Tensile Properties of Crystalline Polymers: Random Copolymers of Ethylene

M. A. Kennedy,[†] A. J. Peacock,[‡] M. D. Failla,[§] J. C. Lucas,[‖] and L. Mandelkern*

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306–3015

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ABSTRACT: Force–elongation curves of a set of random ethylene-1-alkene copolymers have been studied. The comonomers included 1-butene, 1-hexene, 1-octene, and 4-methyl-1-pentene. The copolymers all had the most probable molecular weight and narrow composition distributions. A set of hydrogenated poly(butadienes), random ethyl-branched copolymers, that have very narrow molecular weight and composition distributions were also studied as reference. Only ductile type deformations were studied. Several important generalizations resulted from this work. An important finding was that the molecular weight, copolymer composition, and chemical nature of the co-units have to be considered as independent variables in analyzing the tensile behavior. The nominal stress–strain curves of even modest molecular weights are dominated by strain-hardening. This characteristic is similar to that of very high molecular weight linear polyethylenes. However, the effect is not as large for the ethylene–butenes as compared with the other copolymers. The ultimate properties of the ethylene–butene copolymers also differ from the others. An explanation for these differences can be given by postulating that in the melt structure, and thus in the residual liquid–like region, noncrystalline portions are affected by interaction of the side groups. In contrast, the yield stress and initial modulus do not depend on the chemical nature of the co-unit but only on the crystallinity level. In the regions of overlap there is a substantial difference between the yield stress and initial modulus of linear polyethylene and the copolymers. Different portions of the force–elongation curves are governed by different structural and molecular features indicating the complexity of the problem. The wide range of experimental data that are presented, for thoroughly characterized samples, can serve as a basis for the molecular understanding of the ductile deformation of random copolymers.

Introduction

The tensile properties are an important characteristic of polymers in general and crystalline polymers in particular. They establish the basis for many important end uses of polymers. It is particularly important to understand how stress–strain curves, as well as the key tensile properties, depend on the molecular constitution, i.e. molecular weight, its distribution, and the structural regularity of the chain. Equally important is the role of the key structural variables that govern the structure and morphology of the crystalline polymers.[1,2] These key independent variables are the degrees of crystallinity, the structures of the residual noncrystalline or liquid-like region, the crystallite thickness distribution, the extent and structure of the interfacial region, the overall habit and internal structure of the lamellar-like crystallites, and the supermolecular structure. The tensile behavior of linear polyethylene has recently been studied from this point of view.[3] In order to obtain results that can be given a molecular and structural interpretation it is advisable to work with fractions or samples having well-defined distributions and microstructures.[3,4] From studies of this type some of the general principles that govern tensile behavior are emerging.

When the tensile properties of copolymers are treated in this way several additional factors need to be taken into account. These are the chemical nature of the co-unit, its nominal composition, and the sequence distribution of units. It is also important to establish if the crystalline phase remains pure. If the co-unit enters the lattice, it has to be established whether it does so on an equilibrium or nonequilibrium basis. It is simplest to work with systems with pure crystalline phases that also have well-defined sequence distributions. A copolymer with a random sequence distribution that also has narrow composition and chain length distributions would be ideally suited for study.

It is known that the introduction of noncrystallizing co-units, even in small concentrations, can make significant alterations in the force–elongation curves.[5] Important information has been obtained from previous reports of the tensile properties of random ethylene copolymers.[5–13] However, except for the studies of the hydrogenated poly(butadienes),[14,15] and one set of ethylene–butene fractions of varying chain lengths and compositions,[16] they are of limited utility in developing general principles. The polydispersity in composition and in chain lengths, typical of the copolymers used in the past, introduces major complications. In the present work we alleviate some of these problems by studying the tensile behavior of a set of random ethylene-1-alkene copolymers that have narrow composition and most probable molecular weight distributions.[17,18] Copolymers containing one of four different 1-alkene co-units were used in this study. It has been established that none of the co-units chosen enters the crystal lattice.[19,20a] For reference purposes we have also studied a series of hydrogenated poly(butadienes) which possess both narrow composition and molecular weight distributions.

The main objective of the present work is to assess the influence of the independent structural variables on

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[†] ICI Explosive Canada, Group Technical Center, BePoeil Site, McMasterville, Quebec, Canada J3G1T9.

[‡] Baytown Polymer Center, Exxon Chemical Co., P.O. Box 5200, Baytown, TX 77522.

[§] Planta Piloto De Ingenieria Quimica, 12 De Octubre 1842, 8000-Bahia Blanca, Buenos Aires, Argentina.

[‖] CITIP-INTI, 157, (1650) San Martin, Buenos Aires, Argentina.

