Structure and Properties of Oil Extended Styrene Butadiene Block Copolymers

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The relationships between mechanical properties and structure of rapidly spin cast styrene-butadiene-styrene (SBS) block copolymers diluted with two different types of mineral oil are discussed. Small angle X-ray scattering (SAXS) measurements indicate that both oils go mainly into the rubbery polybutadiene phase. While during rapid spin casting the paraffinic oil improves the phase separation of polystyrene (PS) and polybutadiene (PB), the opposite is true for the aromatic oil. The measurements also suggest that the oils cause a preferential swelling of the superstructure along the longitudinal direction of the cylindrical PS domains. From this, it can be concluded that a larger number of interconnecting PB chains is present in the cross direction than in the longitudinal one. With increasing oil content, a further decrease of interconnecting chains in the latter direction may be the reason for the decrease of the tensile modulus. Furthermore, above a critical value of dilution (33 wt percent for paraffinic oil, 50 wt percent for the aromatic one), more and more spherical domains are formed instead of the cylindrical ones. This morphological transition explains the step present in the double logarithmic plot of the large strain tensile modulus as a function of oil dilution.

INTRODUCTION

Styrene-butadiene-styrene (SBS) triblock copolymers are important materials used as thermoplastic rubbers. It is well known that phase separation takes place in such systems. Depending on concentration and preparation conditions, the phase present in a smaller amount forms well ordered lamellae, cylinders, or spheres within the matrix of the other phase (1). However, a complete phase separation will only occur under processing conditions in which an equilibrium can be reached. If this is not the case, for example, in technological processes such as injection molding and spin casting, the phase separation may remain incomplete. Therefore, there exists much interest in studying the structure and the properties of samples obtained under processing conditions used in manufacturing. Another important problem arises if the SBS block copolymer is extended with mineral oil. This is done in order to reduce the cost of the materials as well as to improve certain mechanical and rheological properties. The question arises as to how the oil influences the structure and mechanical properties.

In previous publications samples of block copolymers extended with different kinds of oil were prepared and, finally, the mechanical properties of these samples as well as the influence of the oil dilution were investigated (2–4). An interesting dependence of the properties on the amount of oil and a difference between the

influence of an aromatic oil and that of a paraffinic one were observed.

In order to explain these results, we have performed investigations of the structure of these materials by means of small angle X-ray scattering (SAXS). In the present work we first summarize some of the earlier results on the mechanical properties which are significant for this investigation. We then present some results on the structure obtained by SAXS and discuss the relations between the structure and the mechanical properties.

EXPERIMENTAL

Tensile properties were determined on standard dumbbell specimens at a jaw separation speed of 0.5 m/min on a Zwick Model 1454 tensile tester. SAXS measurements were carried out using Ni-filtered Cu-k_α-radiation, a Kratky-Compact-Camera, and proportional detector with energy discrimination. Absolute intensity was measured using the moving slit method (5). The data were analyzed following a procedure reported elsewhere (6, 7), which allows a precise determination of the fluctuation background. Some measurements were also performed at HASYLAB (Hamburg Synchrotron Radiation Laboratory). A series of X-ray diffraction patterns were collected while the specimens were continuously extended.

MATERIALS

The polymer investigated is a linear SBS triblock copolymer, the molecular weight, M_n, of the butadiene block being 80,800 g/mole and that of each styrene end-block 21,200 g/mole. The synthesis technique was described earlier (8, 9). The polymer was diluted by two different mineral oils, a paraffinic one called "Oil P" and an aromatic one called "Oil A". Some properties of the two oils are summarized in *Table 1*.

Since SAXS is caused by variations of the electron density within the sample volume and SBS copolymers can be described by the model of a two-phase system, the electron densities of the extender oils were determined and compared with those of pure polystyrene and polybutadiene. Elementary analysis showed that more than 98 wt percent of both oils consists of the two elements, C and H. Neglecting the rest

we computed the C/H-ratio to be 1.90 for the paraffinic and 1.42 for the aromatic oil. This yields electron densities $\rho = 296\ el/nm^3$ for the paraffinic and 336 el/nm^3 for the aromatic oil, using the mass densities. Compared with the electron densities of the two polymer phases, ρ of the aromatic oil is close to the electron density of a pure PS sample (339 el/nm^3) and ρ of the paraffinic oil lies near the electron density of pure PB (301 el/nm^3).

The polymer films were obtained by spin casting from toluene solution containing the necessary amounts of polymer and extender oil. After 4 h the films were dry and could be taken from the heated cylindrical rotating cast mold (2).

MECHANICAL PROPERTIES

In *Fig. 1* some typical stress-strain curves are presented. They show the following features: already at low strains, yielding and drawing is observed. This is followed by a hardening effect at medium strains. Beginning from a certain oil concentration (33 wt percent for paraffinic oil, 50 wt percent for aromatic oil) an inflection in the stress-strain curves at large strains occurs. The higher the oil content, the later the hardening effect will show up.

The chemical composition of the mineral oil has a significant influence on mechanical properties: at constant oil level, the higher the content of aromatic hydrocarbons in the oil, the larger is the stress at any given elongation.

In the following, the "large strain tensile modulus", f, will be considered. In rubber technology this quantity is a widely used parameter describing the elastic properties of elastomers and is defined as the stress at a fixed elongation (usually $\lambda = 2$, 4, or 6). Since calorimetric measurements (3) suggested that the oil goes mainly

Table 1. Properties of Extender Oils.

