the difference between long and short chains (e.g., PE-A) becomes slightly negative at large $Q$ values. The crossover from a positive to a negative difference occurs at $Q \simeq 2/R_{g_A}$, where $R_{g_A}$ is the radius of gyration of the short chain. At much larger $Q$ the difference goes to zero. This occurs in the calculation at $Q \simeq 1/l$, where $l$ is of the order of the monomer bond length. A quantitative comparison of the calculated and the experimental scattering function is not possible since only the diffuse scattering contribution of eq 12 is known from the Monte Carlo calculations and the detailed chain geometry is not taken into account. The atomic structure of the PE and A chains is, however, the same and it should cancel out by taking the difference scattering function (PE-A). The change of the sign of the experimentally determined $\Delta(d\sigma/d\Omega)$ occurs at the $Q$ value predicted by the Monte Carlo calculations, which may serve as an indication for the validity of the simplifications used here.

In summary, the discussion of the measured scattering functions of polyethylene and *n*-alkane melts has shown that no evidence for back-folding of the polyethylene chains was found. Furthermore, details of the molecular conformations in the melt have been explained by effective intramolecular interactions which are attractive at large distances.

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# Stress–Strain Behavior of Thin ABA Poly(styrene-*b*-isoprene) Films

**G. C. Meyer* and J. M. Widmaier**

*Ecole d'Application des Hauts Polymères, 67000 Strasbourg, France.*
*Received November 6, 1980*

ABSTRACT: The stress–strain behavior of thin ABA poly(styrene-*b*-isoprene) films (SIS) was examined as a function of total molecular weight and polyisoprene (PI) content. The Young's modulus was found to increase classically with decreasing PI content, whereas the tensile strength goes through a maximum corresponding to the limit of filmability of the SIS copolymer.

We are currently investigating the adhesive properties of ABA poly(styrene-*b*-isoprene) triblock copolymers (SIS).[1] They are used as heat-activated thin films in simple overlap joints. Their tensile strength and their tensile shear strength have been studied in regard to the molecular characteristics of the SIS copolymers and several other parameters.[2]

The mechanical properties of a joint, mainly its resistance to various acting forces, depend not only on the adhesive forces developed between the adhesive and the substrate but also on their rheological properties. In our work, only undeformable (for the stresses involved) substrates (glass, steel, aluminum, and wood) were used. Therefore the mechanical properties of only the adhesive film could play a role in the overall behavior of the bonded joint. This consideration led us to investigate the tensile properties of thin films of SIS.

In the related literature, the mechanical properties of SIS copolymers have been extensively studied.[3-6] Interest has been mainly in block copolymers of the thermoplastic elastomer type which have over 60% polydiene content. In these copolymers, the polystyrene domains act as cross-linking points, thus reinforcing the mechanical resistance of the materials. Especially stress-strain properties have been investigated on several-millimeter-thick standard test samples. Much less work has been done on SIS with a rigid matrix[5] and, hence, a high Young's modulus. In turn, to our knowledge, there are no investigations on thin copolymer films.

In this paper, we report stress–strain measurements on some 30 thin SIS films (about 0.1 mm). Their tensile strength has been studied as a function of their molecular characteristics.

## Experimental Section

**Synthesis and Characterization of Block Copolymers.** SIS copolymers were prepared in the pilot plant of our Institute[7] by the now classical three-step anionic polymerization, in benzene at 50 °C, using *n*-butyllithium as initiator. Molecular characteristics were determined by gel permeation chromatography (GPC, Waters, in THF) and by ultraviolet spectroscopy (Cary 1501) and appear in Table I. Each copolymer is characterized by its total molecular weight, $M_{tot}$, and its elastomer content, % I.