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the key parameters that describe tensile behavior. For this purpose the present studies have been restricted to one draw rate and temperature. This restriction does not hamper assessing the basic role of molecular constitution and the structural variables. The force−elongation measurements, or nominal stress−strain curves that are obtained here should not be confused with true stress−strain curves.[20b] They are, however, quite adequate for the purpose at hand. This work complements a previous study of linear polyethylene that had a similar objective.[3] Because of structural differences in both the crystalline and noncrystalline regions, copolymers need to be treated separately.[3,4] The connections, if any, in tensile properties of the two types of polymers will become clear from the results of the present study. It is not our objective here to develop procedures that will yield the highest elongation or greatest modulus. These goals will be achieved eventually when the molecular processes that are involved in the deformation are established.

Experimental Section

Materials. The copolymers that were used in this study are similar to those previously used for studies of thermodynamics and phase structure[17,18] supermolecular structures[21] and crystallization kinetics.[22] The ethylene-1-butene (EB), ethylene−1-hexene (EH), ethylene−1-octene (EO) and ethylene−4-methyl-1-pentene (EmP) were prepared following the method of Kaminsky *et al.* using $(C_5H_5)_2ZrCl_2$ as catalyst.[23] This procedure produces random sequence copolymers that have the most probable molecular weight and narrow composition distributions. The hydrogenated poly(butadienes) (ethyl-branched copolymers) that were studied had random sequences and narrow molecular weight and composition distributions. Some of the hydrogenated poly(butadienes) were kindly supplied to us by Dr. W. W. Graessley.[24] Others were purchased from the Phillips Petroleum Co.

Characterization. The molecular characteristics of the copolymers are given in Table 1. The weight and number average molecular weights were obtained by gel permeation chromatography by following conventional procedures. The data make it clear that these samples have the most probable molecular weight distributions. The co-unit content was determined by high-resolution carbon-13 NMR using established methods and assignments that are reported in the literature.[25,26] The data in Table 1 demonstrate that a wide range in molecular weights, co-unit contents and branch types are available for this study.

The heats of fusion were determined with a Perkin-Elmer differential scanning calorimeter (DSC-2B) that was calibrated for temperature and melting enthapy by using indium as a standard. The polyethylenes, and the indium standard, were prepared for the DSC measurements by weighing 1.5−2.0 mg of sample into a preweighed standard aluminum DSC pan. The samples were heated from 40 to 167 °C at a scanning rate of 10 deg/min. The areas of the endotherms were determined by planimetry. The heat of fusion was calculated by comparing the area of the sample with the standard. The degree of crystallinity was then calculated by comparison with the heat of fusion of a perfectly crystalline polyethylene, i.e., 289 J/g (69 cal/g).[27]

The densities were determined at 23 °C in a triethylene glycol/water density gradient that was calibrated with standard glass floats. The degrees of crystallinity, $(1-\lambda)_d$, were obtained from the relationship given by Chiang and Flory.[28]

The fraction core crystallinity, α_c, the liquidlike fraction, α_a, and α_b the fraction of the interfacial region were obtained by analysis of the $900-1600\ cm^{-1}$ internal mode region of the Raman spectra. The spectra were obtained with instrumentation that has been previously described.[29,30] The analysis of the spectra has also been described. It is based on the method given by Strobl and Hagedon,[31] as was further refined in this laboratory.[29,30,32,33]

