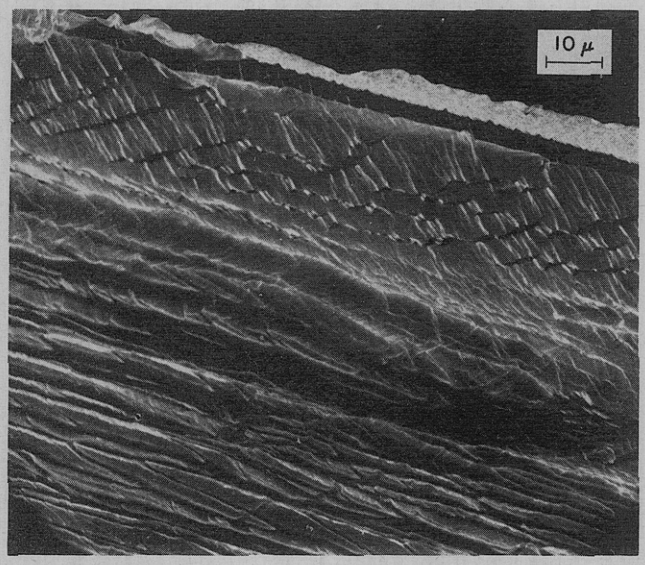

Figure 6. Scanning electron micrograph showing surface structure near the fracture edge. Region II, with coarse surface features, is seen in the foreground; region I and the edge of fracture surface at the top.

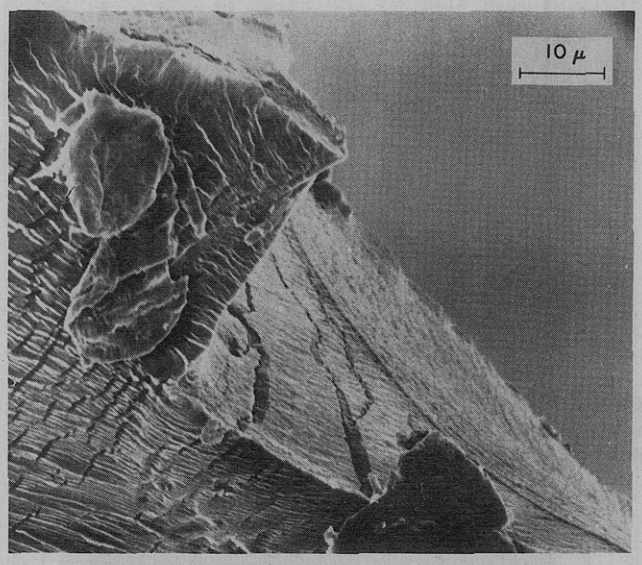

Figure 7. Scanning electron micrograph of the fracture surface in the neighborhood of catastrophic failure.

by the remaining plastic deformation. A narrow zone of material along the fracture is highly briefringent. Using a polarizing microscope with Berek compensator we found a birefringence $\Delta n = 0.030 \pm 0.003$. It is instructive to recall that PP films approach such high birefringence only when drawn to the extreme.[16,17] That this zone is rather different from the regions farther removed from the fracture surface can be seen particularly well in Figure 4, a micrograph obtained with a scanning electron microscope.

The variation in surface sructure suggest three distinct regions: the first is the region far from the fracture plane, with well separated, straight crazes. Closer to the fracture plane the crazes become extremely dense and highly interconnected. The average distance between adjacent crazes is only 2 μ and this is less than the craze thickness under stress in liquid nitrogen. The surface in this second region is very coarse. Considerable thinning of the sample occurs in this region. In the third region, in the already-mentioned narrow zone along the fracture, the surface is relatively smooth again. A schematic cross-section of the sample perpendicular to the crack propagation direction is shown in Figure 5. The dimensions given are average values.

The fracture surface is typically rather smooth where the single crack has propagated gradually, as can be seen at the right of Figure 4. The more rugged features in the fracture surface seen in Figure 4 are somewhat atypical and due to the catastrophic final rupture when the two cracks (Figure 1e) met. At the left of Figure 4 the crack which normally seems to follow a craze appears to have jumped a considerable distance ($\sim$33 μ) to a neighboring craze.