**Obtention of Films and Test Samples.** SIS films were obtained by compression molding for 2 min at 180 °C, followed by rapid cooling. Dumbells (0.1-mm thick) for stress–strain ex-

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Table I
Molecular Characteristics, Average Tensile Strength, and Young's Modulus of SIS Block Copolymers

| SIS sample | $10^{-3}M_{\mathrm{tot}}$ | % I | $\bar{\sigma}_E$, MPa | $\bar{E}$, MPa |
|---|---|---|---|---|
| 344 | 30 | 26.2 | 4.2 | 860 |
| 302 | 35 | 28.6 | 8.8 | 630 |
| 346 | 31 | 29.9 | 7.4 | 700 |
| 330 | 27 | 33.3 | 12.2 | 540 |
| 583 | 31.5 | 40.1 | 9.9 | 380 |
| 564 | 32.5 | 50.6 | 7.2 | 260 |
| 374 | 55 | 12.7 | 20.2 | 1090 |
| 254 | 49 | 18.4 | 22.7 | 890 |
| 514 | 45.5 | 29.7 | 19.8 | 730 |
| 313 | 51 | 33.3 | 15.9 | 900 |
| 320 | 45 | 37.8 | 6.8 | 420 |
| 250 | 48 | 44.0 | 5.5 | 240 |
| 222 | 49.5 | 47.5 | 3.2 | 160 |
| 342 | 52 | 64.8 | 1.3 | 30 |
| 511 | 51 | 67.4 | 0.9 | 10 |
| 378 | 86 | 11.4 | 30.1 | 890 |
| 377 | 98 | 12.2 | 29.3 | 920 |
| 257 | 95 | 20.5 | 26.1 | 1100 |
| 252 | 93 | 26.9 | 20.8 | 820 |
| 558 | 89 | 28.1 | 26.2 | 970 |
| 253 | 85 | 34.1 | 17.8 | 810 |
| 522 | 96 | 45.8 | 13.0 | 500 |
| 314 | 85 | 59.0 | 4.4 | 230 |
| 347 | 98 | 62.3 | 1.6 | 60 |
| 521 | 98.5 | 71.9 | 0.8 | 10 |

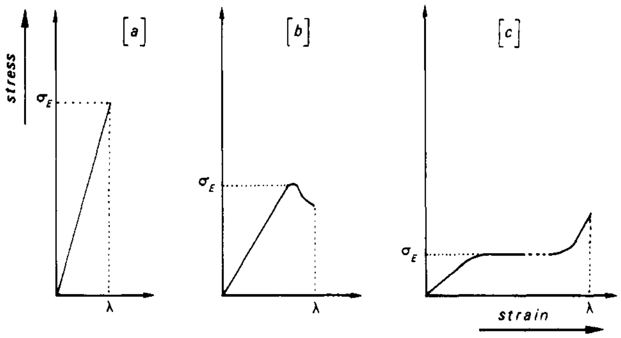

**Figure 1.** Typical stress–strain curves for SIS films, with elastomer content increasing from left to right.

periments were stamped out of these films (overall dimensions, 75 × 12 mm; gage dimensions, 25 × 4 mm). The exact thickness was measured with a micrometer.

**Stress–Strain Experiments.** Stress–strain experiments were carried out on a Zwick testing machine (Model Z13), with a crosshead separation speed of 2 mm/min. For each copolymer, at least 10 dumbells were tested. The average tensile strength $\bar{\sigma}_E$ and the average Young's modulus $\bar{E}$ are listed in Table I. The accuracy, as determined from standard deviation calculations, is around 20%. Though fairly high, such an error is usual in the evaluation of the mechanical properties of polymers.

## Results and Discussion

The stress–strain curves for the various SIS copolymers have the shapes illustrated in Figure 1. They depend, as expected, on the composition of the copolymer: for polyisoprene contents less than about 40%, an elastic behavior with 2–5% elongation appears (Figure 1a); for higher contents, a ductile deformation to failure occurs, preceded by a yield point (Figure 1b); finally, with a still higher polyisoprene percentage, there is an important elongation before break (Figure 1c).

We have also observed these types of curves when breaking adhesive joints bonded with SIS films:[2,8] in that case, the curves obviously ended at the point corresponding to joint failure. For the films used in this work, we have also taken into consideration this value of tensile strength, rather than the usual ultimate tensile strength. It corresponds to the break resistance in Figure 1a and to a yield point in Figures 1b and 1c.

