Hydrogenated linear block copolymers of butadiene and isoprene: effects of variation of composition and sequence architecture on properties

Y. Mohajer and G. L. Wilkes
Department of Chemical Engineering

and I. C. Wang and J. E. McGrath
Department of Chemistry, Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University Blacksburg, Virginia 24061, *USA*

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The effect of variations in molecular architecture and composition on bulk properties is reported for a series of well characterized hydrogenated block copolymers of butadiene (HB) and isoprene (HI), each with a total molecular weight of ~200 000 and a narrow distribution ($Mw/Mn < 1.17$). The polymers were synthesized by sequential anionic polymerization followed by hydrogenation, using *p*-toluenesulphonylhydrazide. The material properties of the homopolymeric HI and HB were also investigated. As expected, HI is rubbery at room temperature and HB is a tough semicrystalline plastic with properties similar to those of a low density polyethylene, LDPE. The crystallinity, density and ΔH_f for all of the block copolymers were found to be linearly dependent on HB content indicating that little mixing exists between the HB and HI blocks in the solid state. Although the solution cast films of the block copolymers were spherulitic, the quenched films displayed no distinct structure on the supermolecular level indicating that the aggregation of the crystallites was more random in these films. The stress–strain properties of triblock copolymers with different block sequence, HBIB and HIBI, and a di-block copolymer, HBI, were similar in bulk behaviour to each other in the high and the intermediate butadiene content (50–90%). This was related to the fact that the mechanical properties were determined predominantly by the behaviour of the more continuous HB phase. For the lower butadiene compositions (7–29%), there was a major difference in the behaviour of polymers with different block architecture. HBIB polymers were thermoplastic elastomers, whereas HIBI polymers behaved like an uncured particulate filled rubber. This difference was related to the presence of permanent 'entanglements' in HBIB polymers. The permanent entanglements which act as a physical crosslink are a consequence of the anchorage of the HB end blocks in the semicrystalline domains. No such arrangement is possible for either the HIBI or HBI polymers. The hysteresis behaviour of HBIB polymers were strongly dependent on butadiene content, decreasing with lowering of the concentration of the semicrystalline HB. This dependence was related to the continuity of the crystalline microdomains. All the members of HIBI series (and the HBI we considered) showed large hysteresis behaviour. This large energy loss during cyclic deformation in these polymers was related to the absence of the permanent anchor points arising from end block crystallization.

Keywords Block copolymer; structure property behaviour; butadiene; isoprene; polymerization; hydrogenation

INTRODUCTION

The ease in attaining a spectrum of properties through the modification of composition and block architecture has been a major factor in advancing the importance and use of block copolymers. The strong interest in block copolymers has produced a large number of publications in this field (e.g. refs 1–4). Although there are some reports on block copolymers containing a semicrystalline block such as poly(ethylene oxide)5[a,b] or even a semicrystalline polypeptide block such as poly(γ-benzyl-L-glutamate)[4,6], the majority of the research has been focused on systems whose blocks are amorphous. The linear amorphous block copolymer of styrene–butadiene–styrene is produced commercially under the trade name of Kraton^R and has been studied most extensively[1–3]. A hydrogenated version of this polymer, where the central block is believed to be of low crystallinity[7], is also available (Kraton G-1650).

Significant modification in properties of polymers and block copolymers containing isoprene and/or butadiene have been reported following hydrogenation of these macromolecules[8–14]. Although the initial motive for this modification of the double bond containing polymers was perhaps directed towards enhancement of the photolytic, oxidative, and thermal stability of these polymers, it was realized subsequently that polymers containing butadiene of low vinyl content produced better mechanical properties[9–14]. This improvement can be attributed to the development of crystallinity in the polyethylene-like segments[8].

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Hydrogenation of the polyisoprene block results in the formation of the amorphous alternating copolymer of ethylene–propylene. The hydrogenated polyisoprene (HI) block possesses a glass transition temperature below ambient temperature ($T_g \simeq -60°C$ by d.s.c., heating rate $10° \min^{-1}$) and is rubbery at room temperature. Exhaustive hydrogenation of the polybutadiene block of low 1,2 microstructure will transform this block to a polyethylene-like structure[8]. Hydrogenation of 1,2 microstructure (present in the parent polymer in around 5–8 mol%)* would result in formation of pendant ethyl groups. Therefore the resultant HB block is more similar in properties to low density polyethylene[15,16] (but not exactly the same as LDPE[17]) than to high density polyethylene. The HB block is thus semi-crystalline but the crystallinity of this block in the quenched samples is lower than 35%. The low crystallinity of this exhaustively hydrogenated HB polymer is due to the presence of pendant side chains.

Duck, *et al.*[8,9], in their extensive studies of the hydrogenation reaction of polybutadiene showed that crystallinity of the product is dependent on the 1,2 content and the extent of hydrogenation. For samples containing 8 mol % vinyl content, considerable crystallinity was developed after 50% hydrogenation. They also showed that the crystallinity was not dependent on the molecular weight of the parent polymers, but was linearly dependent on the extent of hydrogenation[8]. This indicates, as expected, that when a long enough portion of the polymer is hydrogenated, it can aggregate itself into a crystal lattice. Thus segregation of crystallizable and amorphous segments, above 50% hydrogenation, permits formation of microcrystalline domains which serve as physical crosslinks. Moreover, crystallinity which is detectable by X-ray diffraction is developed. At appropriate levels of hydrogenation and per cent 1,2 content, these polymers behave as thermoplastic elastomers. The use temperature must be well below T_m of the crystalline block and above T_g of the other rubbery block component[8].

Falk[10] reported the synthesis of triblock copolymers containing polyethylene-like end blocks and a rubbery central block by the catalytic hydrogenation of triblock copolymers of butadiene, where end blocks were low in 1,2 microstructures but the central block was high in 1,2 microstructure. He was also able to selectively hydrogenate butadiene blocks in copolymers of 1,4-butadiene–isoprene–1,4 butadiene[14]. Hydrogenation of a polybutadiene segment which is rich in 1,4 microstructure will yield a semicrystalline polyethylene-like block whereas the block containing moderate to high 1,2 microstructure produces rubbery structure at ambient temperatures. They investigated effects of variation of composition on tensile properties[10,14].

Hydrogenation of polybutadiene containing high 1,4 microstructure has also been employed for preparation of ‘polyethylene’ of low polydispersity and various studies have been conducted on this polymer. In a series of papers, Graessley *et al.* discussed the preparation and the rheological behaviour of linear and star-branched hydrogenated polybutadiene[15,16,18]. Cowie *et al.* used a series of polybutadienes which had been hydrogenated to different extents in an attempt to determine the glass transition of amorphous polyethylene[19]. The crystallization kinetics[20], elastic recovery and the dynamic mechanical properties[17] of HB have also recently been investigated. The rheology, dynamic mechanical behaviour and the crystallization kinetics of HB were very similar to those of LDPE, but the elastic properties were different. In brief, this change was attributed to the difference in rigidity of the spherulites of HB from that of LDPE.

It is the objective of this work to investigate the effect of variation in block architecture (number and the order of the blocks) on the crystallinity level, morphology, the stress–strain and hysteresis behaviour of this series of polymers. In addition, the composition ratio of the two block types is expected to play a crucial role in determining the bulk material properties of the block copolymers. This is related to the fact that the mechanical properties of block copolymers are typically influenced more substantially by the behaviour of the continuous phase[1,21]. The difference in properties of these polymers of varied architecture was most noticeable in the composition range where the semicrystalline domains are dispersed in the continuous rubbery matrix. Under this condition the HBIB polymer is a thermoplastic elastomer, but both HIBI and HBI behave somewhat as a particulate, partially filled uncrosslinked rubber.

EXPERIMENTAL

Polymer synthesis and characterization

This topic has been extensively discussed in preceding papers[22,23]. However, we will briefly outline the preparative route. The block copolymers were synthesized via ‘living’ anionic polymerization of butadiene and isoprene using sec-butyl lithium as initiator in hydrocarbon solvents under high vacuum. Under these conditions, the mode of addition of butadiene is predominantly 1,4, with between 5–8 mol % of 1,2 structure[14]. Exhaustive hydrogenation of polymers were carried out in the presence of *p*-toluenesulphonylhydrazide[18,24] in refluxing xylene. The relative block composition of the polymers were determined by n.m.r. The relative concentration of the various butadiene microstructures, (1,4 *cis*, 1,4 *trans*, and 1,2 vinyl), were determined from the infra-red spectra of solid films cast on KCl[25]. The 1,2 microstructure content of all the polymers considered in this paper were between 5–8 mol % as determined from the i.r. spectra. Number average and the weight average molecular weight of the polymers were obtained via osmotic pressure and h.p.l.c. The molecular weight of all polymers is around 200 000 g mol^{-1} while the polydispersities were less than 1.17; thus, all of these polymers have a relatively narrow molecular weight distribution. A sample of low density polymer (LDPE) which was obtained from the Union Carbide Corporation (Dex 194) was used for comparison with our polymers. The number and the weight average molecular weight of this polymer, obtained by g.p.c. were 13 900 and 77 500 g mol^{-1}, respectively.

