decrease in intermolecular interaction. The quantity of interest is now the average gain in enthalpy per segment, ΔH_f, when a segment is transferred from the interior of a crystal to a fold. We will estimate the upper limit to ΔH_f. Since the proportion of *gauche* bonds in the fold would be in general larger than in liquid, we assign 0.5 kcal/mol as the maximum possible contribution to ΔH_f arising from the conformational change. Second, we would expect the packing of segments in the fold retains remnants of order carried over from the interior of the crystal, or in other words, the specific volume available per segment of the fold would be somewhat smaller than that in liquid. Still, we assign 0.76 kcal/mol as the maximum possible contribution to ΔH_f from the volume expansion on going from the lattice to the surface. The upper limit to ΔH_f is thus estimated to be 1.26 kcal/mol of segments. Dividing the value of q_e with ΔH_f, we find then that the lower limit to the average number of segments per fold is 18 segments.

Next we consider the observed value of the surface entropy s_e. In order to estimate the upper limit to the entropy excess ΔS_f per segment of a fold over that of the interior segment, we again compare it with the entropy of fusion ΔS_u. Starkweather and Boyd[16] have shown that, of the value of 2.3 eu/mol observed for ΔS_u, 0.5 eu/mol is associated with the increase in volume on melting and the remaining 1.8 eu/mol with the increased degree of conformational freedom available to polymer molecules in liquid. As stated above, we expect that the volume available to a segment of a fold would be smaller than that for an amorphous segment. We will nevertheless assign 0.5 eu/mol as the upper limit to the component of ΔS_f contributed by the increase in specific volume. The conformational degrees of freedom available to segments in the fold is again much smaller than that in liquid because[14] the two ends of the fold are fixed and the space occupied by crystalline lattices is not available for access. Thus, 1.8 eu/mol would be a generous upper limit to the conformational component of ΔS_f. We thus estimate the upper limit to ΔS_f to be 2.3 eu/mol of segments and by dividing the value of surface entropy s_e with it we find a fold to consist of at least 17 CH_2 segments.

The analysis of surface enthalpy and entropy both lead to the conclusion that a fold consists of around 20 segments in the least. The upper limits to ΔH_f and ΔS_f we estimated are, we believe, very generous, so that the number of segments per fold could actually be considerably larger than 20. Such a conclusion is in agreement with those derived by Fischer and Schmidt[17] on the basis of density measurement and by Peterlin and Meinel[18] from the results of nitric acid digestion of single crystals. The number of 20 or more segments we estimate is the average value. Earlier, from consideration of a random flight on lattices as a model for the fold, we calculated[14] that the distribution of fold sizes has to be very broad. In conjunction with the above result, we would then visualize the fold surface to be made up of a large number of fairly short, tight folds which are interspersed with a much smaller number of long, winding folds; the proportions of long and short folds are such that on the average the disordered layers at both surfaces of single crystals are about ten segments or more deep. We note that a picture very similar to the above had been proposed by Flory[19] some time ago and by Peterlin[20] more recently.

---

[16] H. W. Starkweather, Jr., and R. H. Boyd, *J. Phys. Chem.*, **64**, 410 (1960).

[17] E. W. Fischer and G. Schmidt, *Angew. Chem.*, **74**, 551 (1962).

[18] A. Peterlin and G. Meinel, *J. Polym. Sci., Part B*, **3**, 1059 (1965).

[19] P. J. Flory, *J. Amer. Chem. Soc.*, **84**, 2857 (1962).

[20] A. Peterlin, *J. Makromol. Sci. Phys.*, **3**, 19 (1969).

Surface Activity of Polystyrene–Polysiloxane–Polystyrene ABA Block Copolymers

M. J. Owen and T. C. Kendrick

Research Department, Midland Silicones Ltd., Barry, South Wales.

Received March 31, 1970.

ABSTRACT: The surface activity of a series of ABA polystyrene–polysiloxane–polystyrene block copolymers of different compositions has been investigated by measuring the surface tension of their solutions in styrene and their effect on the critical surface tension of wetting of polystyrene. The results suggest a model for the copolymer in the solvent surface where the cross-sectional area of the copolymer is determined by the packing together of distorted A segments.