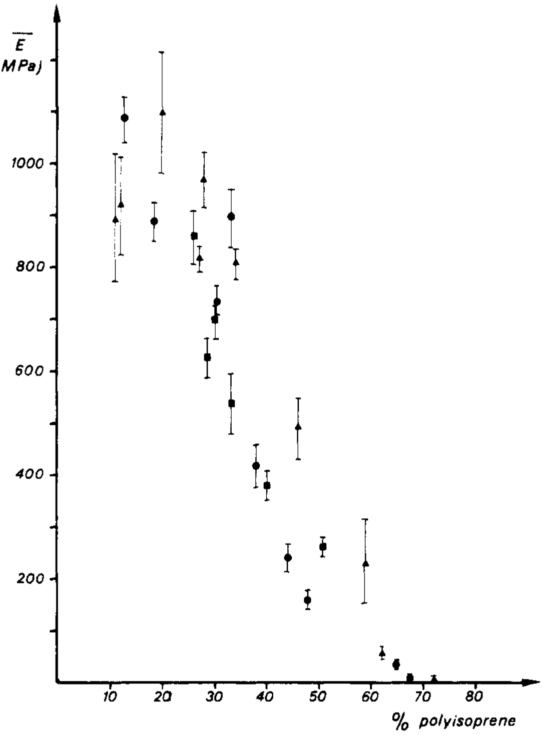

**Figure 2.** Average Young's modulus $\bar{E}$ vs. polyisoprene content.

In Table I the stress value $\bar{\sigma}_E$ and the Young's modulus $\bar{E}$ are listed for SIS copolymers with various molecular characteristics $M_{\mathrm{tot}}$ and % I. The three sections of Table I correspond to series of SIS whose $M_{\mathrm{tot}}$ is centered roughly around 30 000, 50 000, and 90 000. This arbitrary subdivision has been established in order to detect a possible influence of the molecular weight of the copolymers. Table I shows that $\bar{\sigma}_E$ and $\bar{E}$ are very sensitive to the variation of the molecular characteristics. Values of $\bar{\sigma}_E$ fall between about 1 and 30 MPa, and values of $\bar{E}$ between 10 and 1100 MPa.

In Figure 2, the Young's modulus $\bar{E}$ is plotted vs. the elastomer content. $\bar{E}$ increases with decreasing % I and reaches a maximum value near 1100 MPa. The modulus does not depend significantly on the molecular weight. It seems that the lowest $M_{\mathrm{tot}}$ is already high enough to contribute to $\bar{E}$ as much as do the longer chains. For homopolystyrene, considered as the copolymer with 0% polyisoprene content, we have found a modulus of 940 MPa, which fits well with the 1100 MPa obtained for the SIS with the lowest % I. Owing to the weak strain involved at high polystyrene contents, the dispersion of the $\bar{E}$ values is quite large. It may therefore be assumed safely that the maximum value of the modulus for thin SIS films is around 1000 MPa. Note that this value is about half the one reported for stress experiments on copolymer samples having the usual standard thickness of several millimeters.[3]

In Figure 3 $\bar{\sigma}_E$ is plotted as a function of the polyisoprene content; the experimental points fall on three curves, depending on $M_{\mathrm{tot}}$. For the two groups with $M_{\mathrm{tot}}$ around 30 000 and 50 000, a maximum for $\bar{\sigma}_E$ appears, which increases with $M_{\mathrm{tot}}$. This maximum is shifted toward higher % I when $M_{\mathrm{tot}}$ decreases. Such behavior has not yet been observed; it may perhaps be ascribed specifically to thin polymer films.

Obtaining thin polymer films is not always possible, as a minimal molecular weight is required (about 38 000 for

