

Microscopy and laser diffraction investigation of block copolymers used as adhesives

J. M. Widmaier and G. C. Meyer

Ecole d'Application des Hauts Polymères, Louis Pasteur University, Strasbourg, France

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In a previous paper, we established a relationship between the adhesive properties and the chain characteristics of ABA poly(styrene-*b*-isoprene) block copolymers (or SIS). Only copolymers which do not easily undergo phase separation give joints with high tensile lap-shear resistance. By optical and electron microscopy, as well as by laser diffraction, we have now studied the structure of a series of SIS copolymers. We found that a random distribution of small polyisoprene noduli in the polystyrene matrix effectively exists in SIS which show good adhesive properties.

INTRODUCTION

We are currently investigating the utilization of non-compounded ABA poly(styrene-*b*-isoprene) block copolymers (SIS) as heat activated adhesives. Recently, we have shown¹ that high shear resistance is obtained for joints assembled with SIS films having a total molecular weight of about 25 000 and 30% polyisoprene content. Failure is always cohesive, thereby indicating that adhesion to the substrate is at least as high as the cohesive strength of the SIS film itself. Outside of this zone, the SIS copolymers present rather poor adhesive properties.

By examining their molecular characteristics, it can be seen that only SIS with small blocks of nearly equal length show good adhesive properties. Such chain parameters do not favour phase separation², especially when the solubility parameters of the different blocks are close together as they are for polystyrene and polyisoprene³.

All these parameters lead to a high and irregular dispersion of very small elastomeric noduli in the polystyrene matrix, rather than to the well known organization in mesomorphic structures, such as spheres, cylinders and lamellae⁴.

Films obtained from such copolymers therefore, show a rather continuous polyisoprene distribution favouring multiple contacts, and thus good adhesion to the substrate. As stress distribution is uniform over the bonded area, the shear resistance of the joint is improved as well.

This interpretation is a good explanation of our experimental results. In order to establish the relationship we found between the degree of dispersion and the adhesive properties of block copolymers more strongly, we examined SIS films by optical and electron microscopy. Laser beam diffraction experiments were also carried out. Optical polarizing microscopy allows quantitative determination or at least qualitative evaluation of the anisotropy of the SIS films; thus, if very small polyisoprene noduli are randomly dispersed in the polystyrene matrix, the corresponding films appear isotropic. By electron microscopy and laser diffraction, the size of the noduli and their eventual degree of organization can be visualized and evaluated. Moreover, laser diffraction patterns allow detection of microstructures which could not be found by examination of a micrograph.

EXPERIMENTAL

SIS copolymers

SIS copolymers were prepared by the now classical anionic 3 step polymerization, which yields products with low polydispersity⁵. Within experimental error, all the SIS have polystyrene blocks of the same molecular weight. Their chain characteristics appear in *Figure 1*.

Films were usually obtained by compression moulding to 0.10–0.15 mm thickness. Benzene was used when solvent-cast films were needed.

Joint formation and joint breaking were described recently in detail¹ and will only briefly be mentioned here: a simple lap joint was formed, with glass plates as substrates. The film, cut to size, was inserted between the plates and the whole heated at 135°C for 2 h (usual conditions). For each copolymer, 5 joints were tested and the average value of the tensile shear strength at break, \bar{F} (kg/cm²) was calculated.

Optical microscopy

Observations were carried out on a polarizing microscope

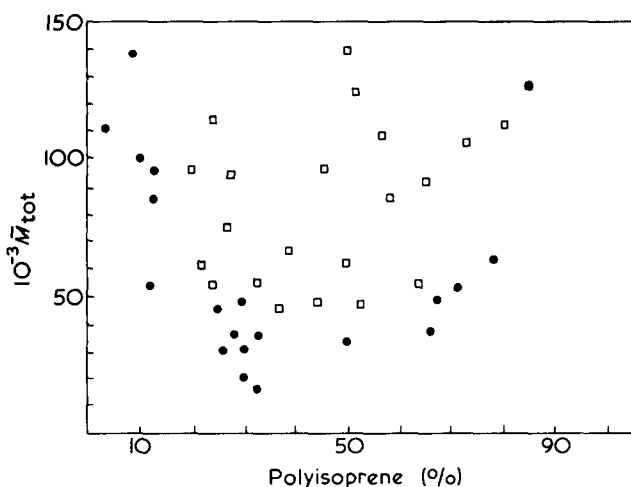


Figure 1 Total molecular weight versus isoprene content. ●, Isotropic SIS films; □, anisotropic SIS films

(model Ortholux, Leitz). Evaluation of the degree of anisotropy was not possible, as phase difference of the samples was too small.