Although the last few years have seen a renewal of interest in the surface tensions of liquid polymers and of polymer solutions, very little is known about block copolymers in this context. This is surprising, for the solution properties of block copolymers are also receiving considerable attention, and many of the results are consistent with the different polymer subchains occupying different domains of the polymer–solvent mixture. For copolymers whose different subchains have different surface energy contributions this should result in a concentration of the more surface active segments in the surface. Such behavior is evident with poly(ethylene oxide)–poly(propylene oxide) block copolymers,[1,2] and with poly(alkylene

---

[1] I. R. Schmolka, "Nonionic Surfactants," M. J. Schick, Ed., Marcel Dekker, New York, N. Y., 1967, p 316.

[2] A. K. Rastogi and L. E. St. Pierre, *J. Colloid Interface Sci.*, **31**, 168 (1969).

TABLE I
COMPOSITION OF THE POLYMERS

Polymer	d*n*/d*c* in benzene, 5461 Å	% Polydimethylsiloxane		Calcd, %			Found, %			Mol wt			Approximate configuration of polystyrene–polysiloxane–polystyrene, number of monomer units
		Calcd from monomer consumption[a]	Calcd from d*n*/d*c*[b]	C	H	Si	C	H	Si	$\bar{M}_n$ Calcd from monomer consumption[a]	$\bar{M}_n$ Estimated from gpc[c]	$\bar{M}_w$ Light scattering	
Homopolystyrene	+0.106[g]	0	0								10,300		
Copolymer A	+0.065	20	19	80.3	7.8	7.6	80.2	8.2	5.2	10,000	9,000	20,200[d]	38–27–38
Copolymer B	+0.027	37	38	70.1	7.8	14.0	65.0	8.2	12.2	9,500	8,000	25,300[d]	29–48–29
Copolymer C	−0.012	59	57	57.0	7.9	22.3	57.0	8.1	21.3	9,700	8,000	18,000[e]	19–77–19
Copolymer D	−0.062	78	80	45.6	8.0	29.5	45.6	8.6	28.7	9,100	10,000	20,900[d]	10–96–10
Copolymer E	−0.013	59	57	57.0	7.9	22.3	57.2	8.0	21.1	7,300	5,000	11,100[e]	14–58–14
Copolymer F	−0.014	58	57	57.6	7.9	21.9	57.3	8.4	20.4	4,800	3,000	9,400[e]	10–38–10
Homopolydimethylsiloxane	−0.104	100	100							14,600[f]			

[a] Assuming each lithium butyl molecule initiates one polymer chain. [b] Assuming linear relation between d*n*/d*c* and per cent composition. [c] Based on homopolydimethylsiloxane calibration. [d] In benzene solution. [e] In styrene solution. [f] Estimated from viscosity data. [g] Data of W. Bushuk and H. Benoit, *Can. J. Chem.*, **36,** 1616 (1958).

oxide)–polydimethylsiloxane block copolymers.[3–5] An extrapolation of these ideas suggested that siloxane–organic block copolymers would be effective integral surface treatments of organic plastics which are liquid at some stage in their production. The use of surface active agents as integral surface treatments has been investigated by Zisman and coworkers,[6,7] who have pointed to the suitability of siloxane-containing materials, although most of their work in this area has been with fluorinated surfactants. We chose initially to study the styrene–siloxane system to test these ideas.

Experimental Section

The surface tensions were obtained with a Rosano Wilhelmy plate surface tensiometer as previously described.[3] Care was taken to obtain equilibrium values of the surface tension, and to use a perfectly wetted blade. Contact angles were obtained using an optical goniometer, modeled on the apparatus of Fort and Patterson.[8] The light-scattering studies were carried out with a "Sofica" photodiffusiometer.

Reagent grade styrene from B.D.H. Chemicals Ltd., Poole, U. K., was used after it had been dried for a few days over a type 4A molecular sieve. The surface tension was taken as a criterion of purity, samples with σ_{LV} less than 31.4 ± 0.1 dyn cm^{-1} at 23° being discarded. Polystyrene chips were obtained from the Distillers Co. Ltd., Barry, Glamorgan, U. K., being the best available grade with greatest freedom from stabilizers, plasticizers, etc. The critical surface tension of wetting of 32.4 dyn cm^{-1} at 23° is in excellent agreement with Zisman's value of 33 dyn cm^{-1} at 20°.[9]

The polystyrene surfaces were prepared by molding the chips into 2 in. × $^1/_8$ in. disks between grease-free aluminum foil using a steam-heated 10-ton press at 180°. The copolymer was introduced by dissolving it in a small amount of hexane and using the solution to wet the polystyrene chips. Before measuring contact angles with various liquids the disks were cleaned by wiping with methanol.