The hydrogenated (H) block copolymers will be designated by giving the butadiene (B) or isoprene (I) block sequence followed by a number which represents the total weight percentage of butadiene in the polymer.

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* 5–8 mol% is obtained from i.r. of polybutadiene according to the procedure given in the text. This is equivalent to 1.3–2.1 ethyl branches per 100 carbon atoms. N.m.r. analysis of the same HB obtained via courtesy of Prof. Mandelkern indicated the presence of ~2% ethyl branch units per 100 carbon atoms

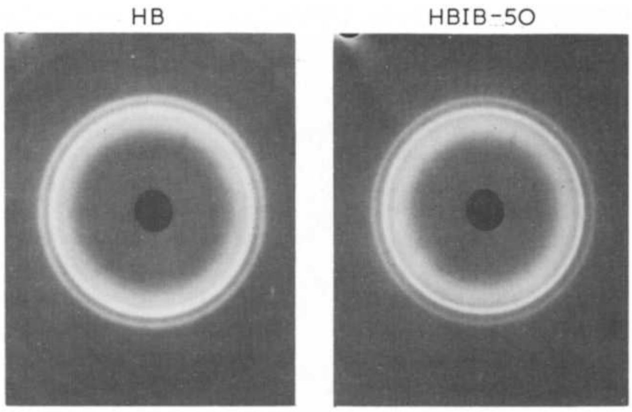

Figure 1 X-ray diffraction patterns of the semicrystalline homopolymer (HB) and a block copolymer (HBIB-50)

For example HBIB-27 is a hydrogenated triblock copolymer of butadiene–isoprene–butadiene which contains 27% butadiene. Since the polymer is symmetric, the relative composition of each block is therefore 13.5% B–73% I–13.5% B.

Sample preparation

Samples for mechanical studies were made by compression moulding the polymers at 150°C between Teflon sheets for 15 min followed by rapid quenching to room temperature in air (these will be referred as PQ samples). Samples for morphology, small angle light scattering (*SALS*) and scanning electron microscopy (*SEM*) studies were prepared from toluene solutions. These films were cast on a Teflon sheet at 80°C from a 1% (by weight) solution in toluene. When the polymer films had solidified (after 5 h), they were stored in a vacuum oven at 80°C for two days to remove residual solvent. These samples will be designated by Tol (solution cast from toluene).

Crystallinity and morphology

The X-ray diffraction patterns of the films were taken with a Phillips PW1720 table-top X-ray unit using a flat plate camera. The *SALS* H_v patterns were obtained using a Helium neon laser and the photographic technique developed by Stein[26]. An ISI Super III-A scanning electron microscope was employed for morphological investigations. Samples were coated with gold using a SPI sputter T.M., Model 13131. The density of the polymer samples was measured using a density gradient column constructed from ethanol and water. Glass beads with known density were used to calibrate the column. The thermal properties of the polymers were measured on a Perkin Elmer differential scanning calorimeter, Model 2C. The heating rate was 10°C per min.

Mechanical properties

The stress–strain and the hysteresis behaviour of the polymers were measured on a Model 1122 Instron using dog-bone samples of 0.28 cm width and 1.0 cm effective length. Based on the initial length, the rate of extension was 100% per min. The mechanical hysteresis of the samples, which is a measure of energy loss during cyclic deformation, was obtained from measurement of the area under loading and unloading curves using a planimeter. The percentage hysteresis was calculated from the following relationship:

$$\%\,\mathrm{Hyst} = 100(A_l - A_u)/A_l$$

where A_l and A_u are the area under the respective loading or unloading stress–strain curve.

RESULTS AND DISCUSSION

As already mentioned, the HB block is semicrystalline and its general behaviour is similar to that of LDPE. The HI block, however, is amorphous and rubbery at ambient temperature. The material behaviour of block copolymers containing HB and HI blocks will now be discussed in the following sections.

Crystallinity and morphology

The block copolymers of essentially completely hydrogenated HBIB, HIBI and HBI, in which the microstructure of butadiene is predominantly 1,4, are semicrystalline. Our measurements indicate that the extent of crystallinity is independent of the architecture of the block copolymer and is linearly dependent on the butadiene content. A comparison of the X-ray diffraction pattern of a homopolymer of HB is given in *Figure 1* along with that from a triblock copolymer HBIB-50. The sharp diffraction rings are clearly indicative of the presence of crystallites in both polymers. Block copolymers containing as low as 8% butadiene have shown basically the same type of diffraction patterns but with a much lower intensity because of lower concentration of butadiene. This indicates that aggregation of crystallizable segments and formation of crystalline domains is not significantly affected by the surrounding noncrystallizable HI block.

Quantitative measurements of the crystallinity content of the block copolymers were made from the determination of the heat of fusion and from the density of the polymer.

The d.s.c. thermograms of several triblock copolymer and homopolymer HB are compared to that of a low density polyethylene in *Figure 2*. The thermograms are those of the first run on quenched samples. Their behaviour is similar except that the temperature of the maximum in the d.s.c. melting peak, T_m, for LDPE (110°C)

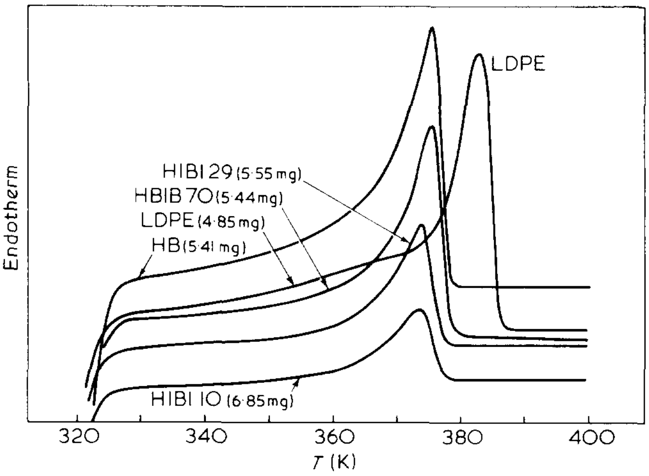

Figure 2 Comparison of the d.s.c. thermograms of the homopolymer HB and various block copolymers to that of the LDPE. The weight of each polymer sample is indicated in the parentheses; the range of the instrument is 2 mcal s^{-1} for all the runs

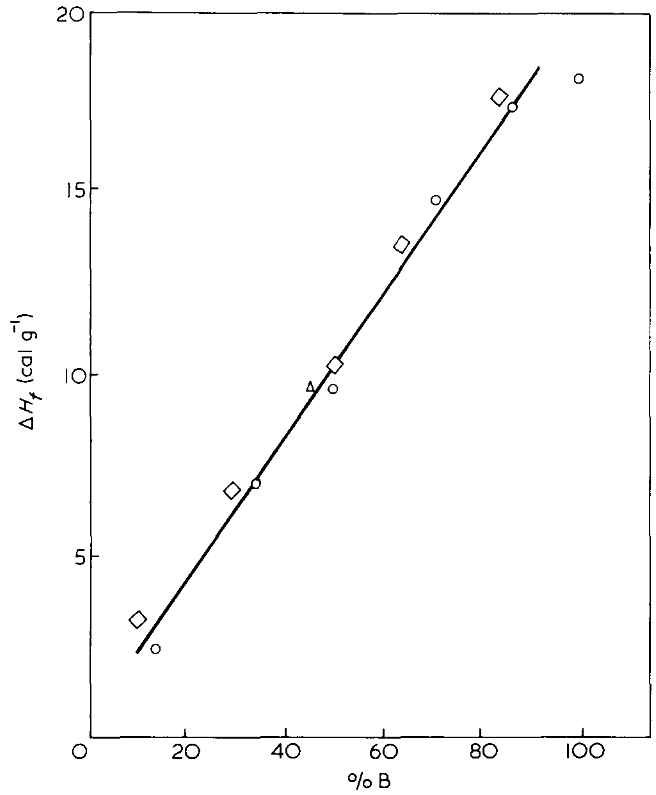

Figure 3 The linear dependence of ΔH_f on butadiene content in the various block copolymers. (⊙) HBIB; (◇) HIBI; (△) HIB