Electron microscopy

Copolymer films were stained using Kato's osmium tetroxide (OsO_4) method⁶. First, the sample was immersed for prehardening in an aqueous 2% OsO_4 solution for about 1 day. Sections of $\sim 500 \text{ \AA}$ thickness were cut on an ultramicrotome Porter-Blum with a diamond knife, at room temperature. The selected sections were further stained in OsO_4 vapour for periods depending on the isoprene content of the copolymer (15 min to 2 h).

Electron transmission micrographs were taken on a Elmiskop model 102 apparatus.

Laser diffraction

This technique was first reported by Fischer, Goddar and Schmidt⁷. It allows direct visualization of periodic structures in a rather simple way. The laser beam was diffracted by the negative electron micrographs and photographs of the diffraction patterns were taken. A Spectra-Physics He/Ne laser, model 161-2 was used at 514.5 nm (green radiation).

RESULTS AND DISCUSSION

First of all, it was important to determine exactly whether the degree of phase separation and/or the structure of the SIS films were due to the chain parameters of the copolymers themselves or to the successive treatments that they underwent. Thus, several preliminary observations of birefringence were made by optical microscopy: no difference was noted

between films obtained by compression moulding or by solvent casting. Neither did the film thickness (up to 1 mm) play any role.

We also checked the influence of the experimental conditions to which the films are subjected, like heating during joint formation, and shear stress when the joint is destroyed. These factors did not cause any change in birefringence. These observations show that for the SIS films used in this study, the history does not influence anisotropy, which hence results clearly from the molecular parameters of the copolymer.

In Figure 1, a point (\bar{M}_{tot} , %I) characterizes a copolymer. Squares and circles correspond to SIS films which appeared respectively isotropic and anisotropic when observed under polarized light. Roughly 2 zones appear: an inner one where

Table 1 Molecular characteristics and properties of some SIS block copolymers. Polyisoprene content of all SIS was near 30% by wt

Sample	\bar{M}_n SIS $\times 10^{-3}$	\bar{M}_{tot} $\times 10^{-3}$	\bar{F} (kg/cm ²)	Film [isotropic (i) aniso- tropic (a)]	Distrib. of PI noduli [random (r); orga- nized (o)]
351	8.5- 7.5- 8.5	24.5	140	(i)	-
346	11 - 9 -11	31	120	(i)	(r)
302	12.5-10 -12.5	35	92	(i)	(r)
514	16 -13.5-16	45.5	73	(i)	-
282	20 -16 -20	56	33	(a)	(o)
316	27.5-19.5-27.5	74.5	31	(a)	-
558	32 -25 -32	89	21	(a)	(o)
309	45 -33 -45	123	18	(a)	-