Liquids used in making the contact angles (θ) reported were methanol–water mixtures of various compositions, covering the surface tension range from 22.6 dyn cm^{-1} (pure methanol) to 49.6 dyn cm^{-1} (50% water). The *n*-alkanes and most other liquids usually employed[10] could not be used because they attacked the surfaces of these disks. Although there are serious disadvantages in using aqueous mixtures for contact angle studies,[10] no other generally applicable set of inert liquids could be found. Because of the problem of solvent evaporation changing surface composition and liquid surface tension, the contact angle was measured as rapidly as possible after placing the drop (no dynamic surface tension changes were noticed using the Wilhelmy plate for several minutes, thereafter the surface tension rose as a result of the evaporation of methanol).

The polystyrene–polysiloxane–polystyrene ABA copolymers were made by sequential anionic solution polymerization of the monomers styrene and cyclic hexamethyltrisiloxane, using butyllithium as the initiator. Details of the polymer compositions are given in Table I. Characterization

---

(3) M. J. Owen and T. C. Kendrick, *Proc. Intern. Congr. Surface Activity, 5th, Barcelona, 1968*, 571 (1970).

(4) B. Kanner, W. G. Reid, and I. H. Petersen, *Ind. Eng. Chem., Prod. Res. Develop.*, **6,** 88 (1967).

(5) W. D. Bascom, L. A. Halper, and N. L. Jarvis, *ibid.*, **8,** 118 (1969).

(6) R. C. Bowers, N. L. Jarvis, and W. A. Zisman, *ibid.*, **4,** 86 (1965).

(7) N. L. Jarvis, R. B. Fox, and W. A. Zisman, *Advan. Chem. Ser.*, **43,** 317 (1964).

(8) T. Fort, Jr., and H. T. Patterson, *J. Colloid Sci.*, **18,** 217 (1963).

(9) A. H. Ellison and W. A. Zisman, *J. Phys. Chem.*, **58,** 503 (1954).

(10) M. K. Bernett and W. A. Zisman, *ibid.*, **63,** 1241 (1959).

Table II
Surface Properties of the Copolymers

	Liquid solution						Solid solution	
				Polystyrene coil dimensions				
	Surface tension at 1% w/w, dyn cm^{-1}	Concn at start of plateau, % w/w	Gibbs limiting area, A_L, Å^2 mol^{-1}	Gibbs radius, r_a, Å	Radius of gyration, $(\bar{s}^2)^{1/2}$, Å	$r_a/(\bar{s}^2)^{1/2}$	Copolymer	Critical surface tension of wetting, dyn cm^{-1}
Styrene	31.4						Polystyrene	32.7
Styrene + A	27.3	>10	670	10.3	18.1	0.57	Polystyrene + 1.0% A	28.3
Styrene + B	25.8	3.5	590	9.7	15.7	0.62	Polystyrene + 1.0% B	27.5
Styrene + C	25.3	2.0	550	9.4	12.8	0.73	Polystyrene + 1.0% C	22.0
Styrene + D	23.5	0.5	280	6.7	9.1	0.74	Polystyrene + 1.0% D	22.0
Styrene + E	25.5	2.0	470	8.6	11.1	0.77		
Styrene + F	25.8	2.0	340	7.4	9.1	0.81		

techniques used were elemental analysis, refractive index increment in solvent solution (dn/dc), and molecular weight by light scattering and gel permeation chromatography (gpc).

Results and Discussion

Equilibrium surface tensions (σ), plotted as a function of concentration (c) for the copolymers in styrene solution, are shown in Figure 1. Comparable homopolymers are also shown. Table II lists the limiting areas, *i.e.*, smallest area calculated from the curves using the approximate form of the Gibbs equation

$$A_L = \frac{-RT}{d\sigma/d\ln c}$$

We are aware of the uncertainties inherent in applying this equation to polydisperse systems. However, it should reveal trends in the behavior if applied to a series of copolymers of different mean composition.

