energy configuration is shown in *Figure 1*. The full line shows the position of the crankshaft in the 'ideal' (i.e. isomeric state) configuration and the broken line shows its position after the dihedral angles have relaxed. We can see quite clearly that the stems are no longer colinear, so that rotation of the crankshaft will produce a disturbance in the rest of the molecule, and that several of the angles are severely distorted from their isomeric state values, e.g. the *trans* bond in the middle of the crankshaft is now at 160° rather than 180°.

The minimum energy path for the rotation of this crankshaft is shown in *Figure 2*. The curve has the expected triple well shape, and the height of the barriers was found to be quite accurately approximated by the sum of the individual barriers encountered by each 'stem' bond rotating separately. *Figure 3* shows the variation in w_6, the first dihedral angle in the crankshaft, with the angle of rotation. Contrary to the hopes of Schatzki, and the calculation of Boyd and Breitling[3], we find that there is quite a variation in the values of all the crankshaft bonds as rotation occurs. The 20° variation illustrated in *Figure 3* is quite characteristic of the behaviour of each of the bonds adjacent to a 'stem' bond.

The effect of this variation in angle and non-colinearity of the stems can be seen in *Figure 4*, where we plot the position of C_{10} which is the carbon atom at the 'fixed' end of the crankshaft, as a function of rotational angle. Distance is measured from the initial relaxed position before the start of rotation. For an ideal crankshaft this particular atom should of course remain motionless, whereas *Figure 4* shows that as the crankshaft passes through the eclipsed position at 270° the carbon atom has been displaced from its equilibrium position by almost 2 Å. This is quite a large displacement when compared to the length of the crankshaft, which is only about 5 Å, and for atoms further down the chain this effect is magnified rather than reduced, the end carbon atom, for example, being displaced from its equilibrium position by as much as 6 Å.

The most appealing aspect of the crankshaft model, when considered in the frame of the rotational isomeric three state scheme, is the completely localized nature of the motion. However our calculations show that when allowance is made for more realistic equilibrium rotational angles this localized nature is lost, and that a crankshaft endeavouring to rotate from one equilibrium state to another through

the lowest energy path would involve considerable movement of the remainder of the polymer molecule. Whether or not the solvent molecules would allow this type of motion is uncertain, nevertheless, we feel that the results described here cast serious doubt on the ability of the crankshaft mechanism to provide a useful description of the local mode process in dilute polymer solutions.

D. A. Jones and D. Pugh

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK
(Received 28 November 1977)

References

1 Schatzki, T. F. *Polym. Prepr.* 1965, 6, 646
2 Scott, R. A. and Scheraga, H. A. *J. Chem. Phys.* 1966, 44, 3054
3 Boyd, R. H. and Breitling, S. M. *Macromolecules* 1974, 7, 855

Effect of hydrogenation on the elastic properties of poly(styrene-*b*-diene-*b*-styrene) copolymers

Introduction

Teleblock copolymers poly(styrene-*b*-butadiene-*b*-styrene) and poly(styrene-*b*-isoprene-*b*-styrene), widely used for their elastoplastic properties, suffer severe drawbacks in their application due to poor ageing properties of the unsaturated soft phase, poor long term elastic properties (stress relaxation as measured by compression set) at temperatures as low as 20°–30°C, short term elastic properties (instantaneous recoverable deformation as measured by tension set) and rapidly decreasing tensile properties as a function of temperature.

In principle, these properties could be improved by introducing saturated soft phases and hard phases with higher

glass transitions or melting points. This can be easily carried out by means of hydrogenation: the soft phase becomes a saturated rubber and the hard phase a polyvinylcyclohexane resin with a glass transition nearly 50°C higher than that of polystyrene. While the effect of the hydrogenation of the soft phase on the ageing properties is well known, no data were reported in the literature, as far as we know, on the effect of hydrogenation of both soft and hard phases on the elastic properties.

Experimental

Samples. Hydrogenation was carried out on two commercial teleblock copolymers, a poly(styrene-*b*-isoprene-*b*-styrene) (SIS) and a poly(styrene-*b*-

hydrogenated high vinyl butadiene-*b*-styrene) (SEBS) with the following characteristics:

	Styrene (wt %)	M_n (osm)
SIS	17	88.200
SEBS	30	58.000

Hydrogenated SIS may be considered as a (VCH–EP–VCH) copolymer and hydrogenated SEBS as (VCH–EB–VCH) copolymer, where VCH indicates a polyvinylcyclohexane block, EP an alternate ethylene–propylene copolymer and EB an ethylene–butene-1 copolymer obtained by hydrogenation of high vinyl polybutadiene.