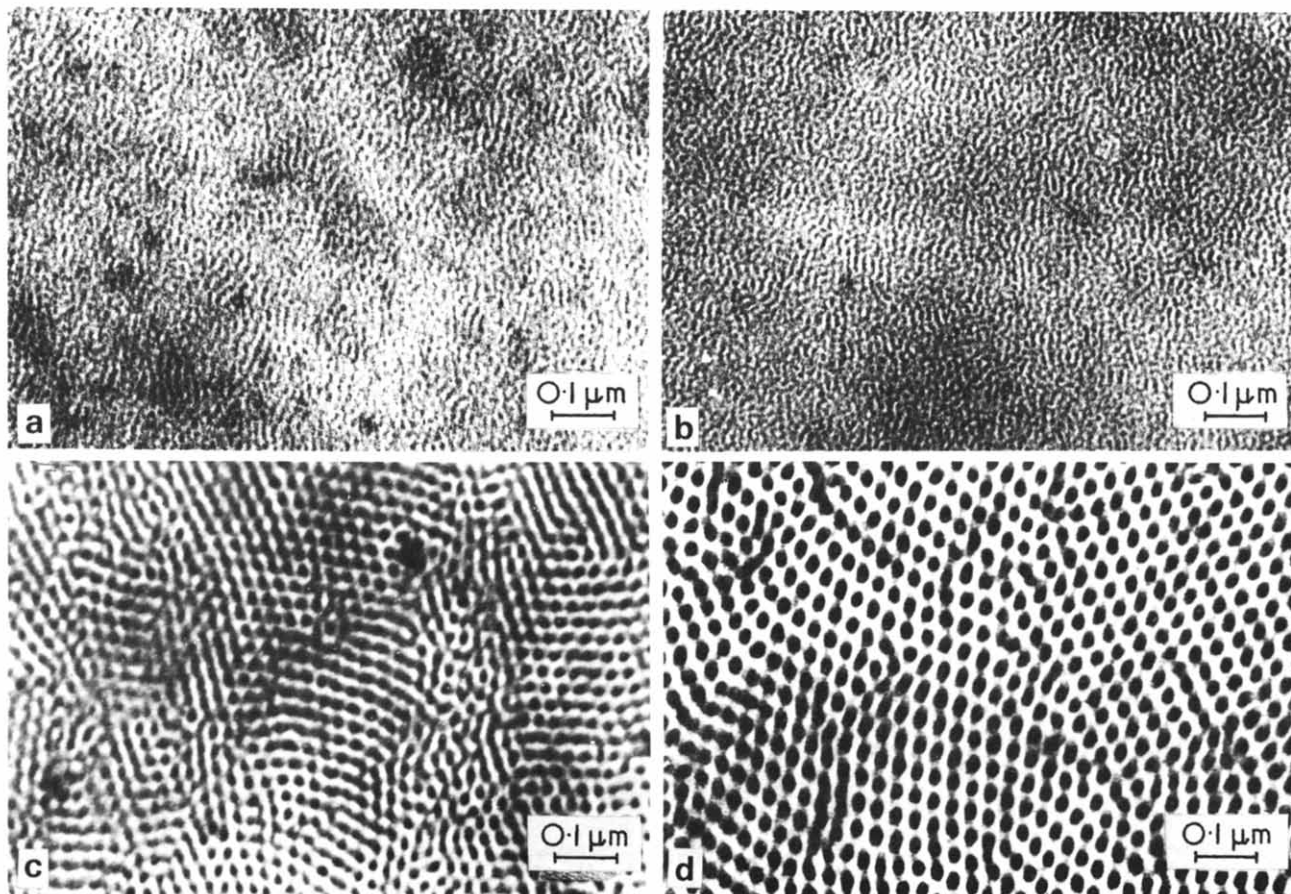


Figure 2 Electron micrographs of SIS films: (a) SIS 346; (b) SIS 302; (c) SIS 282; (d) SIS 558