Property	Oil P	Oil A
Color	colorless	black
Density at 25°C [kg/m³]	866.5	1009.6
Electron density [el/nm^3]	296.	336.
Refractive index	1.4749	1.5785
Viscosity	0.134 (a)	118. (b)
Structural composition (c)		
Aromatic C [wt%]	3.5	45.
Naphtenic C [wt%]	29.9	21.
Paraffinic C [wt%]	66.6	34.

(a) Kinematic, at 37.8°C (m²/h); (b) Saybolt, at 100°C (deg. Saybolt); (c) calculated from refractive index, density and mol. wt.
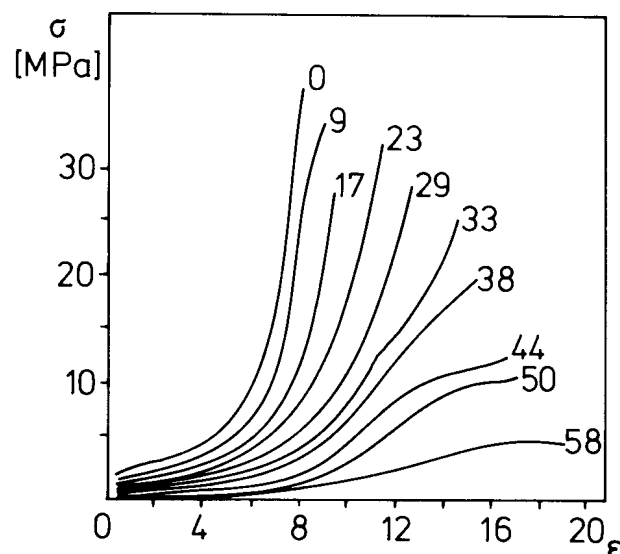

Fig. 1. Stress-strain curves of SBS triblock copolymers diluted with Oil P. Parameter: Oil concentration in wt percent. $\epsilon = \lambda$-1.

into the rubber matrix, the volume fraction of oil in the butadiene phase, ϕ_{OB}, is used to describe the oil dilution of the polymer.

Figure 2 shows the large strain modulus f at $\lambda = 4$ as a function of the volume fraction of oil in polybutadiene, ϕ_{OB}, in a double logarithmic scale. It can be seen that the modulus decreases with increasing dilution, but the dependence is not a linear one: after an initially gentler descent, at higher degrees of dilution a steeper decrease follows. The onset of the transition depends on the chemical composition of the oil (33 wt percent corresponding to $\phi_{OB} = 0.43$ for paraffinic oil; 50 wt percent or $\phi_{OB} = 0.56$ for aromatic oil). Moreover, for aromatic oil dilution a short plateau is observed at the beginning of the curve.

An attempt was made (3, 4) to interpret the stress-strain data in terms of the known constitutive equations for elastomers (Mooney-Rivlin (10) and Guth-Smallwood (11, 12); Holden (13); Leonard (14)). However, no satisfactory results over the whole range of oil dilution were obtained. Since the theories mentioned are restricted to the case of rigid particles of constant shape in an elastic matrix, it seemed obvious that one has to consider changes of the shape of these particles in order to improve the agreement. This was done (3) by multiplying the Mooney-Rivlin equation describing f for unfilled elastomers with a strain amplification factor γ:

$$f = (2C_1 + 2C_2/\lambda)(\lambda - 1/\lambda^2)\cdot\gamma. \qquad (1)$$

C_1 and C_2 are two constants. In the case of rigid rodlike domains γ is given by the Guth function:

$$\gamma = E/E_0 = 1 + 0.67p\phi_S + 1.62p^2\phi_S^2 \qquad (2)$$

with E and E_0 being the Young's moduli of the filled and unfilled elastomer respectively, ϕ_S the volume fraction of the rigid domains and p a shape factor defined as length/diameter. Although *Eq 2* is strictly valid only for rodlike filler particles, the variation of the ratio p/p_0

(p_0 is the shape factor for the undiluted copolymer), can be ascribed to morphological changes of the rigid domains. *Figure 3* shows the ratio p/p_0 as a function of oil content calculated from the data given in (3): with increasing oil content, p/p_0 first remains constant and then decreases. The latter reduction of p/p_0 indicates a transition from elongated domains (lamellae or rods) towards more spherical shapes, taking place at about 33 wt percent for paraffinic oil and 50 wt percent for aromatic oil.

STRUCTURE DETERMINATION

There already exists some knowledge on the structure that can be considered as a base for the further examinations: As the polybutadiene is the major component in the copolymer, polystyrene will form distinct domains within a polybutadiene matrix. Furthermore, for the composition of the undiluted sample in question, the polystyrene particles are expected to be of cylindrical shape. Due to calorimetric results (3), one can also assume that both the paraffinic and the aromatic oil will mainly go into the polybutadiene phase. However, several important questions still arise:

1. What are the shapes and dimensions of the domains formed by the styrene blocks when the polymer is diluted with oil?

2. Does the oil go completely into the polybutadiene matrix or does it also enter the polystyrene phase?

3. How complete is the phase separation between styrene and butadiene blocks?

4. Is it possible to prove the morphological changes indicated by mechanical measurements at a critical value of oil content, by means of other, more direct methods?