Table 1. Molecular Characteristics and Structure of Copolymers

mol % branch pt	M_W	M_W/M_N	superstructure[a]	$(1-\lambda)_{\Delta H}$	α_a	α_b	α_c	L_C
Hydrogenated Poly(butadienes)								
2.1	16 000	1.14	b		0.52	0.12	0.36	67
2.2	108 000	1.31	h	0.18	0.61	0.17	0.22	67
2.2	420 000	2.66	h		0.68	0.13	0.19	69
2.3	24 000	1.1	b		0.54	0.14	0.32	70
2.3	49 000	1.1	c		0.67	0.09	0.24	72
2.4	79 000	1.1	c/h		0.61	0.14	0.25	68
2.7	145 000	~1.1	h		0.65	0.16	0.19	
3.3	50 000	1.2	h	0.20				
3.6	108 000	1.1		0.14				
4.1	50 000	~1.1			0.67	0.19	0.14	
5.5	103 000	~1.1		0.08				
5.7	50 000	~1.1		0.09				
Ethylene-*co*-Butene								
0.3	108 000		a	0.44				
0.8	550 000	~2		0.34				94
0.95	53 000	1.8	a	0.34	0.44	0.16	0.40	87
1.0	244 000	~2	b	0.29				
0.8	33 000	1.9	a	0.40	0.35	0.14	0.51	108
1.2	195 000		c	0.29				84
1.22	71 000	2.1	a	0.29	0.47	0.17	0.36	80
1.26	90 000	2.2	a	0.31	0.46	0.17	0.37	93
1.9	78 800	2.2	c	0.26				
2.05	125 000	2.3	h	0.24	0.62	0.11	0.27	72
2.8	93 700	2.1	h	0.19				
Ethylene-*co*-hexene								
0.4	305 000			0.32				
0.5	160 000			0.30				
0.6	56 000	~2	c	0.41	0.48	0.12	0.40	95
0.97	307 000		h	0.24				74
1.1	23 000	~2	c		0.42	0.14	0.44	93
1.1	58 000		b	0.35	0.46	0.18	0.36	82
1.1	201 000			0.25				
1.14	68 000	2.1	c	0.31	0.50	0.16	0.34	80
1.2	48 800	1.87	h	0.32	0.51	0.11	0.38	77
1.2	104 000	2.39	c		0.58	0.10	0.32	77
1.4	54 000			0.28				77
1.4	18 900	2.39	b		0.43	0.11	0.46	75
1.5	240 000	2.17	h		0.61	0.10	0.29	75
1.7	121 000		h	0.22				77
1.7	69 400		h	0.28				77
2.2	88 000		h		0.68	0.12	0.20	62
2.6	28 000			0.16				70
2.7	221 000	1.7	h	0.17				
2.8	57 000	1.8	h	0.17	0.71	0.10	0.19	60
2.9	112 000			0.17				
3.2	12 460	1.9		0.18	0.70	0.10	0.20	58
3.3	42 000			0.23				
3.3	50 600	1.9	h		0.66	0.21	0.13	57
3.5	62 700	2.2	h	0.12	0.67	0.18	0.15	57
3.8	15 860			0.11				
4.7	109 000							
Ethylene-*co*-Octene								
0.15	153 600		c	0.32				
0.7	117 000		h	0.34	0.47	0.13	0.40	87
1.4	38 000	1.9	h	0.29	0.47	0.19	0.34	80
1.4	79 000		h	0.27	0.52	0.20	0.28	78
2.0	125 000			0.22				
1.9	28 000		b/c		0.51	0.15	0.34	78
3.7	122 000			0.21				
4.6	149 000	2.5	h	0.08	0.82	0.11	0.07	45
Ethylene-*co*-4-Methyl-1-pentene								
0.7	127 000		h	0.40	0.55	0.08	0.37	72
1.0	169 000	2.65	h	0.43				
1.2	36 000		c	0.39	0.44	0.17	0.39	82
1.3	137 000		h	0.38	0.61	0.12	0.27	67
1.6	26 000		h	0.39	0.58	0.06	0.36	73
1.8	273 000		h	0.24	0.62	0.18	0.20	59
1.9	83 000	2.35	h	0.35				
2.0	88 000		h	0.27				
2.0	106 000		h	0.28	0.55	0.19	0.26	
2.1	252 000	3.00	h	0.25	0.63	0.16	0.21	64
2.1	38 000		h	0.26	0.59	0.20	0.21	67
2.4	28 000	2.28	h	0.26				
2.4	238 000	2.45	h	0.24	0.65	0.17	0.18	64
3.6	63 000		h	0.19	0.67	0.22	0.11	50

[a] Designation of superstructures are the same as in ref 41.

The crystallite thickness, L_C, was obtained from the Raman low-frequency acoustical mode (LAM). The instrumentation used, the experimental procedures, and the method of analysis that were followed, have also been described.[34] The LAM data were analyzed by following the methods given by Snyder and co-workers.[35,36] The value of 2.9×10^5 MPa was taken for the Young modulus.[37,38] The thickness of the interlamellar region, L_A, was calculated from the Raman spectra.[39]

The supermolecular structure of the crystallized films was determined from small-angle light scattering patterns. The type of patterns that are obtained, and their interpretation, has already been discussed in detail.[21,40,41]

The phase structure characteristics and crystallite thicknesses of the samples are also given in Table 1.

Sample Preparation. Films for the tensile measurements were prepared by compression molding of the samples at 150 °C in a Carver press. The samples were molded between 0.9 mm thick copper plates that were spaced with 0.2 mm thick brass sheets. On removal from the press, the plates were rapidly plunged into a dry-ice saturated solution of 2-propanol (−78 °C). This rapid crystallization procedure (quenched) was adopted deliberately. It enables a rational comparison to be made between different samples. After either slow cooling, or isothermal crystallization from the melt, the level of crystallinity that is observed at room temperature is dependent on the details of the cooling process.[42] Even at a constant cooling rate, the co-unit concentration plays a crucial role in determining the sequences that actually crystallize and thus on the macroscopic properties. Therefore, it is difficult to make a meaningful comparison between the properties of different samples after either isothermal or slow crystallization.

Tensile Measurements. For the tensile measurements small dumbbell-shaped specimens, with a gauge length of 4 mm, were stamped from the films using a mallet handle die. The width and thickness of the gauge region of each specimen was measured to an accuracy of 2.5 μm. Sample thickness was in the range 0.15−0.3 mm and the width was about 2 mm.