In conventional nonionic surfactants the break in the σ/log c curve to an almost constant low value of surface tension is often identified with the onset of micellization, and a point of interest was to see if our block copolymers aggregated at this point. Figure 2 shows the light scattering, refractive index, and surface tension plot for copolymer D in benzene, establishing that there is no aggregation occurring at this concentration. The presence of micelles at such concentrations in a solvent such as benzene, which is a good solvent for both homopolymers, is not expected, but it has recently been demonstrated for AB polysiloxane–polystyrene block copolymers, when a nonsolvent for one of the homopolymers is added.[11]

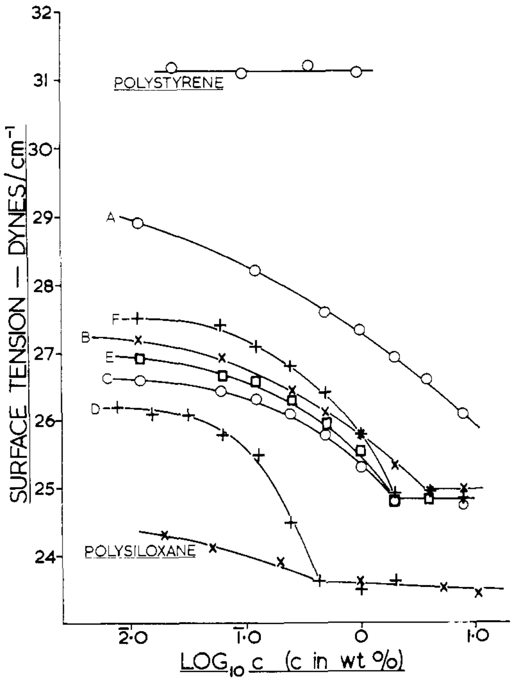

Figure 1. Surface tensions of the copolymer solutions in styrene.

The surface tension at this point is dependent on the copolymer composition—the higher the siloxane content the lower the value. But even with the siloxane homopolymer the value is not as low as 21 dyn cm^{-1}. Evidently this value is a function of the configuration of the copolymer in the surface and the amount of solvent associated with it. The lowest values of 21 dyn cm^{-1} will only be obtained with solvent in which the siloxane is insoluble, *cf.*, the poly(alkylene oxide)–polysiloxane block copolymers in water.[3] The low surface tension plateau of copolymer D is reached in benzene at 1% and in styrene at 0.5%, the values being 25.3 and 23.5 dyn cm^{-1}, respectively. Moreover, the limiting value of the surface area appears to be greater in benzene than it is in styrene. All this is consistent with the copolymer being more surface active in styrene

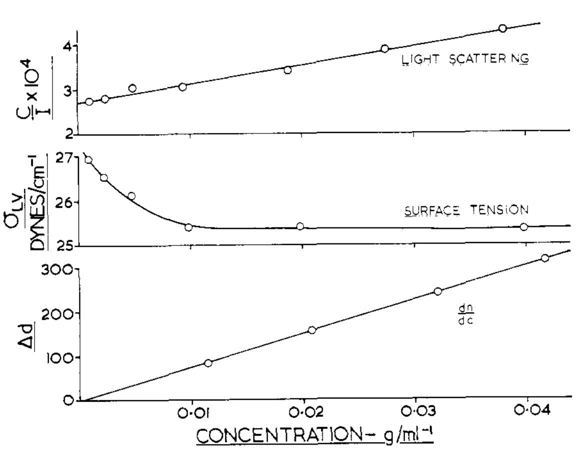

Figure 2. Light scattering, surface tension, and refractive index of solutions of copolymer D in benzene.

---

(11) J. C. Saam, D. J. Gordon, and S. Lindsey, *Macromolecules*, 3, 1 (1970).

than it is in benzene. Presumably the siloxane portion is less soluble in styrene than in benzene.

The general trend is for the Gibbs limiting area to decrease as the percentage of polysiloxane increases. For the poly(alkylene oxide)–polysiloxane ABA block copolymers we have proposed a model where the surface layer consists of closely packed coiled A segments with the siloxane chains extending out of solution. Applying this model to the present case, we can obtain the radius of the adsorbed polystyrene coils r_a from the Gibbs limiting area $r_a = (A_L/2\pi)^{1/2}$. This can be compared with the radius of gyration $(\bar{s}^2)^{1/2}$ of the polystyrene chain in solution, calculated from the well-known equations for a Θ solvent

$$[\eta] = KM^{\alpha} = \frac{\Phi(6\bar{s}^2)^{3/2}}{M}$$

when $\alpha = 0.5$, where $[\eta]$ is the intrinsic viscosity, M molecular weight, and Φ the universal constant $= 2.1 \times 10^{-21}$. For polystyrene in a mixture of methyl ethyl ketone and isopropyl alcohol (6:1), at 25°, $\alpha = 0.5$ and $K = 7.3 \times 10^{-4}$ dl g^{-1}.[12]

Table II shows the ratio $r_a/(\bar{s}^2)^{1/2}$, illustrating that the coils in the surface are compressed or distorted, although in a good solvent. Our model for the poly(alkylene oxide)–polysiloxane materials assumed a rather loose coil due to solvation which was distorted such that it was longer than it was wide. Such a postulate seems appropriate here. This type of chain distortion in the surface of the solubilizing coil thus occurs in two quite different systems (there is no hydrogen bonding in the present case) and is probably quite general. Burns and Carpenter[13] have carried out a similar comparison to this for homopolystyrene adsorbed from cyclohexane solution onto aluminum. Their compression factors $r_a/(\bar{s}^2)^{1/2}$ were similar. However, their molecular weight range was much higher and because of the great differences in the two systems, and the many approximations that we have made, it is unwise to pursue this comparison.