Shape, Dimensions and Superstructure of PS Domains

An attempt to determine the shape of the domains by electron microscopy (15) was not successful. It turned out that no contrast was
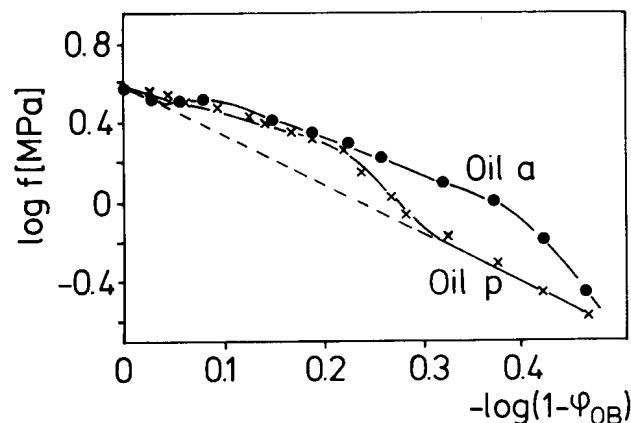

Fig. 2. "Large strain tensile modulus" f at $\lambda = 4$ of the SBS copolymer as a function of the volume fraction ϕ_{OB} of oil in the PB phase. Volume additivity of the oil and the polybutadiene is assumed. (×): paraffinic extender oil; (●): aromatic extender oil.
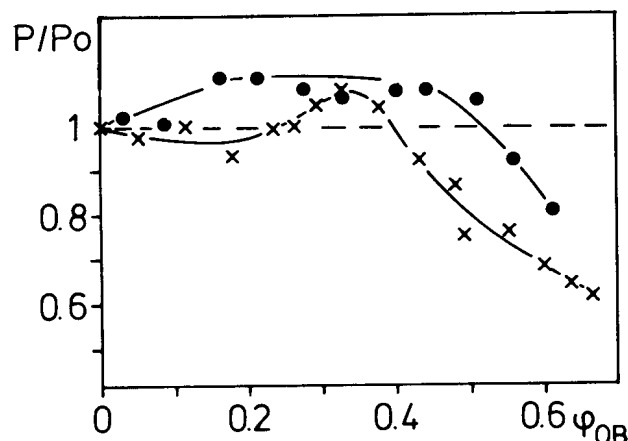

Fig. 3. Variation of the shape factor, p/p₀, as a function of oil content, ϕ_{OB}, at $\lambda = 4$. (×): paraffinic extender oil; (●): aromatic extender oil.

obtained by usual staining techniques, probably because the phase separation of styrene and butadiene is not complete (see section 3). Therefore, we tried to get results by SAXS.

Figure 4 shows the SAXS curves for the pure block copolymer, as well as some curves for samples extended with paraffinic oil. Similar curves were obtained for the case of aromatic oil. The patterns are typical for such triblock copolymers, showing just two relatively broad peaks. If the superstructure formed a completely regular arrangement, it would be possible to distinguish between different morphologies. In this case, due to distortions in the regular arrangement, this attempt with the sample investigated here would be questionable. In any case, by means of the Bragg equation, from the position of the first strong maximum it is possible to calculate the most probable interdomain distance, the long period L. With the sample without oil, a value of $L = 43$ nm is obtained.

Drawing the sample will cause the superstructure to orient, thus allowing more parameters to be determined. *Figure 5* shows one of the SAXS pictures obtained under sample stretching at HASYLAB. In this case, a layer line pattern is obtained: a series of parallel narrow lines perpendicular to the stretching direction, whose intensity envelope gives rise to an ellipsoidal pattern with its longitudinal axis parallel to the lines. In *Fig. 6* a structural model is visualized, in which all these results are
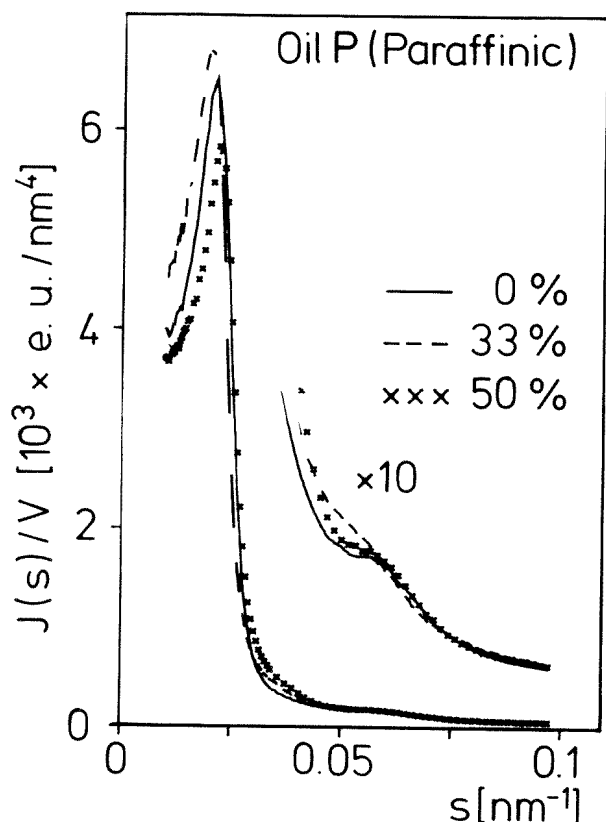
taken into account. It shows polystyrene cylinders of height h and diameter d in a polybutadiene matrix. As usually assumed, the long period obtained by SAXS for the unstretched sample is considered to be the distance between cylinders in lateral dimension, designated by L in *Fig. 6*. From the SAXS pattern of the oriented material, a rough approximation for the dimension of the polystyrene particles and the distance L_1 between them can be obtained (16). This gives, for the undiluted polymer and $\lambda = 6$, cylinders of height $h = 39$ nm, and diameter $d = 24$ nm at a distance of $L_1 = 230$ nm in the stretching direction. If we now describe our unstretched system using the so obtained cylinder
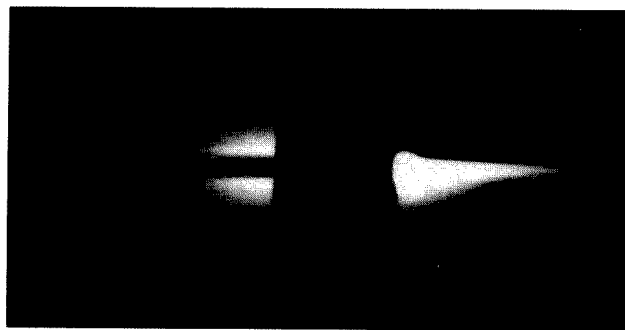