Hydrogenation was carried out at

Table 1 Mechanical properties of examined ABA copolymers

Polymer	Modulus at 100% elonga- tion(MPa)	Modulus at 300% elonga- tion(MPa)	Tensile strength (MPa)	Elonga- tion at break (%)	Tension set at 20% strain	Tension set at 100% strain	Tension set at 200% strain
SEBS	2.2	3.0	24.1	550	1.1	4.0	8.5
VCH—EB—VCH	2.8	5.8	22.5	525	2.0	3.5	8.5
SIS	0.5	0.6	15.3	1200	0.5	1.5	7.5
VCH—EP—VCH	1.5	1.8	8.9	650	0.6	3.1	10.0
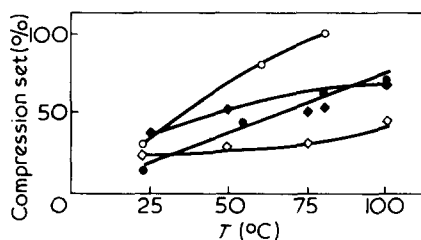
Figure 1 Plot of compression set vs. temperature for the ABA copolymers studied. ○, SIS; ●, VCH—EP—VCH; ◇, S—EB—S; ◆, VCH—EB—VCH

230°C in cyclohexane under H_2 pressure (80 atm at r.t.) for 20h. 10% polymer solutions and a catalyst of Pd dispersed on C (10% Pd) were used in a polymer/catalyst ratio of 10.

Hydrogenation was tested by i.r. and n.m.r. measurements.

After hydrogenation neither gel formation (from solubility measurements) nor noticeable decrease in molecular weight (from osmosis measurements) was observed.

The samples were compression moulded at 180°C for SIS and SEBS samples and 230°C for copolymers with VCH phases.

Tensile tests were performed according to DIN 53 504 at a tension speed of 50 mm/min, using a DIN-S 3 die. Tension set tests were carried out according to ASTM D 421, compression set tests according to ASTM D 395 — Method B. Samples were kept relaxed ½ h at the measurement temperature instead of room temperature. Dynamic and mechanical measurements were made by means of Rheovibron viscoelastometer from Toyo Instruments at 110 Hz frequency with an automatic control of temperature provided by TNO (Delft). The moduli (E' and E'') were not corrected for the effect of the grips and the sample length.

Results

The elastic properties of elastoplastic copolymers depend on time, temperature and deformation. The effect of these factors has been tested by means of simple standard test methods. The effect of the deformation was evaluated

by means of measurements of stress—strain and permanent set after a quick tensile deformation (tension set) at room temperature (see *Table 1*).

The effect of time was deduced from comparison of the compression set, i.e. permanent deformation after a 25% compressive deformation for 22 h (see *Figure 1*), with the tension set, permenent deformation after a 20% tensile deformation for 10 min. The effect of temperature was derived from measurements of the storage modulus E', tan δ (from *Figures 2* and *3*) and compression set (see *Figure 1*) at varying temperatures.

Discussion

Hydrogenation of the polystyrene segment increases the glass transition of the hard segment by approximately 40°—50°C (see *Figure 3*) in both samples. However, the effects of the T_g increase on the long term elastic properties as a function of temperature are different for the two copolymers. In fact the copolymer obtained by hydrogenating SIS shows compression set values lower than the 'parent' copolymer, whereas those for the copolymer obtained by hydrogenating SEBS are higher (see *Figure 1*). Therefore the variation of glass transition is not sufficient to explain the compression set vs. temperature plots.

Hydrogenation of an unsaturated rubber causes a decrease of the solubility parameter δ; in fact for polybutadiene values[1] of δ range from 8.4 to 8.6 $(cal/cm^3)^{1/2}$, while for hydrogenated polybutadiene a value of 8.1 $(cal/cm^3)^{1/2}$ is reported[2].