is higher than that of HB (102°C). The depression of the melting point brought about by the presence of 5–8 mol % of the hydrogenated 1,2 butadiene adduct (equivalent to 1.3–2.1 ethyl branches per 100 carbons) far exceeds the theoretical value based on Flory's work[27a]. Polyethylene containing methyl, ethyl and n-propyl groups have also shown higher depression of the melting point than the theoretical value and thus the behaviour of our system is not unique[27a,b]. However, the depression of the melting point brought about by the presence of 1.3–2.1 ethyl branches per 100 carbons in our system ($\Delta T = 36°C$ with respect to T_m of HDPE) is still higher than that produced by the same amount of ethyl or even n-propyl branches ($\Delta T = 22°C$ for 2.1 n-propyl branch per 100 carbon atoms as measured by Richardson *et al.*)[27a]. We do not have the exact reason for the behaviour of our system, but it is possible that the higher depression of the melting point is caused by a very small amount of remaining unsaturation and/or the presence of some *p*-toluene sulphonyl adduct produced during the hydrogenation of the double bonds. We have recently reported that the addition of a phenolic antioxidant such as Irganox 1010 effectively decreases the minor but the detectable side reaction[23]. We are currently investigating the effect of reducing the sulphonyl adduct concentration on T_m of the HB polymers. The preliminary results indicate that a decrease in concentration of the bulky adduct increases the T_m of the polymer, as expected. Other workers have also reported a lower T_m for HB polymers[17,20] and postulated that the depression of the melting temperature, as compared to HDPE, is due to presence of ethyl branches and some remaining unsaturation in the main chain[17]. Lowering of T_m with an increase in the number of ethyl side chains has been observed in copolymers of ethylene–butene[27c]. Although the melting temperature of HB has been reported to be inversely related to molecular weight[20] and hence on chain length, our block copolymers do not show such a dependence on HB sequence length. The 'peak' melting temperatures of all of the block copolymers, regardless of chain architecture or butadiene composition, are in the vicinity of 102 ± 2°C for the quenched samples. The reader may recall that for a given total molecular weight, an increase in butadiene content is followed by an increase of butadiene block chain length. Thus, neither the architecture nor the butadiene block chain length (at least in the ranges that we have studied) affects the melting behaviour of the polymer. This is contrary to the finding of O'Malley, *et al.* who studied the effect of the changes of composition of tri and diblock copolymers of styrene ethylene oxide block copolymers[27d]. They attributed the decrease of T_m of the crystalline polyethylene oxide block with the increase of styrene content to the decrease of the perfection of the crystalline PEO lamella. In light of this result, the independence of T_m on composition in our own systems could be rationalized in the following way. The crystallites of HB are generally embedded within the amorphous HB phase and thus are not significantly affected by the rubbery HI block. In fact, there is an indication from our dynamic mechanical studies that there may well be phase separation between the HI and HB blocks in the amorphous regions. Thus the environment experienced by the HB crystallites is the same (unlike the previous work[27d]) and therefore their perfection (and hence T_m) is not influenced by the composition variation of HI.

Regarding crystallinity contents, the heat of fusion ΔH_f, obtained from the area under the d.s.c. melting curve, (and subsequently the percentage crystallinity calculated from ΔH_f) is found to be linearly dependent on butadiene content, and independent of the polymer architecture. This is shown in *Figure 3*. Also, the density of the block copolymers was found to be linearly dependent on butadiene content (see *Figure 4*). The linear additivity

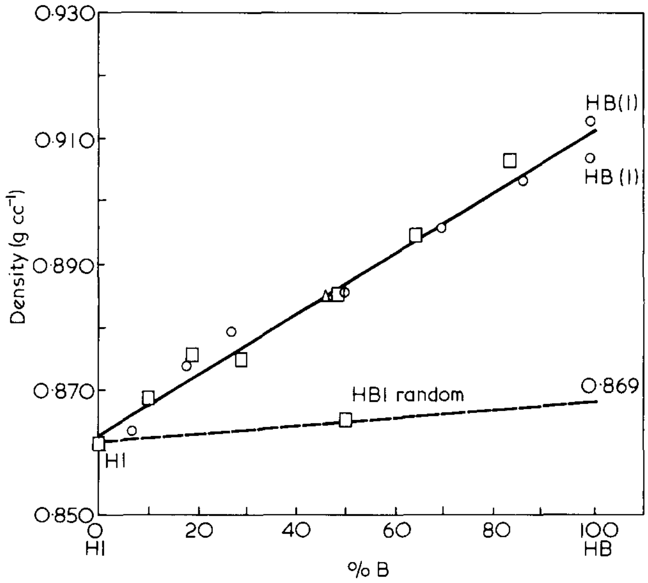

Figure 4 The linear dependence of density on butadiene content in the various block copolymers. The density of amorphous HB (polyethylene) is estimated from the extrapolation of the density of HI through that of the random copolymer HBI-50 to axis where butadiene content is 100%. (⊙) HBIB; (□) HIBI; (△) HBI

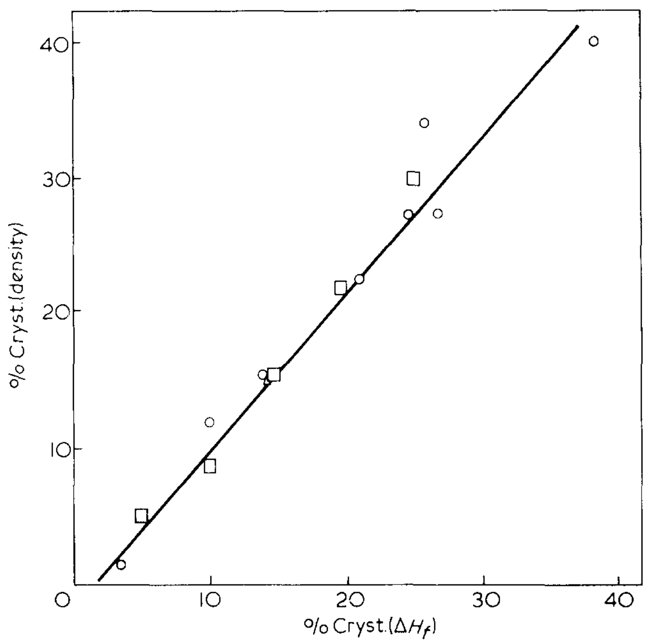

Figure 5 A comparison of % crystallinity obtained from density to that obtained from ΔH_f for the various block copolymers. (○) HBIB; (□) HIBI; (△) HBI

of density (specific volume) has been observed by other workers for incompatible block copolymers of styrene and butadiene indicating that very little change in density from that of pure components has occurred on forming the block copolymers[28]. While the above statement is somewhat plausible, these workers have utilized the small positive deviation from the linear additivity law to estimate the thickness of the boundary in SB block copolymers[28].

In *Figure 4*, the density of a random hydrogenated copolymer of butadiene–isoprene containing 50% butadiene is also given. The X-ray diffraction pattern and the d.s.c. thermogram of this polymer indicates that it is totally amorphous. Extrapolation from the density of HI to the density of this random HBI-50 to the axis corresponding to 100% hydrogenated butadiene would give the density of amorphous HB (or that of amorphous 'polyethylene'). The value of the density for amorphous polyethylene obtained in this way is about 0.869 g cm^{-3} as compared to 0.855 g cm^{-3} obtained from the extrapolation of molten PE[29]. In our calculation of the percentage of crystallinity from density measurements, we have used this value of 0.869 g cm^{-3} for the density of amorphous PE (rather than the literature value of 0.855 g cm^{-3}), 0.862 g cm^{-3} for the density of hydrogenated isoprene (amorphous), and 1.00 g cm^{-3} for the density of crystalline PE[30a]. While our extrapolated density for PE might be somewhat questionable based on our limited data, the value of crystallinity obtained using the above values is nearly identical to that found from ΔH_f. This value is at least 12% lower than that found using the relationship of Chiang and Flory where the density of the amorphous and crystalline PE are taken at 0.8518 and 0.9995 g cm^{-3} respectively at 25°C[30b]. The per cent crystallinity was also obtained from the areas of the endothermic peaks in d.s.c. graphs using a ΔH_f value of 69 cal g^{-1} for completely crystalline polyethylene[31]. A comparison of crystallinity values obtained from density to those from ΔH_f is made in *Figure 5*. The correspondence of the data from both methods is excellent. It is noteworthy that the behaviour of LDPE also falls in this range, even though the crystallinity of this sample is much higher. It is of interest to point out that Hser and Carr have reported percentage crystallinity of a series of HB of different molecular weight using X-ray diffraction methodology. The density of all of their samples were ~0.915 g cm^{-3} and for samples in the molecular weight range 60 700 to 340 000 the ΔH_f were 21.7 to 17.4 cal g^{-1} respectively. These ΔH_f values correspond to a percentage crystallinity varying from 31.4 to 25.3%, whereas the respective percentage crystallinity values from the X-ray method were 43 and 46%. That is, there is little correlation in their crystallinity values obtained from the ΔH_f and X-ray methods used in their work. While we do not attempt to explain their discrepancy, it stands in contrast to our own data. An increase in crystallinity in our series of block polymers is only dependent on the butadiene content and bears no relationship to the block architecture.