Fig. 5. SAXS layer line pattern of undiluted SBS sample, oriented by stretching to $\lambda = 6$.

Fig. 4. Absolute SAXS intensities for the SBS sample diluted with different amounts of paraffinic oil. Parameter: weight percent of oil.
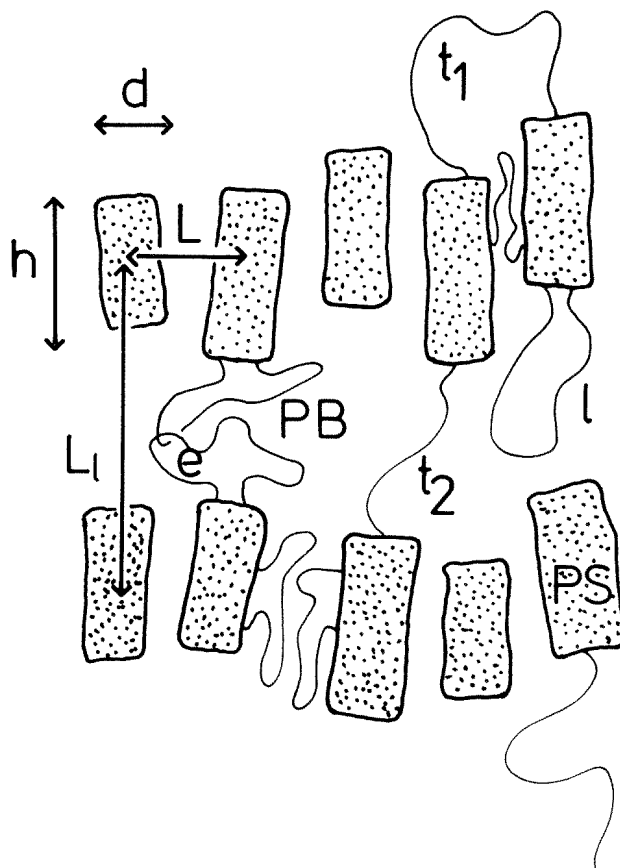

Fig. 6. Structural model of the arrangement of the PS domains in the PB matrix. In order to avoid confusions, only a few PB chains are shown.

dimensions and a hexagonal superlattice, we can even compute the distance L_1 for the unstretched sample. We find $L_1 = 55$ nm. A more complete analysis of drawing data will be reported elsewhere (16).

How does the structure change if oil is added? *Figure 7* shows the long period L as a function of the amount of oil for both oils. If the dimension of the PS domains do not change, the slow increase of L with increasing oil dilution is not compatible with an affine swelling of the superstructure. In order to explain the smaller increase of L we have to assume a preferential swelling of the matrix along the longitudinal axis of elongated polystyrene domains yielding an increase of L_1. Under the above mentioned assumption of preferential swelling the value of L_1 for a sample diluted with 50 wt percent of aromatic oil would be increased from 55 to 140 nm. In case the height of the cylinders decreases from 39 to 33 nm, as suggested by some preliminary measurements (16), L_1 would increase only to 135 nm, the anisotropic effect becoming much smaller.

Let us speculate in order to find a possible reason for such an inhomogeneous swelling. The two styrene blocks of each molecule may lie either in the same cylinder or in two different cylinders. In the first case, the PB block forms a loose loop 1 (*Fig. 6*). If, however, the two PS blocks of a molecule are lying in different cylinders, the included PB block must form a tie chain connecting these cylinders. They may connect either two blocks in cross direction, like the chain t_1 in *Fig. 6* or two blocks in longitudinal direction, like t_2. By simple entropy considerations one can deduce that tie chains of the type t_1 will occur much more frequently

than those of the type t_2: The first ones are part of molecules, which are quite close to the most probable coil conformation, for example the distance in cross direction between two cylinders, L-d, agrees quite well with the average end-to-end distance of a PB block. In contrast, the chains of the type t_2 belong to molecules, which are considerably extended. Due to the large decrease of entropy with extension, the formation of such tie molecules is improbable. In the longitudinal direction, the cylinders are held together by entanglements between loops (*e* in *Fig. 6*) rather than by tie molecules.