Rastogi and St. Pierre[2] have observed that above a certain length of the more surface active poly(propylene oxide) chain in poly(propylene oxide)–poly(ethylene oxide) surfactants the surface tension of the block copolymers (neat) is that of poly(propylene oxide). The same was found to be true for our poly(alkylene oxide)–polysiloxane block copolymers. Litt and Herz[14] have demonstrated this effect for solid surfaces. They showed that the critical surface tension of wetting σ_C of block copolymers of poly(N-lauroylethylenimine) and poly(N-acetyltrimethylenimine) ranging from 25 to 75% poly(N-lauroylethylenimine) was always 22 dyn cm^{-1}, the value of the more surface active poly(N-lauroylethylenimine). This effect is observed in the present case as well. Films of all our copolymers cast from hexane give uniformly low critical surface tensions of wetting of ~22 dyn cm^{-1}, the value for dimethylsiloxanes. For the polysiloxane–poly(alkylene oxide) series we deduced that a degree of polymerization of at least 20 was necessary before this lowest possible value could be attained—all the present copolymers have siloxane segments of greater degrees of polymerization than this.

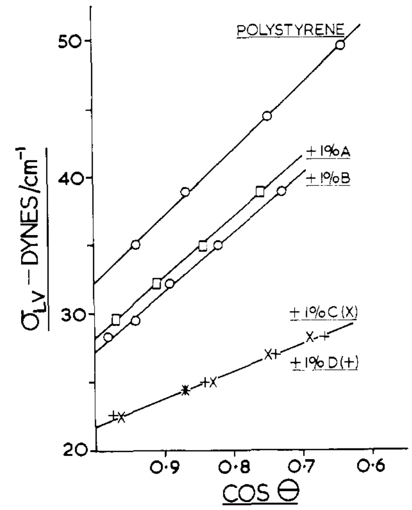

Figure 3. Contact angle plots for the polystyrene disks.

Figure 3 shows the contact angle plots for polystyrene disks containing 1.0% each of the four copolymers of $\bar{M}_n$ ~ 10,000 and also an untreated disk. Values of the critical surface tension of wetting σ_C are included in Table II. Those copolymers with the highest proportion of polysiloxane gave the lowest σ_C as expected, and we thus have the means of varying the wettability of the plastic surface progressively down to what is effectively a silicone surface. Copolymer D gave a rather greasy feel to the surface. A greasy surface was not obtained with copolymer C, although the copolymer had the same low critical surface tension of wetting. Presumably copolymer D has too high a siloxane content for overall compatibility—polysiloxanes dissolve in styrene but are not compatible with polystyrene.

The relative compatibility of the polymers involved crucially affects surface behavior. Copolymer B, which at 1.0% only lowers σ_C of polystyrene to 27.5 dyn cm^{-1}, lowers σ_C of an acrylic resin-based paint from 28 to 22 dyn cm^{-1}. Presumably the copolymer is less compatible with the acrylic resin than with the polystyrene. It is, however, firmly fixed in the surface and cannot be wiped out by methanol in contrast to polysiloxane–poly(alkylene oxide) block copolymers in the same paint system; where it is clear that the treatment dissolves in the contact angle test liquids since moderate wiping with methanol soon removes all trace of the treatment from the surface. Consequently by controlling the overall size of the copolymer, the relative proportions of the polysiloxane and organic polymer segments and the nature of the organic portion new selective surface treatments for plastics, rubbers, resins, paints, etc., become possible.

---

(12) S. R. Rafikov, S. A. Pavlova, and I. I. Tverdokhlebova, "Determination of Molecular Weights and Polydispersity of High Polymers," Israel Programme for Scientific Translations, 1964.

(13) H. Burns, Jr., and D. K. Carpenter, *Macromolecules*, **1**, 384 (1968).

(14) M. Litt and J. Herz, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **10**, 905 (1969).