The accumulated data from X-ray, ΔH_f and density measurements thus far indicate that there is good separation of the crystallizable HB block from that of amorphous HI block, regardless of molecular architecture. We as yet have no direct evidence to determine what is the specific morphological nature of the crystalline structure; specifically, as to whether they are composed of fringe micelle or folded chain structures. Dimarzio *et al.* have carried out calculations of lamella thickness in diblock copolymers where one of the components is crystalline; they have reached the conclusion that chain folding is a stable form in such block copolymers[32]. This is contrary to homopolymers where chain folding is metastable and annealing reduces chainfolding[33]. In order to gain some insight into possible arrangement of the crystalline domains on a higher order level, i.e., superstructure, we have applied the *SALS* technique. The H_v patterns for solution cast films of HB and a series of HBIB polymers are shown in *Figure 6*. Both the HIBI and HBI polymers produce the same kind of patterns and are not shown here. Polymers with high and intermediate butadiene content show the typical cloverleaf H_v pattern which is associated with the spherulitic structure[34]. In this composition range, the size of the spherulites as calculated from the angle of the maximum intensity in the H_v four-leaf clover scattering patterns, range from 0.5 to 3.0 μm. The *SALS* patterns suggest that there is a deterioration of the spherulitic perfection with an increase in HI content, and indeed sample HBIB-7 no longer displays a cloverleaf pattern, but rather a more rod-like or sheaf type pattern.

SEM micrographs of two member of these polymers (HB and HBIB-50) are shown in *Figure 7*. One can directly observe the surface of the spherulitic structure of the HB homopolymer as well as in that of the copolymer HBIB-50. The H_v patterns shown in *Figure 6* display an important trend. The best formed spherulitic structure is that of homopolymer HB. When the concentration of butadiene decreases in the series of the HBIB copolymers the perfection (anisotropic ordering) of the spherulites is also decreased. Indeed, in the polymer HBIB-7, which contains only 7% butadiene, one can no longer see the H_v scattering pattern as is observed for well developed spherulites. The formation of the spherulitic structure is strongly dependent on the method of film preparation.

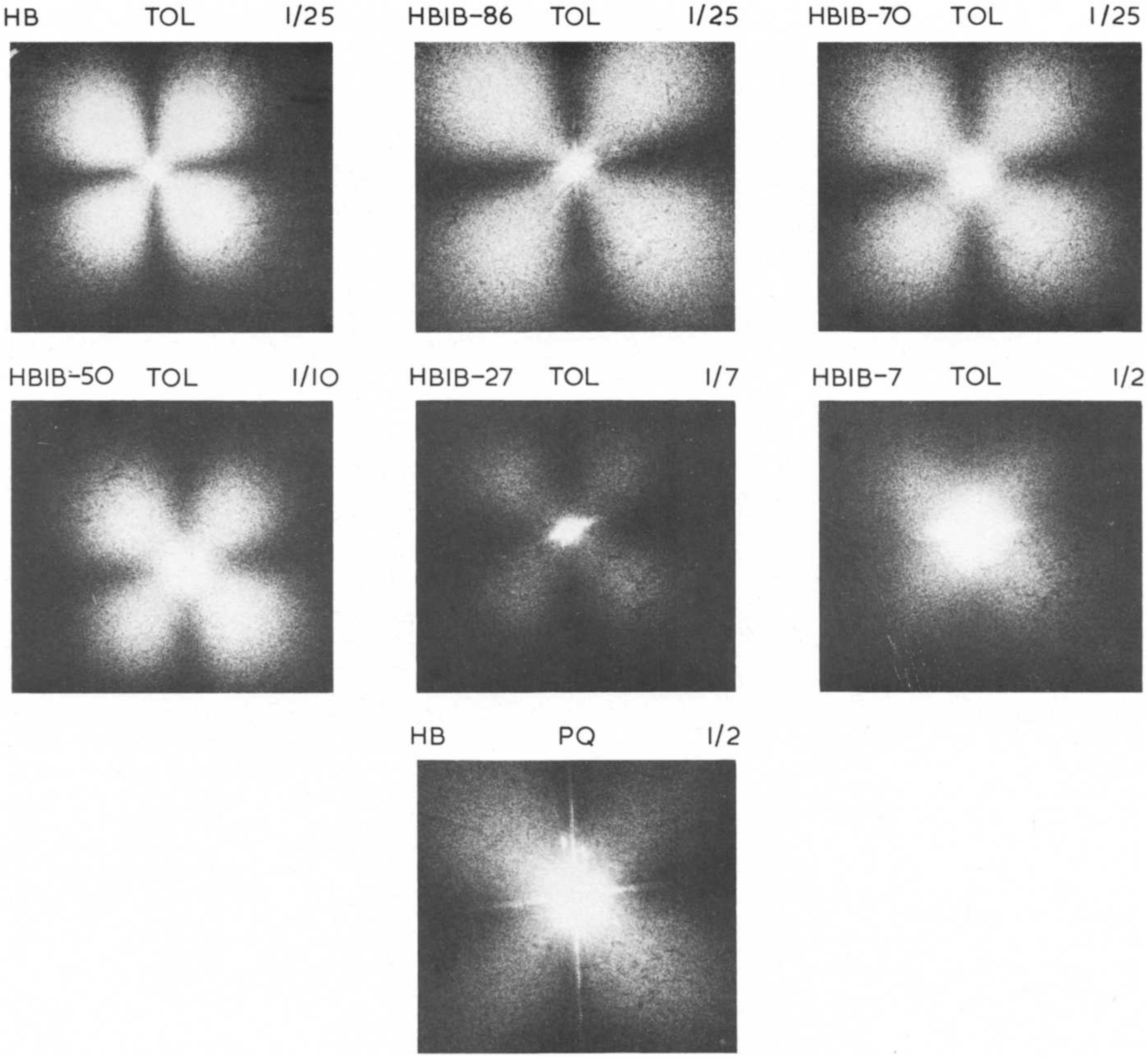

Figure 6 *SALS, H_v* light scattering patterns of homopolymer HB and the triblock copolymers HBIB of different compositions (indicated in the top left corner). The method of film preparation of T.C., cast from toluene (Tol) or press-quenched (PQ), is indicated on the top of the pictures. The exposure time (in fractions of a second) is indicated in the right hand corner of each picture

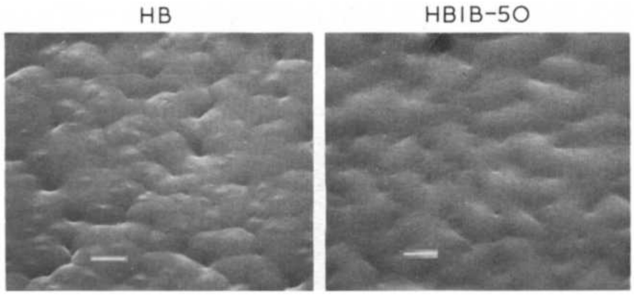

Figure 7 *SEM* of the surface of films cast from toluene for HB and HBIB-50

The well developed spherulitic structure shown in *Figure 6*, HB or HBIB-86 for example, were produced when the films were cast from solution (Tol). By contrast, press-quenched samples (PQ) did not show well developed spherulitic structure. Even the HB homopolymer produced an ill-defined spherulitic pattern when the film was prepared by quenching the pressed film (*Figure 6*). Mandelkern *et al.* have studied supermolecular structure of linear polyethylene fractions and reported that high molecular weight fractions (3–8×10^6) do not form well developed spherulites if they are crystallized rapidly[35]. These same polymers can, however, produce spherulitic structure if they are crystallized from highly swollen solutions[36].

It should be reemphasized that although our block copolymers do not display spherulitic morphology when they are press-quenched, they are nevertheless crystalline. Hence, this indicates that under this mode of film preparation, aggregation into well developed superstructure is apparently kinetically limited.