The long period L in the cross direction is defined by the principle of maximum entropy of the tie chains t_1. The so-defined long period strongly resists any changes imposed by other influences like addition of oil. On the other hand, the long period in longitudinal direction can be changed more easily, as there are almost no tie chains.

In this model the oil concentration between the cylinders in the cross direction may be somewhat lower than between the cylinders in the longitudinal direction. This can be explained by the fact that there arises an additional pressure in the cross direction due to some elongation of the t_1 molecules. In the longitudinal direction this pressure is not present.

The decrease of the large strain tensile modulus with increasing oil content may be explained by a decrease in the number of entanglements between the loops (*e* in *Fig. 6*).

Phase Separation in the Undiluted Polymer

An important quantity is the scattering power, Q, defined as the absolute intensity integrated over all angles. For a two-phase system the measured Q can be expressed in terms of the electron densities, ρ_i, and the volume fractions, ϕ_i, by:

$$Q = (\rho_2 - \rho_1)^2 \cdot \phi_1 \phi_2. \qquad (3)$$

For the pure triblock copolymer ϕ_1 is the volume fraction of polystyrene, ϕ_2 that of polybutadiene and ρ_1 and ρ_2 are the electron densities of the two materials. Thus $\Delta\rho = (\rho_2 - \rho_1)$ is 38 el/nm^3 and ϕ_1 is 0.31. From this, one obtains $Q = 309$ el/nm^3. From our experimental data we have obtained a value of 119 ± 2 el/nm^3. From this, by means of *Eq. 3*, the electron density difference $\Delta\rho = 23.5$ el/nm^3 is obtained. Thus $\Delta\rho$ of undiluted SBS obtained by SAXS, is far below the theoretical value mentioned above.

These data show that the initial SBS-block-copolymer cannot be treated as an undisturbed two-phase system, in which both phases behave like pure PS and PB. The phase separation seems to be incomplete. This result is in agreement with electron microscopy observations. As mentioned above, electron microscopy failed to visualize the superstructure in rapidly cast SBS films like the ones studied here (15). The stain-
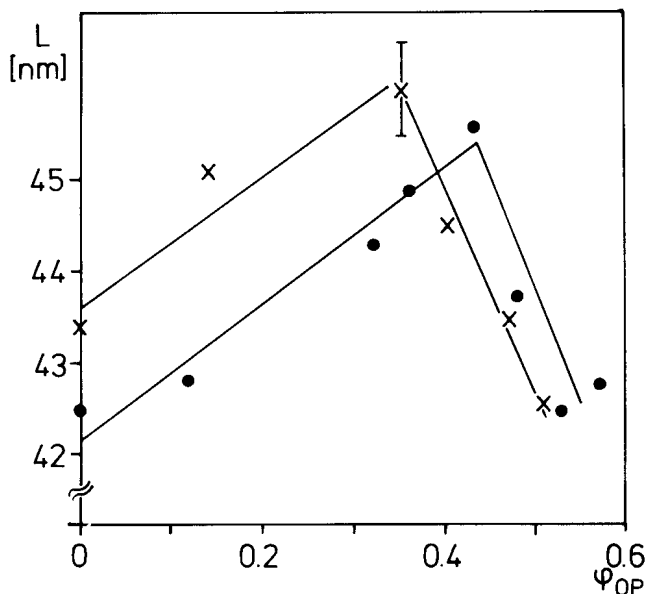

Fig. 7. Long period L as a function of the volume fraction of oil in the polymer. Additivity of the volumes is assumed. (×): paraffinic extender oil; (●): aromatic extender oil.

ing agent seems to couple not only to the PB phase, but also to the PS phase. Therefore, this phase obviously is contaminated by PB.

One can try to estimate which amount of PB is mixed with the PS cylinders and vice versa. If one assumes a pure PB phase and a mixed PS/PB phase, one obtains that 23 vol percent of PB is present in the PS domains. On the other hand, if one has a pure PS phase, one obtains that 16 vol percent of PS is present in the PB domains. For $\Delta\rho$ this yields values of 22 el/nm^3 in the first and 31 el/nm^3 in the second case.

In which phase does the oil go?

The scattering power Q has been also determined for the samples diluted by oil. *Figure 8* shows Q as a function of the volume fraction of oil in the polymer, ϕ_{OP}. As can be seen, one obtains a constant value with the paraffinic oil and a linear decrease with the aromatic one. For $\phi_{OP} = 0$ the value $Q = 119.5$ el/nm^3 mentioned before is obtained.