Hydrogenation of polystyrene causes a decrease in the solubility parameter: for polystyrene δ values of 9.1 $(cal/cm^3)^{1/2}$ have been found[3], while for polyvinylcyclohexane a value of 8.7 has been calculated[4] on the basis of a density of 0.94 g/cm^3, using the molar attraction constants of Van Krevelen[5] and Small's method. These data show that phase separation is more easily obtainable when the copolymer is composed of a styrene hard phase and a saturated soft phase for which

the difference between the solubility parameters is greatest.

It is well known that the broadness of the boundaries between two phases[6] is one of the physical causes of the stress relaxation of these materials, which show no equilibrium moduli but rather a continuous, although slow, relaxation of the applied stress. The relaxation mechanism is unknown, but one of the most valid interpretations is that the detachment of the individual segments from the hard phase and the restricted mobility of the entanglement network in the soft phase are responsible for such behaviour.

Relaxations which occur in times shorter that the deformation time in the compression set measurement (22 h) are responsible for the high values for the compression set of these materials. The above mentioned relaxation mechanism is probably accelerated by a less sharp phase separation (increase of interface thickness), as occurs upon hydrogenating the S—EB—S copolymer. In the case of the SIS copolymer the positive effect of hydrogenation on the compression set of the soft phase is greater than the negative effect of the polystyrene hydrogenation, since the compression set of the VCH—EP—VCH copolymer is lower than that for SIS (see *Figure 1*).

On the contrary the effect of hydrogenation on the tension set at varying strains is very small (see *Table 1*).
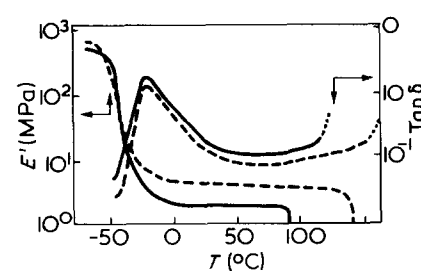

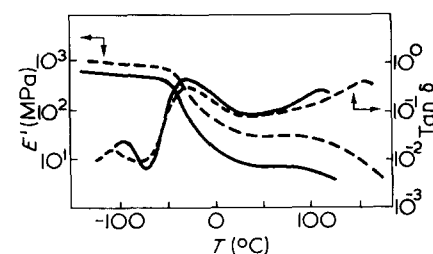*Figure 2* Dynamic—mechanical spectra of the SIS (———) and VCH—EP—VCH (— — —) copolymers

Figure 3 Dynamic—mechanical spectra of the S—EB—S (———) and VCH—EB—VCH (— — —) copolymers

Letters

Conclusion

In spite of the limitations due to the unknown morphology of the hydrogenated copolymers and to the non-selective hydrogenation catalyst used (not suitable for obtaining the S—EP—S copolymer), we think that an interesting conclusion stands out from this work.

Long term elastic properties (compression set) and their variation with the temperature do not depend only on the glass transition of the hard phase, but also on the degree of compatibility of the two phases. A less definite phase separation gives rise to a relaxation

mechanism that increases the compression set values. Hydrogenation of the soft phase of a SBS or SIS copolymer increases the difference between the solubility parameters of the hard and soft phases and the sharpness of the boundaries; it causes, therefore, an improvement in long term properties.

Further hydrogenation of polystyrene increases by $40°-50°C$ on the glass transition of the hard phase, but decreases the differences in solubility parameter between the hard and soft phase; so on one hand the length of the 'rubber plateau' increases, while on the other hand the long term elastic properties worsen.

L. Zotteri and G. P. Giuliani

*Snamprogetti SpA,
Direzione Ricerca e Sviluppo,
Polymer Research Laboratories,
San Donato Milanese, Milano, Italy
(Received 30 November 1977)*

References

1 Small, P. A. *J. Appl. Chem.* 1953, 3, 71
2 Mongaray, D., Patra, S. and Rashid, S. *Makromol. Chem.* 1963, 67, 84
3 Mongaray, D., Bhatnagar, S. K. and Rah, S. B. *Makromol. Chem.* 1963, 67, 75
4 Anon. *Mat. Plast. Elastomeri* 1973, 7, 545
5 Van Krevelen, D. W. 'Properties of Polymers: Correlation with Chemical Structure', Elsevier, New York, 1972, Ch 6
6 Helfand, E. *Acc. Chem. Res.* 1975, 8, 295