Stress–strain properties

A comparison of the stress–strain properties of the

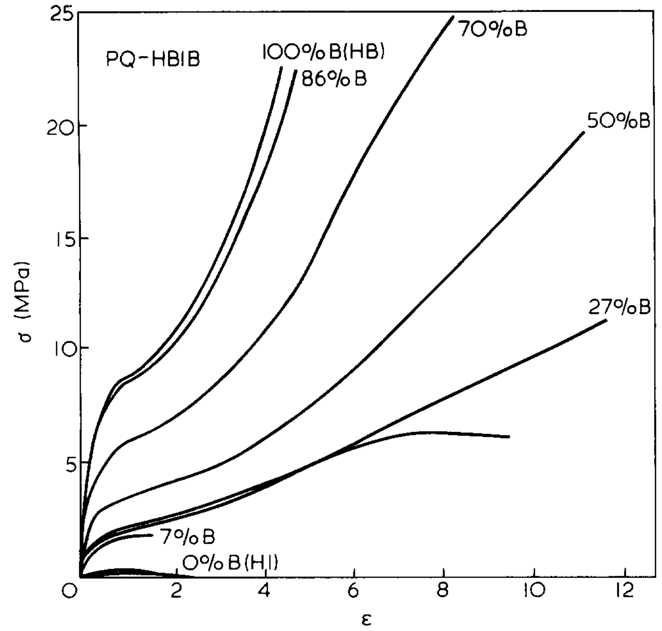

Figure 8 Comparison of the stress–strain properties of the press-quenched films of HBIB to those from the homopolymers HB and HI. The composition of each polymer is denoted by giving the butadiene content next to the graph

press quenched tri-block HBIB copolymers to those of the homopolymers HB and HI of the same molecular weight (~200 000) are made in *Figure 8*. The stress–strain properties of the inverted triblock copolymers HIBI are given in *Figure 9*. As might be expected, the stress–strain properties of HB are very similar to that of low density polyethylene. Perhaps linear low density polyethylene (LLDPE) would be an even better model. The major difference that we have observed is that the initial modulus of HB is lower than that of LDPE (75 vs. 170 MPa respectively) and there is also a lower stress displayed in the region where plastic deformation begins which is likely associated with yielding phenomenon involving crystallite reorientation. Both of these differences are at least partially accountable by the lower crystallinity of the press-quenched samples of HB relative to that of low density polyethylene (the crystallinities are approximately 30 and 40% respectively, see *Figure 5*). Onogi *et al.*, however, have reported that the material properties of HB are different from that of LDPE, the most remarkable difference is the higher elastic recovery of the former[17]. They attribute this difference to a 'looser' structure of spherulites of HB which allows crystallites to orient in a reversible manner. We have not observed significant differences in the nature of the stress-strain behaviour of HB polymers relative to those of LDPE. Indeed, when a sample of HB was prepared by solution casting from toluene, the crystallinity of this film was very close to that of a quenched sample of LDPE. The stress–strain plot of this solution cast film closely resembled that of quenched LDPE, indicating, as mentioned before, the earlier difference is principally due to the difference in the crystallinity level in contrast to molecular weight distribution discrepancies, etc. One should comment that the ultimate tensile properties of the HB systems are excellent.

The mechanical properties of HBIB block copolymers are significantly affected by the increase in the proportion of the central rubbery HI block. For example, HBIB-86 (14% isoprene) shows a lower modulus; some yielding behaviour is still present but elongation to break is significantly improved. A further increase in the rubbery HI content (e.g. from 14 to 82%) produces a modulus which is sharply decreased, but the elongation to break is again increased. HBIB-70 and HBIB-50 are very tough plastics; the former has even a higher stress to break than the initial HB. However, the behaviour of HBIB-27 is typical of a thermoplastic elastomer. HBIB-18 also has elastomeric behaviour but it fails earlier than HBIB-27 indicating that the three dimensional network of physical crosslinks (crystallites) is less well developed. The behaviour of HBIB-7 is somewhat like a particulate filled and uncrosslinked rubber of low filler content. The last member of this series, the homopolymer HI (or HBIB-0), is and behaves as an uncured rubber. It does not show any strain hardening indicating that, as expected; no strain-induced crystallization occurs.

The general stress–strain behaviour of our HBIB series has some similarity to those of the SBS block copolymers[3]. However, there are two prime differences between these two systems. Styrene is a brittle glass at room temperature, but HB is a semicrystalline plastic above its T_g and therefore is rather ductile. Therefore, a block copolymer of SBS containing as much as 20% butadiene is still brittle and often breaks at very low elongation. By contrast, HBIB-86 or even HB itself can be extended to above 400% elongation before failure occurs. The other difference is that the block copolymers of SBS may show considerable amounts of drawing (necking) in the concentration range of 39–65% styrene, whereas none of the members of HBIB display this behaviour.

The stress–strain properties of the inverted triblock copolymers HIBI are shown in *Figure 9*. Analogous measurement on the diblock copolymer HBI-50 are not shown but were almost identical to that of HIBI-49.

As expected, an increase in isoprene content from the

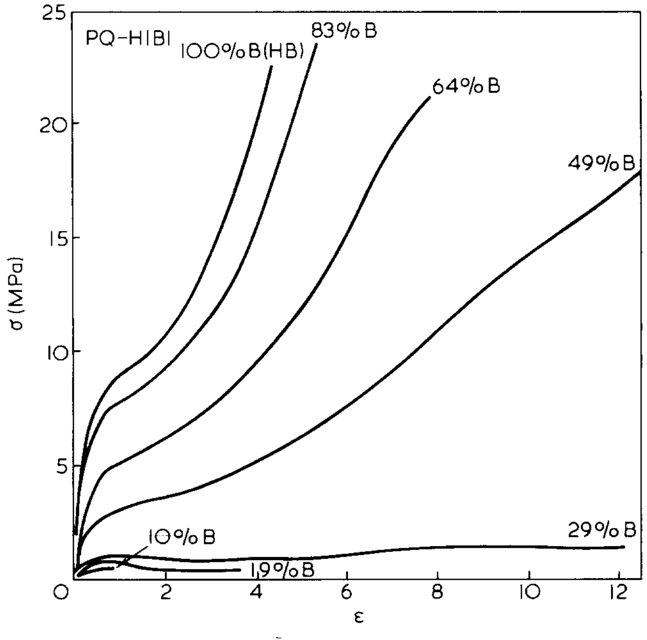

Figure 9 Comparison of stress–strain properties of the press-quenched films of HIBI block copolymers to those of homopolymer HB. The butadiene content is indicated next to each graph

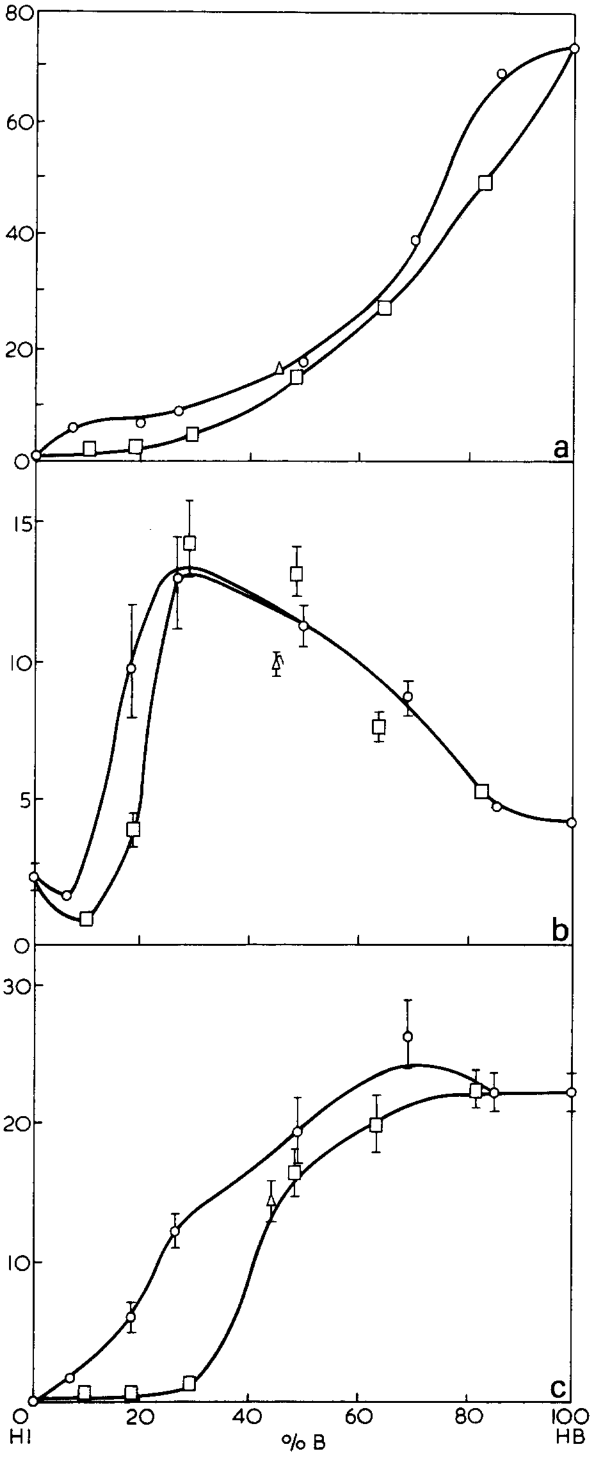

Figure 10 (a) The dependence of Young's modulus on butadiene content for the various copolymer architectures. (b) The dependence of strain to break on the butadiene content for the various copolymer architectures. (c) The dependence of the ultimate stress on the butadiene content for the various copolymers architectures. PQ samples: (○) HBIB; (□) HIBI; (△) HBI