In *Table 2* the electron densities of the polymers and the oils are summarized. According to these values, if the oil A went into the PS phase, both the electron density difference $\Delta\rho$ and $\phi_1\phi_2$ would remain almost constant. As a consequence (*Eq 3*), Q should not change very much. This is obviously not the case. On the other hand, if one assumes that the oil A is going into the PB phase, $\Delta\rho$ and therewith Q should decrease. Therefore, the results indicate that the oil A is going into the PB phase. Let us next consider the oil P. If it went into PS phase, $\Delta\rho$
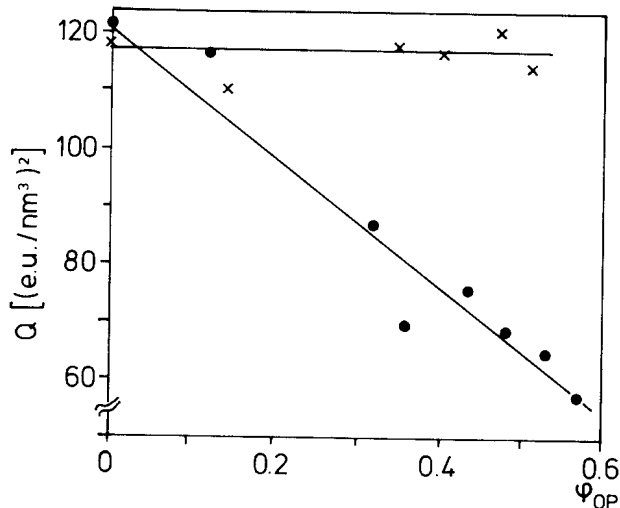
would strongly decrease, while $\phi_1\phi_2$ would remain almost constant. A rapid decrease of Q would be expected, in contrast to the results. If, on the other hand, the oil goes in the PB phase, $\Delta\rho$ is constant, while $\phi_1\phi_2$ slightly decreases. This is in much better agreement with the results of a constant value of Q.

For a more quantitative analysis, from *Eq 3* the electron density difference $\Delta\rho$ was calculated under the assumption that the oil goes into the PB matrix and that the volumes are additive. The results are shown in *Fig. 9*. One can see that $\Delta\rho$ considerably increases with increasing amount of paraffinic oil. With aromatic oil $\Delta\rho$ first remains constant, then decreases and eventually increases again. As mentioned in section 1) of this chapter, the phase separation between PB and PS is incomplete. If we assume a pure PS phase in which some PB is present and, further, that the oil only enters the PB phase, we would get the curve indicated by the dashed lines in the figure. If, moreover, the PB is assumed to contain some PS, the slope of the line is slightly changed. In a very rough approximation the experimental data follow the theoretical lines, so that it can be concluded that the assumption

Fig. 8. *Absolute scattering power Q as a function of the volume fraction of oil in the polymer. Additivity of the volumes is assumed. (×): paraffinic extender oil; (●): aromatic extender oil.*

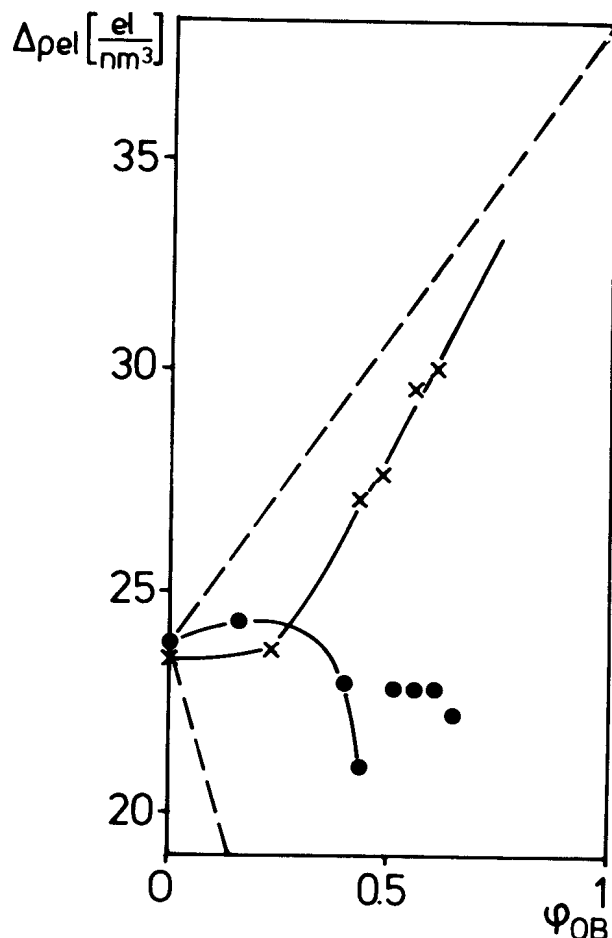Fig. 9. *Electron density difference $\Delta\rho$ between the two phases of oil diluted SBS copolymers as a function of the volume fraction of oil in the polymer. Additivity of the volumes is assumed. (×): paraffinic extender oil; (●): aromatic extender oil.*

Table 2. Electron Densities of the Polymers and the Oils.

	PS	PB	Oil P	Oil A
electron density [el/nm^3]	339	300	296	336

that the oils only enter the PB phase is correct. However, the deviations from the theoretical behavior observed are far beyond the experimental error. How can these deviations be explained?

Let us first consider the paraffinic oil, if one extrapolates the experimental results to $\phi_{OB} = 1$, one obtains a value of $\Delta\rho = 38\ el/nm^3$, which is the theoretical value calculated for pure PS and PB. As the electron density of this oil is close to that of PB, one has to conclude that in this extrapolated situation the phase separation of PS and PB would be complete. Therefore, we can state that an increasing amount of paraffinic oil improves the phase separation between PS and PB domains.

At small concentration no increase of $\Delta\rho$ is observed. This suggests that for such small concentrations of oil the additivity of volumes is not strictly valid: small amounts of oil can enter some "holes" in the PB matrix.