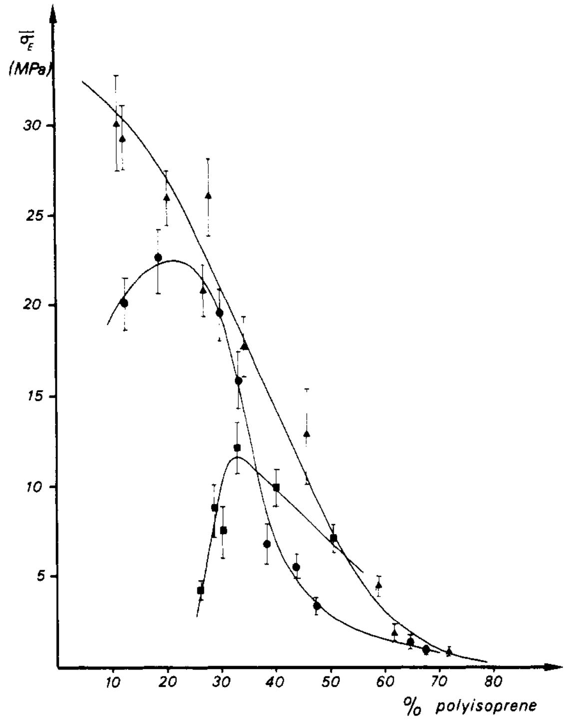

**Figure 3.** Average tensile strength $\bar{\sigma}_E$ as a function of polyisoprene content: (■) $M_{tot}$ = 30 000; (●) $M_{tot}$ = 50 000; (▲) $M_{tot}$ = 90 000.

PS), below which the cohesive strength decreases, as chain entanglement is no longer realized.[9] That limit may be lowered by addition of low-modulus particles such as a polydiene.[10] But a reinforcement by this method is only observed when the elastomer is able to form discrete phases. When both phases are chemically bound, as in block copolymers, the reinforcing effect is even enhanced. Thus, for SIS copolymers with low $M_{tot}$ or low content in one phase, there is no phase separation and the corresponding films are not very cohesive and difficult to handle.

We now consider the two curves in Figure 3 presenting a maximum. For a $M_{tot}$ of 30 000, the polyisoprene content at the maximum is 30%, hence corresponding to a central block of 10 000; for SIS with an $M_{tot}$ of 50 000, where the maximum is located at 20%, we also find 10 000. This value is precisely the molecular weight predicted by several authors,[11] above which styrene–isoprene block copolymers exhibit phase separation.

For SIS copolymers of still higher molecular weight, around and over 90 000 (corresponding to the upper curve in Figure 3), a maximum in $\bar{\sigma}_E$ would be expected to appear at less than 10% polyisoprene content. This is difficult to verify, as there are insufficient experimental points in this range. Nevertheless, for homopolystyrene, we have obtained approximately the same value as for the SIS film with the lowest elastomer content. This seems to favor our assertion that, for a given $M_{tot}$, $\bar{\sigma}_E$ increases up to a point where the % I becomes too low for a good film to form. Beyond this limit, films show microscopic defects, especially crazes, and $\bar{\sigma}_E$ decreases rapidly.

## Conclusion

Our experiments show that the total molecular weight influences the tensile strength of thin SIS films, but not their Young's modulus. Classically, $\bar{\sigma}_E$ and $\bar{E}$ are expected to increase continuously with increasing hard-phase content. The observed maximum in $\bar{\sigma}_E$ corresponds to the point from which film formation is no longer possible due to a decrease in cohesive strength of the polymer material.

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# Nuclear Magnetic Resonance Study of Norbornene End-Capped Polyimides. 1. Polymerization of *N*-Phenylnadimide

**A. C. Wong and W. M. Ritchey***

*Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106.*
*Received November 16, 1979*

ABSTRACT: Carbon-13 and high-field proton NMR were used to study the thermally induced polymerization of *N*-phenylnadimide. In addition to the exo–endo isomerization, *N*-phenylnadimide undergoes a retro-Diels–Alder reaction to produce cyclopentadiene and *N*-phenylmaleimide. Two major isomers are found via Diels–Alder reaction from cyclopentadiene and *exo*-*N*-phenylnadimide. Their isomeric forms are determined by empirical calculation of the $^{13}C$ chemical shifts. These products and the two phenylnadimide isomers polymerize with *N*-phenylmaleimide to give stereochemically and sequentially irregular polymer chains which contain no olefinic functional groups.

## Introduction

Thermal polymerization is one of the areas of polymer science that is still not well understood. While many monomers appear to undergo spontaneous polymerization when heated in the absence of catalysts, on careful investigation, such polymerization is often initiated by homolysis of the impurities present in the reaction mixture.[1]

A group of oligomers which appear to undergo spontaneous polymerization when heated thermally are the aro-

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