homopolymer HB to the HIBI block copolymers and finally to the hompolymer HI greatly influences the mechanical properties. An increase in the rubbery HI content is again followed by a decrease by modulus. In the range of 23–49% butadiene, the polymers show higher extension to break than the pure HB. They can be viewed as tough plastics and require a larger input of energy (higher area under the stress–strain curve) to break. The next member of the series, HIBI-29, shows a great deal of extensibility, but it is extremely weak. A further increase in isoprene concentration results in polymers which are not only weak but also break at low extensions (HIBI-19 and HIBI-10). Now that the effects of variation of composition on the mechanical properties of each member of the two series has been examined, the influence of architecture alone on properties can be considered. A comparison of some specific properties for the polymers of various architecture and different compositions are made in *Figures 10a–c* and *Figure 11*. As in the case of *Figure 10a*, an increase in HB content, i.e., a rise in the concentration of the semicrystalline blocks, is always followed by a rise in the modulus of the polymers. This type of block copolymer behaviour has been expressed in terms of composite theories and the knowledge of the modulus of the component blocks (HI and HB). To do so, however, one has to know the geometry of the microdomains in the system considered. Calculation of the modulus of block copolymers using the modified composite theories developed by Nielsen[37,39] and Lewis[38] have been reported on SBS triblock copolymers[40,2] and will not be repeated here.

An interesting observation derived from *Figure 10a* is that modulus of the triblock copolymer HBIB is always higher than that of the inverted block copolymer HIBI. This difference in modulus is believed to be due to the presence of more permanent entanglements in HBIB copolymers since these endblocks can be partially tied down in the semi-crystalline domains, as shown schematically in Figure 12. Of course, it is realized that amorphous regions in HIBI also form entanglements, but since the end blocks are not mechanically anchored these entanglements can be lost when the sample begins to undergo deformation.

The ultimate properties, that is the elongation and stress at break for copolymers with various architectures and compositions, are given in *Figures 10b* and *c* respectively. The elongation at break ε_β goes through a maximum for the block copolymer when the composition is varied from pure HI to that of HB as shown in *Figure 10b*. The maximum is achieved around 30% butadiene content. Since the ultimate properties are often controlled by crack initiation and crack propagations[41,42] the improvement in ε_β here suggests that this catastrophic failure has been reduced by the composition variable. The principal mechanism is believed to be the termination or

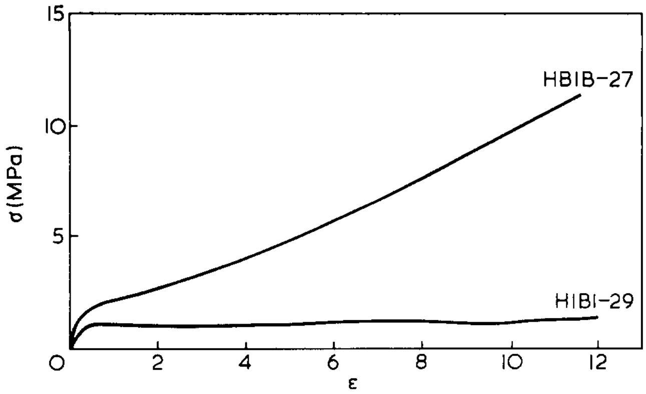

Figure 11 A comparison of the stress–strain properties of the thermoplastic elastomer HBIB-27 to that of the inverted block copolymer HIBI-29

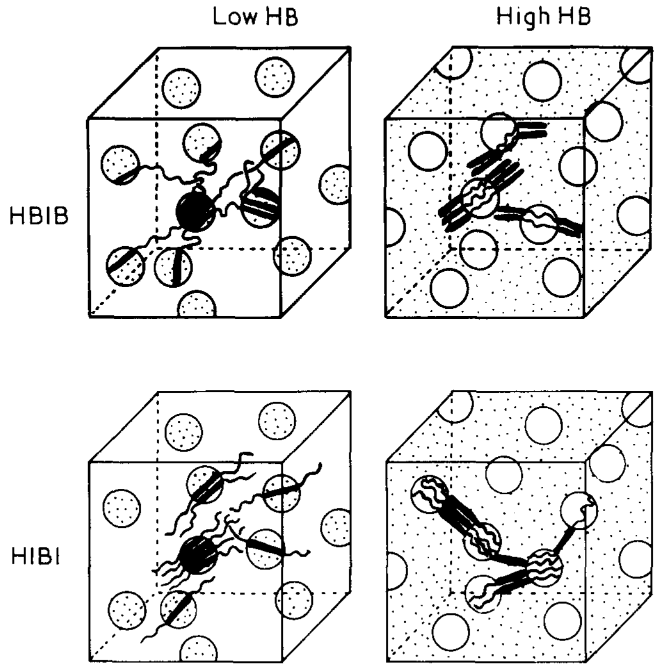

Figure 12 Oversimplified schematic representation of the morphology of HBIB and HIBI block copolymers in the low and high butadiene concentration ranges. Formation of 'physical crosslinks' by the anchorage of the chain ends in the semicrystalline domains and production of the 'permanent' entanglements is shown in the HBIB block copolymers. No such arrangement exists for the inverted polymer HIBI. No attempt has been made to show possible chain folding, or superstructure development of their absence. (—) Semicrystalline block; (~) amorphous block

slowing down of the crack front at the boundary between the crystalline and noncrystalline regions. Thus in the composition range of 30–40% butadiene content, the morphology of all the polymers, HBIB, HIBI and HBI, is perhaps in an optimum condition for arresting catastrophic failure. Therefore all these polymers have high extension in this concentration range. Above this concentration range ε_β is decreased approximately in the same way for all chain architectures. Below this value, the ε_β is also decreased, but now there is a considerable difference in behaviour of HBIB from that of HIBI polymers. In the 10–20% butadiene range HIBI polymers fail at lower elongation than HBIB polymers and this behaviour is related to the morphological structure of the polymers as discussed shortly. The stress to break, σ_β, does not seem to go through a significant maximum, but rather there is a considerable increase in σ_β with an increase in butadiene from the low value of HI. The behaviour of the polymers with regard to ultimate stress falls into two categories. In the low to intermediate concentration range of butadiene (from 10–40% B) the behaviour of the HBIB polymers is quite different from that of the inverted HIBI copolymers and is most pronounced in the 20–29% range. In the high concentration range (40–100% B), the σ_β for HBIB and HIBI is much closer. A comparison of the stress–strain properties for HBIB and HIBI polymers, in this concentration range, is made in *Figure 11*.

The HBIB-27 polymer behaves like a thermoplastic elastomer, whereas HIBI-29 behaves like a particulate-filled uncured elastomer. These differences are clearly related to the morphology and structure of these polymers. To describe the behaviour of these polymers of various architecture and containing different levels of semicrystalline HB block, an oversimplified morphological model of these systems, was made at the two extreme ranges in concentration*. In polymers where the relative concentration of butadiene is high (*Figure 12*), the continuous phase is the semicrystalline HB (or the polyethylene-like structure). The mechanical properties of the polymer are controlled primarily by this continuous dominant phase. The rubber HI domains are dispersed within this semicrystalline phase. There is no major difference between HBIB, HIBI of HBI block copolymers because the properties are determined by the continuous semicrystalline structure. The behaviour of this system is somewhat similar to that of rubber modified polystyrene[1]. The main function of the dispersed rubbery phase is to lower the modulus and to allow higher extensibility by terminating or reducing crack propagation. A schematic drawing for the intermediate concentration of butadiene is not shown but the behaviour is similar since under this condition (of course, depending on the film processing condition) both phases are continuous. But the behaviour of the polymer is again controlled by the dominant semicrystalline phase.

