of 207 000 was used. *Figure 1a* shows a peak at about 1.2 MeV in the as-cast film blend containing 25 wt% block copolymer. This peak results from silicon at and near the surface of the film, indicating that there is substantial segregation to the surface as the film dries. *Figure 1b* shows the same film after annealing for 24 h at 160°C . The surface peak has narrowed and increased in height. *Figure 2* shows the areal chain density Σ of this block copolymer at the surface as a function of annealing time. The kinetics of segregation are rather slow and probably reflect the fact that most of the block copolymer in the bulk of the film is in the form of micelles, thus decreasing the concentration of block copolymer that is free to diffuse, and slowing equilibration. In some cases it was observed that the surface silicon peak was followed by a layer underneath that was noticeably depleted in silicon (i.e. depleted in block copolymer); this depletion layer persisted to long annealing times, much larger than the times expected if the kinetics were controlled by simple diffusion of the block copolymer. (An upper limit for the time for equilibration by simple diffusion was estimated from the tracer diffusion coefficient of polystyrene of the same degree of polymerization as the block copolymer.) Such effects have been observed

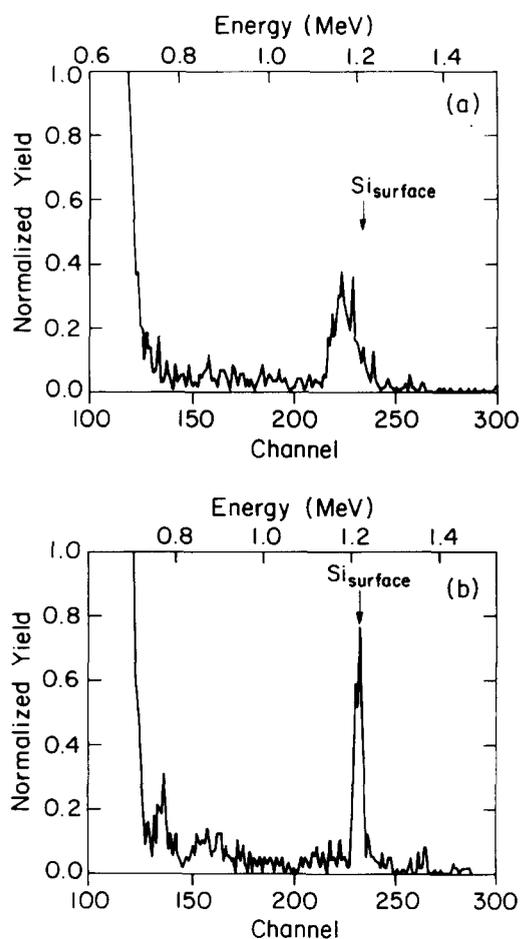


Figure 1 Rutherford backscattering spectra from (a) an as-cast film containing 25 wt% siloxane-modified block copolymer; (b) an identical film after annealing for 24 h at 160°C

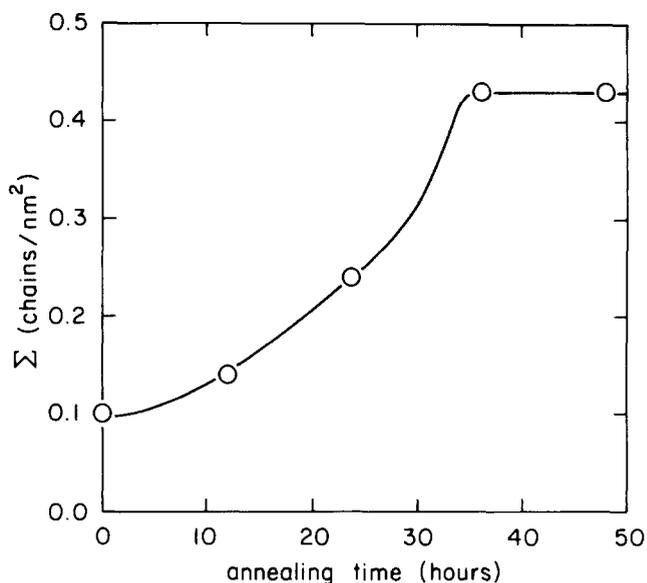


Figure 2 Surface areal chain density of the siloxane-modified block copolymer as a function of annealing time

previously in equilibration of block copolymer segregation at polymer interfaces⁵. Qualitative analysis of the segregation behaviour showed that with low molecular weight polystyrene matrices, segregation was rapid enough that a surface excess occurred during spin casting that was little affected by annealing. The intermediate

molecular weight matrices showed significant effects of annealing on segregation, as mentioned above. For blends with the highest molecular weight homopolystyrene, little additional segregation was observed to take place during the annealing cycle.

The nature of the fluorinated surface of the fluorinated block copolymer was examined using XPS, since RBS is too insensitive to fluorine to be very useful in its analysis. The XPS measurements using the Cornell instrument could only show ratios of the amounts of different elements within the top 100 Å. The ratios of C bonded to either F or Si *versus* C bonded to H were therefore studied, and found to be roughly double the expected stoichiometric ratios in the pure fluorinated block copolymer sample (i.e. considering both polystyrene and modified polyisoprene blocks), suggesting that uniform coverage of the surface to a depth of up to 100 Å by a perfluoroisoprene microdomain layer is possible. The presence of Si in this microdomain is of course due to the use of the hydrosilane to introduce the perfluoroalkyl segment. In view of the strong effects of surface energy in inducing preferential order near the surface of other microphase-separated block copolymers^{13,14}, our results seem reasonable.

In the blend of 25% fluorinated block copolymer in homopolystyrene, the samples showed roughly stoichiometric amounts of F and Si, from which we may deduce that the thickness of the outer perfluoroisoprene layer is less than the 100 Å sampling depth and that coverage of the outer microdomain in the pure block copolymer may not be as uniform. The sample with 10 wt% fluorinated block copolymer in homopolystyrene had approximately 50% of the expected stoichiometric ratio, suggesting that the thickness of the outer perfluoroisoprene layer is even thinner or less uniform than for the 25% sample. These results seem reasonable since the integral excess increases with increasing copolymer concentration in the bulk, and this increase must logically be accompanied by an increase in the thickness of the outer perfluoroisoprene layer.

The structure of the low surface energy components of the modified blocks is somewhat different from that usually built into such materials. Most siloxane-based polymers have silicon placed in the polymer backbone. Similarly, most fluorinated polymers are constructed with fluorinated backbones and short fluorinated substituents, if any^{15,16}. Only a few methacrylate and acrylate polymers make use of the pendent 'finger' structure we have introduced into these materials. The attachment of the low surface energy groups via a spacer consisting of the vinyl group from the isoprene block and the silane

gives the low surface energy 'finger' a significant degree of mobility. One can infer from the contact angle measurements that this strategy is very successful in producing a low energy surface. While we have no evidence that the perfluoro groups stand up perpendicular to the surface, it may be that this flexibility enables the siloxane and perfluoro segments to self-organize in the same fashion that similar groups have been shown to organize on oxide surfaces modified with self-assembled monolayers¹⁷. Additional studies exploring these sorts of low surface energy materials are now underway.

Acknowledgements

The authors acknowledge the Office of Naval Research (MIMI Program) for support of this work. S. P. also thanks the Department of Defense for a DOD fellowship administered through the Army Research Office. Also acknowledged is the use of the Central Facilities of the Cornell Materials Science Center which is funded by the NSF-DMR-MRL Program.

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