The almost complete disappearance of crazes in the narrow zone along the fracture surface, with some fine isolated markings left, may permit the speculation that the crazes coalesced in the stress direction by complete transformation of the original matrix into a drawn material of void content somewhere between that of normal polymer and that of the single craze. This is probably made possible by the high density of crazes or, expressed another way, the small thickness of the layer of uncrazed material between crazes. At the crack tip, these thin layers may become drawn out and transformed into oriented fibrils. The lateral coalescence of craze voids may then account for the reduced thickness of the sample in this region.

At higher magnification, a new system of surface markings is resolved in the narrow zone along the fracture (Figure 6). This consists of fairly large steps whose edges subtend an angle of about 30° with the crack propagation direction, and, more or less perpendicular to these, a system of smaller steps. The bright object at the top in Figure 5 is a thin membrane of material such as can be frequently seen overhanging the edge of the fracture surface.

Figure 7 shows the jump in the fracture surface already seen in Figure 4, now at higher magnification. The catastrophic rupture that has taken place not far from this point has caused cracks in the fracture surface; such cracks are not present in regions of slow crack propagation.

In conclusion, the foregoing microscopic evidence shows that stress crazing and final fracture of smectic PP in liquid nitrogen involve considerable plastic deformation. When the polymer is stressed and fractured at the same temperature −196°, but under vacuum, it behaves brittly and practically no plastic deformation is observed. This further shows that liquid nitrogen acts as a plasticizer, as has been recently contended.[14]

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Characterization of Styrene–Isoprene Block Copolymers by Gel Permeation Chromatography

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The advent of anionic polymerization techniques, specifically those involving the organolithium systems, has made possible the preparation of many novel linear block

Table I
Molecular Characteristics, GPC Elution Volume (at the Peak Maximum) and Intrinsic Viscosities of the Samples

Sample	w_{ps}[a,b]	$M_n \times 10^{-5}$	$[\eta]$ 35° (dl/g)	Elution Vol (ml)
Polystyrene	1.00	0.49	0.278	129.7
		0.96	0.452	123.1
		1.64	0.663	118.1
		3.92	1.24	105.3
		7.73	2.02	95.6
		17.8	3.68	87.5
Polyisoprene	0	1.49	1.22	114.0
		2.26	1.68	108.1
		3.19	2.18	103.5
Two-block copolymer	0.48	0.95	0.654	119.8
	0.50	2.21	1.19	109.1
	0.48	8.8[b]	3.60	92.5
	0.25	0.581	0.512	126.3
	0.24	5.3	3.20	97.5
Three-block copolymer	0.65	1.54	0.826	114.0
	0.63	5.1	2.26	97.9
	0.40	1.96	1.23	111.6

[a] Weight fraction of polystyrene in the samples. [b] Calculated from the polymerization data.

copolymers of interesting physical and mechanical properties. These materials are generally of narrow distribution in both composition and molecular weight but, in some cases, suffer from contamination by homopolymers or other materials of smaller block number than desired. Although this type of macromolecule has been investigated for many years now, their molecular characterization is still a very challenging field of work. In fact, while basic techniques such as osmometry or light scattering have been successfully extended to block copolymers, little is known concerning the validity of the more practical methods already well established for homopolymers such as viscometry or gel permeation chromatography.

The main reason for this lack of knowledge is the great difficulty encountered by many investigators in preparing suitable material for a sufficiently systematic study; this requires a large series of samples with wide ranges of molecular weights and compositions in which one of the parameters is constant. Fortunately, recently we have been able to design such a material from styrene and isoprene monomers. The molecular weight of monodisperse styrene–isoprene two- and three-block copolymers of known composition can be evaluated[1,2] from their intrinsic viscosities in both good and preferential solvents such as toluene, cyclohexane, and dioxane. In fact, their systematic study has shown that their intrinsic viscosities are closed to the weighted average of the corresponding homopolymers of equal molecular weight

$$[\eta]^{2/3} = w_a[\eta]_a^{2/3} + (1 - w_a)[\eta]_b^{2/3} \quad (1)$$

Therefore, knowing the weight fraction w_a of constituent A and the Mark–Houwink parameters of the homopolymers A and B make this equation most useful to calculate the molecular weight of the block copolymers. We have interpreted the validity of eq 1 as an evidence for a molecular conformation having a small number of heterocontacts. Here, we should recall that similar behavior has been previously observed by other investigators[3] for two-