A schematic drawing of the morphology of the block copolymers in the low butadiene range is given in *Figure 12*. In this concentration range the behaviour of the HBIB polymers is very different from that of HIBI or HBI. The continuous phase in this case is the rubber HI segments and the semicrystalline domains are dispersed throughout the sample. The semicrystalline domains in the case of HBIB not only act as a filler, but also tie down the end blocks of the polymer producing physical crosslinks. The entanglements in the HI blocks can no longer be lost by complete slippage of the chain, and are therefore of a more permanent nature. The behaviour of HBIB polymers under this condition is that of a thermoplastic elastomer. The HIBI or HBI polymer cannot form this kind of physical cross-link, the HB block which has formed the semi-crystalline domain can only act as a filler and therefore these polymers behave more like an uncured rubber. This type of behaviour has also been observed for SBS block copolymers[3].

Hysteresis behaviour

The hysteresis behaviour of the HBIB triblock copolymers is given in *Figure 13a* and of that of the inverted HIBI block copolymer is given in *Figure 13b*. The difference in the behaviour of these two series of block copolymers is tremendous. The origin of these differences are again directly related to the morphology and the architecture of the polymers. The hysteresis behaviour of HBIB is strongly dependent of the composition of polymer. The first member of this series is the homopolymer HB which contains the highest (100%) concentration of the semicrystalline segment and therefore exhibits the highest hysteresis. That is, during each cyclic loading and unloading, a considerable amount of energy is lost as heat. Moreover, irreversible rearrangement of the crystalline domains occurs during this plastic deformation.

Introduction of the central rubbery HI block decreases

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* These drawings are not meant to infer that no superstructure or chain folding may exist but only to depict the general differences in the continuity of the two components as well as the nature of the localized end blocks

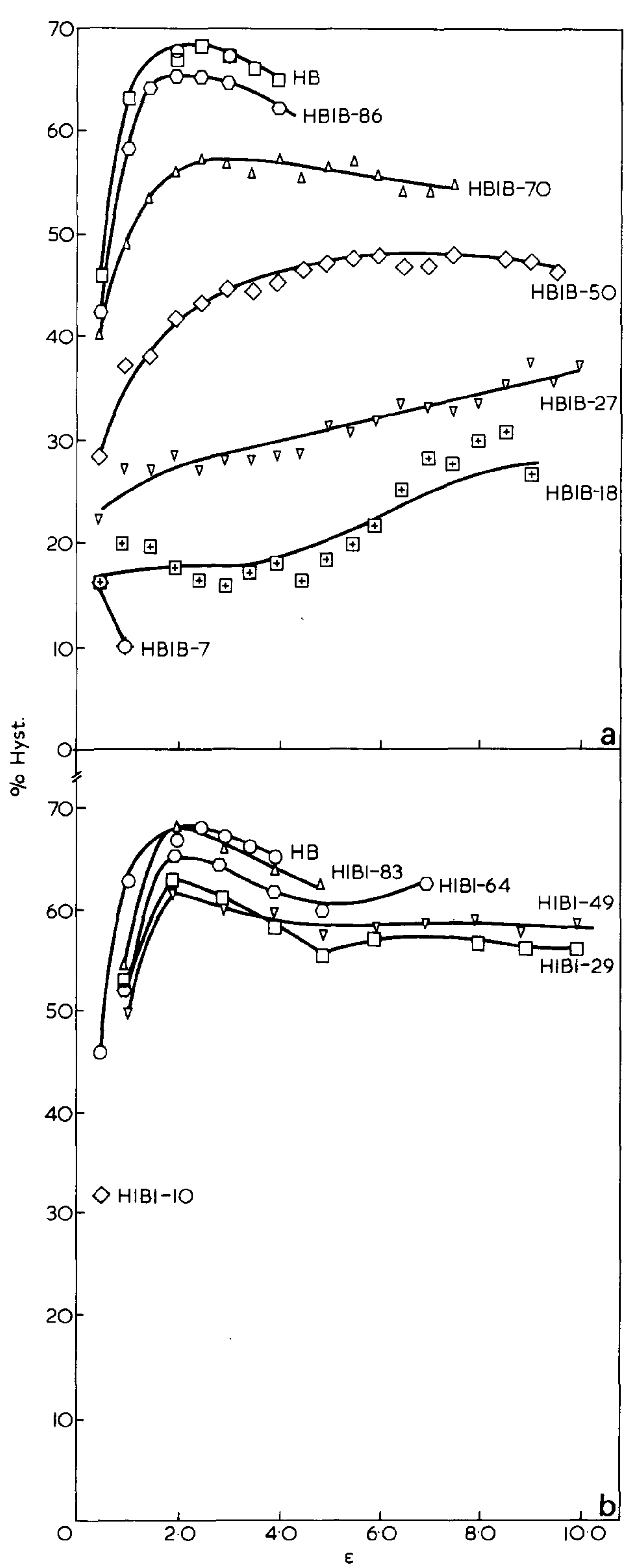

Figure 13 (a) The hysteresis behaviour of the HBIB polymers. (b) The hysteresis behaviour of the HIBI polymers

the continuity of the semicrystalline domains and results in a successive decrease in hysteresis behaviour. Similar behaviour has been observed in segmented polyurethanes when the hard segment content has been varied[43]. Thus, an increase in HI block content (or a decrease in the concentration of the semicrystalline HB) is always followed by a considerable decrease in the hysteresis behaviour. The lowest hysteresis is observed for HBIB-7 which contains the lowest butadiene content, but this sample is not very extensible and fails early because, as mentioned before, there are not enough crystalline domains to form a three dimensional network of physical crosslinks. HBIB-18 and HBIB-27 which are both thermoplastic elastomers, show considerable extensibility but low hysteresis behaviour. The hysteresis behaviour of the above two elastomers is much lower than that of the conventional segmented poly(urea-urethanes)[44]. An increase in the butadiene content of the other members of the HBIB series results in the crystalline HB domains developing more continuity. This alteration in morphology leads to a high hysteresis. Further support of the above argument extends from the recent work of Séquéla and Prod'homme who investigated the properties of SIS and SBS block copolymers[45]. They have shown, as expected, that the best hysteresis behaviour is obtained for samples in which the hard styrene block has formed microdomains which are well isolated from each other[45]. This was also demonstrated much earlier by one of the authors[47]. The mechanical behaviour of such a system is similar to that of unfilled crosslinked rubber. If, however, the samples were made such that there was connectivity between the hard blocks, the mechanical properties deviated from that of cross-linked rubber. A similar observation has been made with respect to the hysteresis behaviour in segmented urethanes as a function of composition and domain morphology.

The hysteresis behaviour of the HIBI series is shown in *Figure 13b*. All of the samples have much higher hysteresis than the corresponding member (with respect to composition) of the HBIB series. Although there is a noticeable decrease in the per cent hysteresis with an increase in rubbery HI content, the hysteresis does not fall below 55% at high extensions.

The hysteresis behaviour of the diblock copolymer HBI-50 is not shown but is very similar to that of HIBI-49. In summary, the difference in hysteresis behaviour of the HBIB series to that of HIBI and HBI is related to the ability of the members of the first series to form permanent entanglements, by entrapment of the end blocks in the semicrystalline domains, whereas no such arrangement is possible for neither HIBI nor HBI series. The permanent entanglements by entrapment of the end blocks in the semicrystalline domains whereas no such arrangement is possible for neither the HIBI nor HBI. The permanent lower energy lost as heat.

Crystallization kinetics

Changes in the composition of the block copolymers affects their rate of crystallization. To indicate this, a plot of the time of onset of maximum crystallization rate. t_{xtal}, is plotted against the degree of supercooling in *Figure 14a.* The parameter t_{xtal} is that time period between the onset of crystallization and that time when the rate is a maximum. This was determined from isothermal d.s.c. traces and observing the change in the heat capacity with time. The supercooling is defined as the melting temperature minus the crystallization temperature. In this study, we have taken the temperature of the exothermic maximum of the d.s.c. curve as the melting temperature, being sure to use the same scan rate for each material. In the above plot, the polymer with a faster rate of crystallization will have a curve which is shifted closer to the origin. The rate of