A completely different behavior is observed in the case of the aromatic oil. Here, a decrease of $\Delta\rho$ with increasing oil content is observed. This decrease is, however, considerably smaller than would be expected theoretically. Apparently, the volume of the PB/aromatic oil blend increases more rapidly than the volume additivity would suggest. This can be explained by the incompatibility between the aromatic oil and PB. The later increase of $\Delta\rho$ from $\phi_{OB} \approx 0.5$ might be ascribed to a true phase separation of oil and PB.

From the tails of SAXS curves, the fluctuation of the electron density within each phase averaged over both phases, I_{Fl}, can be calculated. This quantity is a measure of the homogeneity within the phases. Figure 10 presented the values obtained from our data. As can be seen, with paraffinic oil dilution, I_{Fl} remains almost constant, while it strongly increases under aromatic oil extension. This confirms that the paraffinic oil homogeneously mixes within the rubber phase. On the other hand, the steep increase of I_{Fl} for aromatic oil shows that this oil considerably raises the inhomogeneity when it goes into the PB phase. As aromatic oil mixes in even parts, the fluctuation background has a sudden drop. We assume that a critical concentration has been reached at which a phase separation between oil and PB can occur. During this phase separation, already suggested by the behavior of $\Delta\rho$, larger homogeneous oil regions (clusters, droplets) are formed within the PB phase.

An alternative explanation of the abrupt drop of I_{Fl} would be that from this concentration some oil enters the PS phase. SAXS is not able to distinguish between these two assumptions.

Morphological Changes

The onset of a morphological transition of the PS domains is more or less directly suggested by the trend of different parameters.
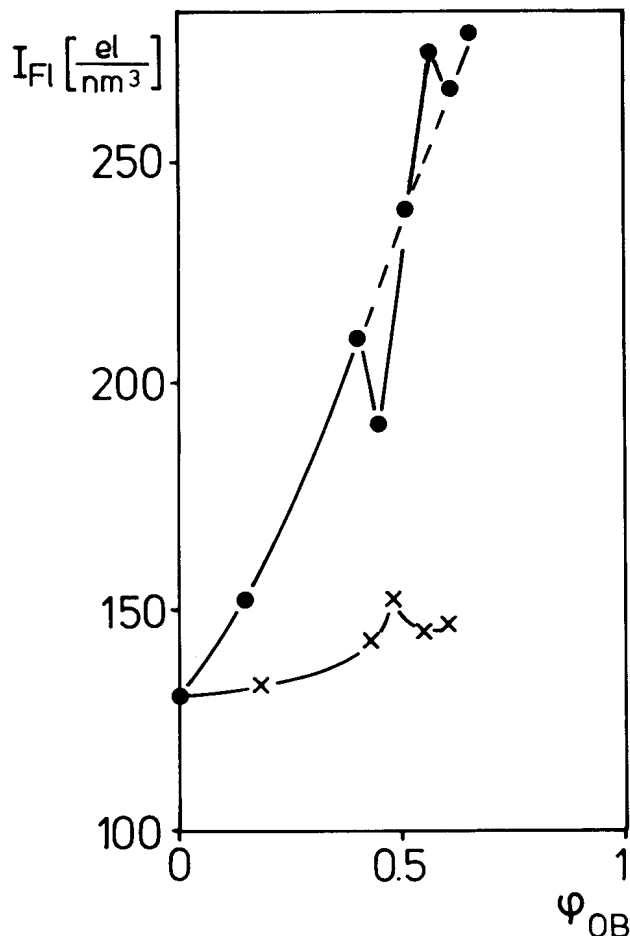

Fig. 10. Absolute electron density fluctuations I_{Fl} of oil diluted SBS copolymers. (×): paraffinic extender oil; (●): aromatic extender oil.

A rather sharp decrease of the long period L (Fig. 4) is observed for both oils at a certain critical value of dilution. These critical values (33 wt percent for paraffinic oil and 50 wt percent for aromatic oil) are the same ones at which a change of the shape factor is obtained in the investigation of the mechanical properties.

Also, sharp variations in the fluctuation background (Fig. 10) correlate with the points suggested for the morphological transitions.

A more direct indication is obtained by segment length distributions, calculated from the experimental SAXS curves (18, 19, 20).

CONCLUSIONS

The study showed that, even for films rapidly cast from solution, SAXS was able to detect a two-phase system similar to that found with slowly cast SBS films.

The following conclusions can be drawn concerning the structure and its relation to mechanical properties.

1. The polystyrene forms cylinders lying in a matrix of polybutadiene.

2. The phase separation between polystyrene and polybutadiene is incomplete.

3. Both oils enter mainly the polybutadiene phase.

4. Paraffinic oil favors the phase separation of PB and PS.

5. The local density fluctuations within one phase increase considerably if aromatic oil is added, while they remain constant upon dilution with paraffinic oil. This indicates that the compatibility of PB and the aromatic oil is bad.

6. Decrease of modulus with increasing oil content is explained by a decrease of entanglement density. Paraffinic oil is more effective because of its better miscibility with polybutadiene.