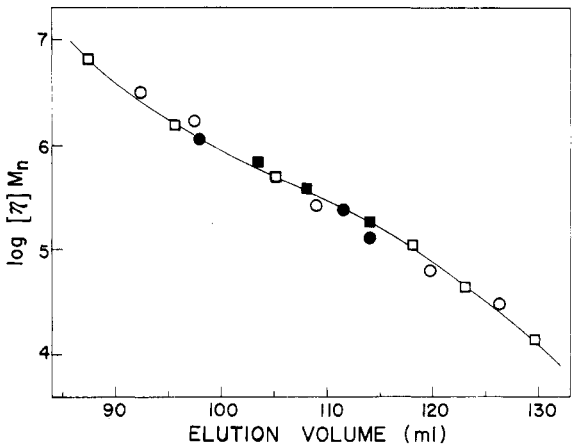

Figure 1. Plot of log $[\eta]M_n$ *vs.* elution volume at 35°: (□) polystyrene, (■) polyisoprene, (○) styrene–isoprene two-block copolymers, and (●) styrene–isoprene three-block copolymers.

and three-block copolymers of styrene and methyl methacrylate. In the present paper, we intend to extend this investigation to gel permeation chromatography.

Until now, GPC analysis of block copolymers has been primarily used to detect presence of extraneous materials and, as far as we know, very few authors consider the GPC application to molecular weight determination of block copolymers. The methods introduced for converting the experimental elution volume to molecular weight employ log M *vs.* elution volume calibration curves for homopolymers. In all cases the knowledge of copolymer composition is needed. For instance, in their investigations of styrene–isoprene and styrene–butadiene block copolymers, Cramond *et al.*[4] and Runyon *et al.*[5] suggested that the molecular size of block copolymer expressed as log M_c is given by the weighted average of molecular sizes log M_a and log M_b of the corresponding homopolymers at the same elution volume

$$\log M_c = w_a \log M_a + (1 - w_a) \log M_b \quad (2)$$

More recently, Chang[6] applied a slightly different method on styrene–butadiene and styrene–methyl methacrylate block copolymers requiring linear relationships between log M and elution volume for the corresponding homopolymers. Both of these methods suppose implicitly that the hydrodynamic volume of the block copolymer sequences are additive, an assumption which implies a negligible interaction between unlike segments.

In the well-known general GPC investigation of Benoit, Grubisic, and coworkers,[7] it has been demonstrated that one common plot of log $[\eta]M$ *vs.* elution volume is obeyed by structurally different polymers including some graft copolymers of styrene and methyl methacrylate. Moreover, they have shown that when porous glass beads are used as the stationary phase, the calibration based on $[\eta]M$ gives a single curve for thermodynamically different

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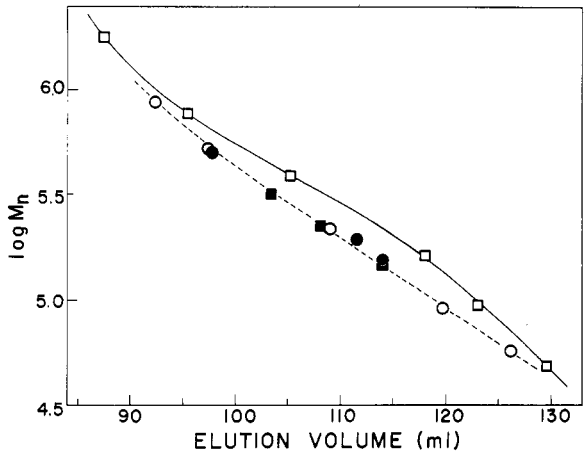