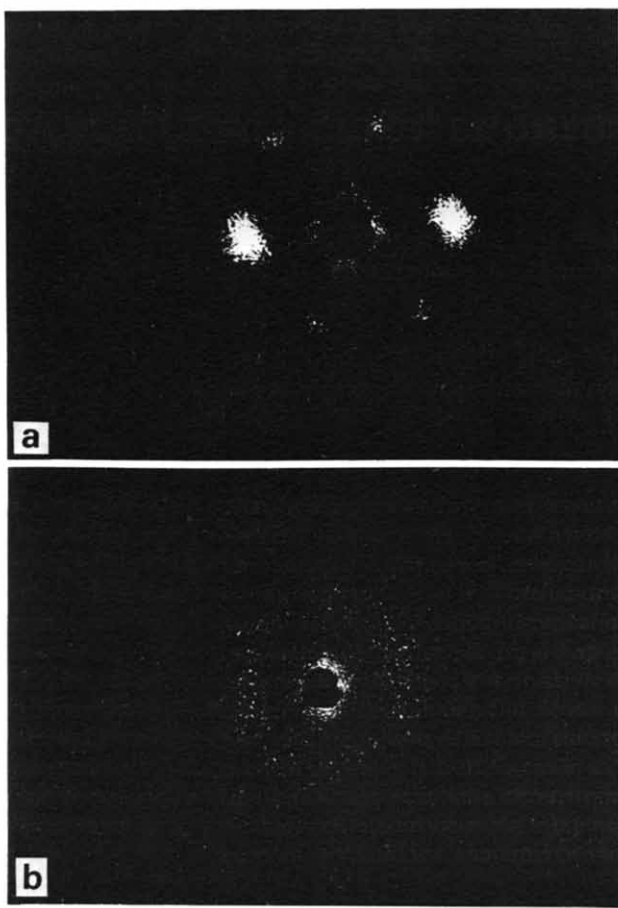


Figure 3 Laser diffraction patterns: (a) SIS 558; (b) SIS 302

films exhibit anisotropic behaviour, and an outer one, where isotropic films are present. This latter zone may be further divided into two categories. The first includes the SIS that have up to around 20% polystyrene or polyisoprene content and therefore show the well-known organization in spherical domains⁴. The second contains the SIS with a small overall molecular weight.

We found that the SIS which have good adhesive properties belong to this second category. However, as mentioned previously, low molecular weight alone does not impart adhesive strength: a polyisoprene content of around 30% is also required. For copolymers with low molecular weight, isotropy is due to the fact that phase separation occurs at a nearly molecular level, and even some phase mixing cannot be excluded. This kind of macroscopic isotropy can result from either an absence of any organized structure or the existence of very small organized structure, randomly distributed throughout the copolymer film.

Electron microscopy was therefore used to investigate some SIS films whose molecular characteristics are listed in Table 1.

Figures 2a and 2b show some representative micrographs corresponding to isotropic SIS films: no organization is visible. These figures can be compared to micrographs 2c and 2d which show SIS with higher molecular weights, but the same isoprene content. Here, as expected, a cylindrical structure appears clearly. Sections cut in different directions, fully confirmed the cylindrical structure. As may be seen in Table 1, high shear resistance corresponds well to SIS without structure, and *vice versa*.

Even at the electron microscopy scale, simple visual examination of micrographs like Figures 2a and 2b does not always allow one to determine whether an ordered structure exists or not. Laser beam diffraction by electron micrograph negatives proved to be helpful: the resulting diffraction pattern, like the ones obtained by small-angle X-ray diffraction, reveals the possible existence of a periodic structure.

Figure 3a shows the diffraction pattern corresponding to SIS 558, a copolymer with a cylindrical structure: a hexagonal organization appears, whereas no order can be detected for SIS 302 (Figure 3b). This fact confirms that copolymers like the latter have a rather uniform and random distribution of polyisoprene nodules in the polystyrene matrix.

These results evidently prove that the chain characteristics are one of the main factors governing the adhesive properties of SIS block copolymers. For the shear resistance to be high, a rather continuous repartition of the adhesive component throughout the film is necessary. This in turn requires chain parameters which do not favour phase separation, i.e. low total molecular weight, and not too great a difference in the solubility parameters. In addition, when the different blocks are of equal lengths, phase separation is the most difficult².

Recently, we were able to draw the same conclusions on the structure-adhesive properties relationship in another way, by studying star-shaped copolymers with SIS as branches⁸.

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REFERENCES

- 1 Widmaier, J. M. and Meyer, G. C. *Polymer* 1977, **18**, 587
- 2 Meier, D. J. *J. Polym. Sci. (C)* 1969, **26**, 81
- 3 Dawkins, J. V. in 'Block Copolymers', (Eds. D. C. Allport and W. H. Janes) Appl. Sci. Publ., London, 1973
- 4 Aggarwal, S. L. *Polymer* 1976, **17**, 938
- 5 Fetters, L. J. in 'Block and Graft Copolymerization' (Ed. R. J. Ceresa), Wiley, New York, 1972, vol 1
- 6 Kato, K. *J. Polym. Sci. (B)* 1966, **4**, 35
- 7 Fischer, E. W., Goddar, H. and Schmidt, G. F. *Kolloid Z. Z. Polym.* 1968, **226**, 30
- 8 Meyer, G. C. and Widmaier, J. M. *Polym. Eng. Sci.* 1977, **17**, 803