ACKNOWLEDGMENTS

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LIST OF SYMBOLS

C_1, C_2	constants
d	diameter of cylindrical polystyrene domains
$\Delta\rho$	electron density difference between the two phases
e	entanglement between chain loops
E	Young's modulus
E_0	Young's modulus of the unfilled elastomer
f	large strain tensile modulus
ϕ	volume fraction
ϕ_S	volume fraction of polystyrene
ϕ_{OB}	volume fraction of oil in polybutadiene
ϕ_{OP}	volume fraction of oil in polymer
γ	strain amplification factor
h	height of cylindrical polystyrene domains
I_{F1}	density fluctuation background
$J(s)/V$	absolute SAXS intensity
L	SAXS long period
L_1	lattice constant in longitudinal direction of the cylindrical polystyrene domains
l	loose chain loop
λ	draw ratio
M_n	number average of molcular weight
p	shape factor (length/diameter)
P_0	initial shape factor (sample without oil)
Q	scattering power
ρ	electron density
s	scattering vector ($s = 2 \sin (\Theta)/\lambda$
t_1	tie chain in cross direction
t_2	tie chain in longitudinal direction
Θ	half of scattering angle

DISCUSSION: H. G. ZACHMANN

M. XANTHOS: Some years ago there was similar work done on SBS attempting to correlate the mechanical properties with various models, e.g. considering the material as short fiber reinforced composites. Could you treat your system in a similar way and compute the modulus of polybutadiene phase plasticized by oils? There are good theories for composites. The computed values could then be compared with experimental variation of modulus of plasticized polybutadiene.

H. G. ZACHMANN: I was concerned with the structure investigation. The mechanical properties which we reported were not of prime interest. I indicated that some of the mechanical properties can be explained by means of the shape change of the dispersed phase. In the literature SBS was treated as a rubber with rigid particles in it. For rubbers, the Mooney theory and that by Guth, allows calculation of modulus variation with particle content, as well as of that with aspect ratio (see *Ref. 4* in our paper). Using this theory we concluded that the dispersed phase undergoes transition from spheres to cylinders.

M. XANTHOS: Have you done any T_g measurements?

H. G. ZACHMANN: My co-author published these data. It was shown that T_g of polystyrene did not change upon addition of the oils, concluding that the oils go into polybutadiene phase.

M. A. VALLANCE: Trying to explain different non-equilibrium moduli (dependent on the rate of strain) one has to consider the entanglement density at the temperature relative to T_g for the oil impregnated material. Would it not be better

to test these materials at different absolute temperatures but always the same vis-a-vis T_g?

H. G. ZACHMANN: This is a point worth considering. Actually with polybutadiene we are high above $T_g \simeq -100°C$ and even higher for oil extended SBS. According to rubber theory at high enough temperatures above T_g the elastic constant should be proportional to the absolute temperature. Therefore, we expect that T_g is not of influence.

M. A. VALLANCE: When you start the loading experiment and then stop it the material will relax indicating that it was not at equilibrium. The entanglements will also relax out. So the entanglement argument does not seem to be valid.

H. G. ZACHMANN: We think that entanglements exist by virtue of the postulated two interpenetrated loops and they are permanent.

L. A. UTRACKI: George Hadziioannu working on his PhD thesis in Strasbourg found that in order to perfect the SBS morphology, a dynamic shear field of specific character had to be imposed for rather a long time. He constructed a special shearing device and optimized the dynamic parameters, amplitude, and frequency, to achieve nearly perfect pseudo-crystalline structures. However, the problem is so difficult, that after he left CRM for several years nobody seemed to be able to achieve similar degree of perfection of SBS morphology using the same equipment, conditions, and samples. Apparently, development of an equilibrium structure in SBS with the spacing calculable from the molecular parameters is not easy. The morphology which you have with the low value of the scattering power parameter Q may in effect be evidence of the imperfect phase separation, a sort of locking of one phase within the domain of another. This can be verified by using SBS samples with different molecular weights and/or developing similar methods of phase perfectioning as that used by Hadziioannu.

H. G. ZACHMANN: We agree that we are far from equilibrium with respect to phase separation of the polybutadiene and the polystyrene phase. We have just started to investigate SBS-samples prepared in other ways. Here, Q was still smaller by a factor of 5. We have also prepared specimens using Peterman's method. The new specimens had all higher Q-value than those prepared by our old method, but while the increase for the new samples was large that for the samples discussed in this paper was hardly significant. This shows that equilibrium is approached at different extents in the various samples. Why would you expect the molecular weight to make a difference?

L. A. UTRACKI: Diffusion rate and solubility.

H. G. ZACHMANN: I do not think that this is a solubility effect. I think that the sample cast from solution does not easily reach phase equilibrium. By adding the paraffinic oil the rate of phase separation is increased.

L. A. UTRACKI: Perhaps one should also look at solubility. Addition of paraffinic oil can play a role of a nonsolvent, precipitating the small quantity of polystyrene from the polybutadiene phase.

H. G. ZACHMANN: We did not think of that but we will consider it.

A. CERVENKA: Was your SBS sample one of the Shell Kraton resins?

H. G. ZACHMANN: No, it was a copolymer made in Roumania. We have another one from China. But if you have an interesting SBS we would like to have one from Shell too.

A. CERVENKA: Another important parameter to consider is the number of blocks. There are samples with two, three, four, and multi-blocks available, linear and star-shaped. Furthermore, polybutadiene can be hydrogenated into ethylene and/or butylene copolymer. Hydrogenation may give you a better contrast. Finally, the styrene-polybutadiene copolymer may have a tapered composition, not a sharp change from 100 percent styrene block to 100 percent butadiene block but a gradual one. From the thermodynamics point of view this would reduce phase separation tendency.

H. G. ZACHMANN: These are very good suggestions.