Figure 2. Plot of log M_n *vs.* elution volume at 35°; (□) polystyrene, (■) polyisoprene, (○) styrene–isoprene two-block copolymers, and (●) styrene–isoprene three-block copolymers.

solvents. The universal calibration of GPC has been widely discussed for the past few years and although some improvements of the Benoit and Grubisic method have been suggested,[8] the use of $[\eta]M$ is still very attractive for its correctness and its simplicity. In the present paper we apply this method to well-characterized styrene–isoprene two- and three-block copolymers of various compositions and molecular weights.

Experimental Section

Measurements were carried out at 35° on a Waters Associates Model 200 GPC instrument. A series arrangement of three Waters columns containing porous silica beads (Porasil) with upper porosity designation 10^6, 10^5, and 5×10^4 Å was used. The solvent was reagent grade toluene. The flow rate was 1 ml/min and 2 ml of solution at a concentration of approximately 0.005 g/cm^3 were injected. The polystyrenes used were narrow distribution samples supplied by Waters Associates. The anionic synthesis and the characterization of the two-block and the three-block copolymers have been described previously.[1,2] These samples are of narrow distribution ($M_w/M_n < 1.1$) and contain less than a few per cent of extraneous materials. The polyisoprene samples were prepared under the same conditions. All polymers gave symmetrical peaks with a width at half-height of approximately 2 counts (10 ml). The reproductibility of peak position was better than 1%.

Results and Discussion

Table I summarizes the molecular characteristics, the GPC elution volume (at the peak maximum) and the intrinsic viscosities of the samples studied. The use of a number-average molecular weight is anticipated to be of weak consequence since all the samples are of narrow distribution. Figure 1 shows the plot of log $[\eta]M_n$ *vs.* elution volume. The smoothed calibration curve is drawn through the data points for the polystyrene standards. It is satisfying to note that the data points for the polyisoprene samples coincide well with the calibration curve. In the case of block copolymers, the fit to the polystyrene calibration curve is perhaps not as close as might be wished, but a close examination shows that the block copolymer molecular weights evaluated from this curve are correct inside a margin of 20% for all the samples except one. Of course, the magnitude of the error depends on the accuracy of the calibration line and an alternative procedure would have been to draw a calibration curve through all the data points. Such a curve, which is not shown in Figure 1, reduces considerably the apparent scatter of the data.

It is also of interest to compare the present universal calibration procedure to the molecular weight calibration procedure, *i.e.*, log M_n *vs.* elution volume, as illustrated in Figure 2. Here, the samples appear to fall into two groups. The upper line represents the data points for the polystyrene standards and the lower dashed line approximates well the data points for both the polyisoprenes and the block copolymers. It is not easy to explain why a single curve groups together these samples of different compositions unless there is a small increase of hydrodynamic volume due to heterocontacts in the present block copolymers. Thus, for a given value of the elution volume, the actual molecular size log M_c will be smaller than the weighted average of molecular sizes log M_a and log M_b of the corresponding homopolymers. From this comparison it seems that the $[\eta]M$ universal calibration is a better procedure because of its ability to take into account the heterocontact effects which are small but not completely negligible in styrene–isoprene block copolymers.

Recently, Urwin and Girolamo[9] have reported that the plots of intrinsic viscosities *vs.* temperature for two-block copolymers of styrene and isoprene exhibit a discontinuity in cyclohexane and other poor solvents for polystyrene. This phenomenon which appears in the region of 15–30° in cyclohexane was attributed to an intramolecular phase separation. Unfortunately, as we have already shown,[2] our samples, among which some present the same molecular weights and compositions as those investigated by Urwin and Girolamo, failed to show this behavior in both cyclohexane and toluene. We are led to believe that the copolymers under consideration have different architectures. At first glance, this was thought to be due to the differences in the synthesis approach, but a recent viscometric study of a two-block copolymer prepared in our laboratory according to the Urwin and Girolamo procedure also gave no sign of phase transition between 10 and 60°.

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