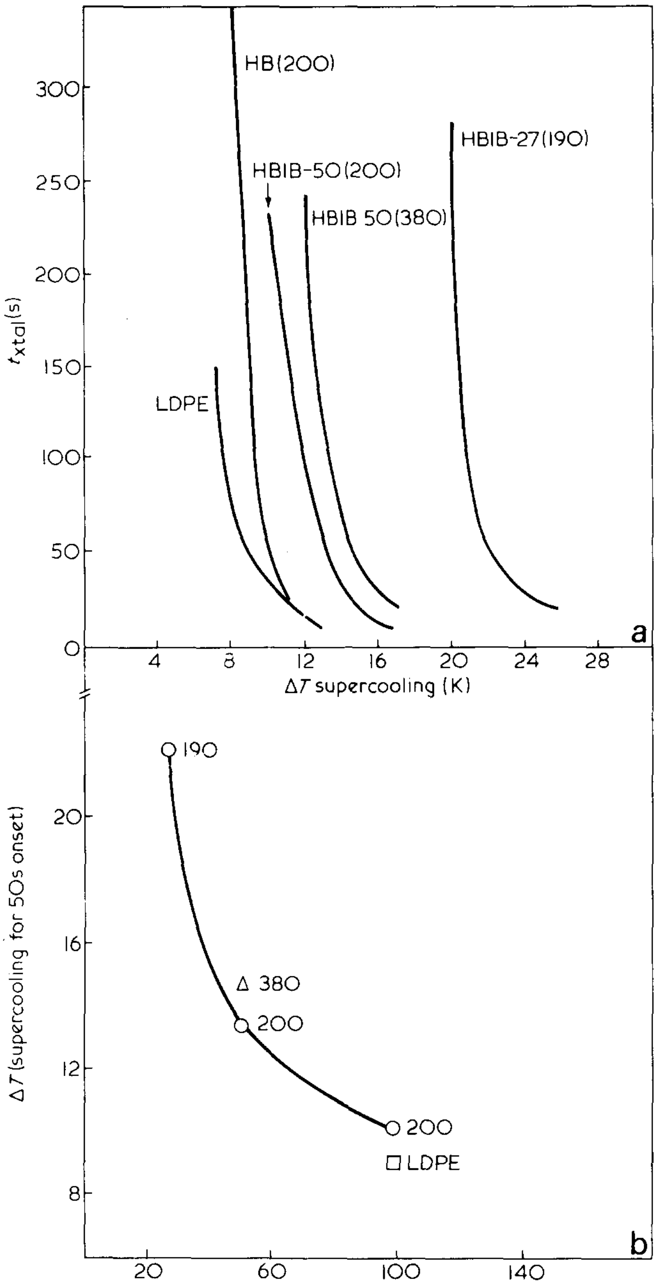

Figure 14 (a) A comparison of the rate of crystallization for homopolymer HB and some of the triblock copolymers HBIB contrasted to that of LDPE. The molecular weight of the homo and the block copolymers ($\times 10^{-3}$) are indicated in the parentheses. (b) A comparison of the supercooling to produce the onset of crystallization at 50 s for LDPE, the homopolymer HB and some of the triblock copolymers of various compositions

crystallization of the homopolymer HB and block copolymers of HBIB are compared to that of our LDPE sample in *Figure 14a*. It is noted that the LDPE crystallizes faster than the HB and the rate of crystallization of the block copolymers is lower than that of the homopolymer HB and decreases with an increase in HI content. This plot can also be utilized in two different ways. At any given supercooling, the sample with a faster crystallization rate will require a lower value of t_{xtal}. The other way of describing the relative rate of crystallization is to determine the supercooling required for a given t_{xtal}; in this case samples with a faster rate will require a lower supercooling. *Figure 14b* is based on using this latter method of comparison. In this plot we have arbitrarily chosen the time window of t_{xtal} to equal 50 s. Observe that the LDPE requires a 9 degree supercooling and has a faster relative crystallization rate than HB which requires a 10 degree supercooling. HBIB-50, in turn, requires a higher supercooling than HB. It is noted that the rate at this butadiene content also seems to be dependent on the molecular weight. The sample with a higher total molecular weight crystallizes more slowly as might be expected. However, with the limited samples studied, this latter point should be viewed only as speculation.

The slowest rate of crystallization is observed for HBIB-27, whose molecular weight is around 190000. Thus, the general trend indicates that the increase in rubbery block content (and therefore a decrease in crystallizable block content) results in a slower rate of crystallization. The melting temperature on the other hand is $\sim 102 \pm 2$°C for all of these polymers and does not depend on the block composition and the architecture. This latter data, combined with the earlier observations on linear additivity of density and heat of fusion, supports the suggestion that in the final solid there is a good phase separation between HB and HI blocks. Thus because of this phase separation, the environment felt by the polyethylene like crystallites in the domains containing the HB blocks is ambivalent to the total concentration of the HI in the block copolymers. Furthermore, the dynamic mechanical studies suggest that even the amorphous region of the HB and HI blocks are not mixed to any major extent in the solid state.

Thus, if the decrease in the crystallization rate of the block copolymers is not caused by an increase in the relative concentration of a mixed phase, the question would be what is causing the difference in the values of t_{xtal} with a change in composition? There is no simple answer to this question since many factors may concurrently be responsible for this observed behaviour. First it must be recognized that the absence of mixing of the two blocks in the solid state does not exclude mixing in the melt. It is likely that there is a tendency for mixing between the HB and HI blocks when above the melting temperature of the semicrystalline HB block. This statement rests on the fact that the nonhydrogenated block copolymers display compatibility in the solid state[48,52,53]. If indeed we assume mixing occurs for the hydrogenated system in the melt, a possible explanation that may partially account for the observed crystallization kinetics is as follows. Specifically the glass transition temperature of the HI block is around -60°C, while that of the HB block should be comparable with that of polyethylene (T_g of PE for example is taken at ~ -75, -81, and -100°C, respectively, according to refs 19, 49 and 50). This indicates that the mobility of the HB chain is somewhat greater than that of the HI chain. Hence, if mixing between the two blocks is allowed when the polymer is in the molten state, then the T_g of the mixed blocks (and thus the molecular mobility) will be dependent upon the composition ratio. That is, block copolymers of higher HI content will have a somewhat higher rigidity and thus a lower diffusivity in the melt. Hence, the rate of crystalline growth will be slower for a given supercooling[51]. To help verify the above explanation, melt rheological studies will be carried out to note if any sign of a hetereogeneous melt exists.

Another plausible answer, though highly speculative, may be the lowering of the rate of nucleation of the crystalline domains caused by their separation from each other due to the rubber HI phase. This requires, however, that phase separation in the melt state occurs. As indicated earlier, we do not think such phase separation exists. The second explanation has some similarity to the crystallization kinetics behaviour of polyethylene droplets suspended in oil. In our case, the amorphous HI phase plays the role of the oil. Even if there might be no change in the rate of primary nucleation and crystal growth, the bulk crystallization of polymer droplets in oil will be reduced. The reduction of the crystallization of the bulk of the polymer is due to the physical separation of the droplets (or HB domains in our case) because the propagation of crystallization will be restricted to the droplet in which the crystallization nucleus is initiated. The reduction of mass crystallization rate thus will be related to the lack of mechanism of transfer of crystallization from one domain to the neighbouring regions. Further detailed crystallization and morphological studies will hopefully shed light on this phenomenon.

CONCLUSIONS

The mechanical properties of block copolymers composed of rubber HI segments and the semicrystalline HB chains are dependent both on the composition of the polymers and the architecture of the blocks. The density, ΔH_f, crystallinity and the morphology of the block copolymers, on the other hand, are primarily dependent on butadiene content and show little dependence on architecture. This is tentatively indicative of the fact that in the solid state there is a very good phase separation between the HB and HI blocks. Although the solution cast films show a spherulitic morphology, the quenched films do not show distinct structures indicating that the arrangement of the crystallites at the supermolecular level is not well organized.

At high and intermediate concentrations of HB, the semicrystalline HB block forms the continuous or one of the continuous phases. When the continuous phase is a tough semicrystalline block, the mechanical properties are dominated by this phase. At these compositions, the stress–strain properties are not much different, although there is a difference in modulus behaviour between members of varied architecture. The hysteresis behaviour is significantly varied indicating that the permanent end block entanglements produced in the HBIB series play an important part in retracting the sample once the extension load is removed. The difference in mechanical properties between polymers of different architecture is most apparent when the HB content is low. At this composition, where the rubbery HI has formed the continuous phase and the semicrystalline blocks are dispersed in more discrete or isolated domains, the behaviour of HBIB becomes that of a thermoplastic elastomer. The HIBI and HBI polymers, however, cannot behave as crosslinked elastomers because they are not capable of forming permanent endblock anchorage. The stress–strain properties of HIBI and HBI are similar to that of modified particulate filled uncured rubber. These polymers, however, have high extensibility, probably due to crack termination at the interphase. But contrary to HBIB polymers, they do not show any strain hardening and are very weak materials. The hysteresis behaviour of HIBI and HBI polymers is also very different from that of the HBIB polymer. The former polymers show much higher energy loss during cyclic deformations, and these differences are again interpreted as being related to the ability to form permanent entanglements.

The observed isothermal crystallization kinetics do show a dependence upon composition with a slow rate noted as the HI block concentration increases. Speculation is given as to the possible origin(s) of this phenomenon.

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