The force−length studies were carried out using an apparatus that was designed and built in our laboratory. Its characteristics have already been described in detail.[6] One advantage of this instrument is that only 150 mg of sample is required for ten repetitive experiments. This enables one to study materials that are in short supply, such as molecular weight and composition fractions and polymers of narrow, defined distribution. The specimens were deformed at ambient temperature (24−26 °C) at the draw rate of 1 in./min. The deformation was carried out to fracture. Equidistant ink marks, spaced at intervals of 1 mm, were placed on the underformed samples in order to facilitate the measurement of the draw ratio during deformation and after break. Ten specimens were tested for each sample.

The tensile parameters of interest here are the initial modulus, the yield stress, the draw ratio after break, and the ultimate tensile stress. These quantities were determined in the manner described previously.[3,6] The mean values, and the standard deviation were calculated for each of these parameters. The standard deviations are in the range 5−15% for the initial modulus; 2−8% for the yield stress; 4−8% for the draw ratio after break; and 5−20% for the ultimate tensile stress.

Results and Discussion

Structural Characteristics. The compilation of data given in Table 1 shows that the levels of crystallinity obtained from enthalpy of fusion measurements and the Raman internal modes, the core crystallines, are very similar to one another. This result is in accord with previous ones.[1,18] In contrast the crystallinity levels obtained from the densities, $(1 - \lambda)_d$, are greater than the core crystallinity levels. This difference in crystallinity levels has been previously observed in the polyethylenes,[1,43] as well as in other polymers.[44−46] It can be attributed to the contribution of the interfacial region to the measured density but not to the core crystallinity.

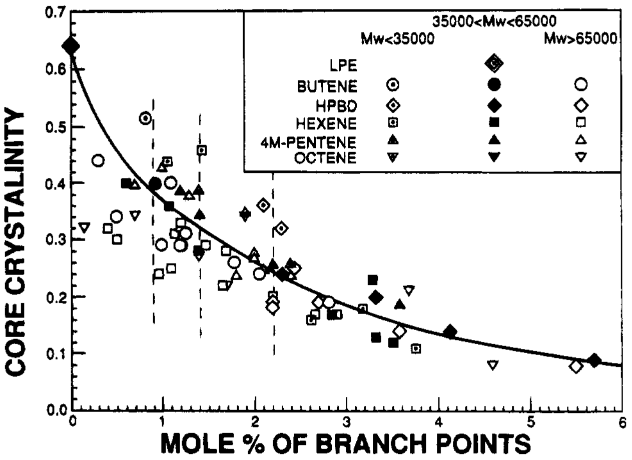

Figure 1. Plot of core crystallinity against mole percent branch points for random ethylene copolymers. Symbols for molecular weights and branch types are indicated. The dashed vertical straight line delineates changes with molecular weight at a fixed branch concentration.

A plot of the core crystallinity against the mole percent of branch points is given in Figure 1 for the five different types of copolymers that were studied. The expected rapid decrease in the crystallinity level with the concentration of branches is observed. The level of crystallinity of a fraction of linear polyethylene of $M \simeq 50\,000$ is about 0.65 under these crystallization conditions.[47] It decreases smoothly to about 0.10 for copolymers containing about 6 mol % branch points. The solid curve that is drawn in the figure represents data for $M \simeq 50\,000$. The apparent scatter of the data about this curve reflects the influence of molecular weight on the crystallinity level.[18] With just a few minor exceptions, the data points that lie above the solid curve represent lower molecular weights while those below represent molecular weights greater than 65 000. The influence of molecular weight on the crystallinity level is delineated in more detail by the dashed vertical lines that are drawn in the figure. For example, for hydrogenated poly(butadiene) having 2.2 mol percent branch points the crystallinity level decreases from 0.36 to 0.19 as the molecular weight increases from 16 000 to 420 000. For ethylene−hexene copolymers having approximately 1.4 mol % branch points the crystallinity level decreases from about 0.45 to 0.25 as the molecular weight increases from 23 000 to 201 000. A similar behavior is observed for copolymers having about 1.0 mol % branches. It has been shown that molecular weight and co-unit content act as independent variables in influencing thermodynamic and structural properties.[18] The influence of molecular weight and copolymer composition on properties must, therefore, be considered separately. For the different type co-units, we examine the case where the molecular weight is held fixed and the co-unit content is varied as well as that where the co-unit content is varied and the molecular weight is kept constant.

Stress−Strain Curves: Influences of Molecular Weight. In the following discussion of the nominal stress−strain curves only the ductile type deformation will be considered. The conditions for brittle failure and the transition between a brittle and ductile deformation will be detailed in a separate communication.[48] As a general rule, the type of copolymers that are studied here display a ductile deformation for molecular weights

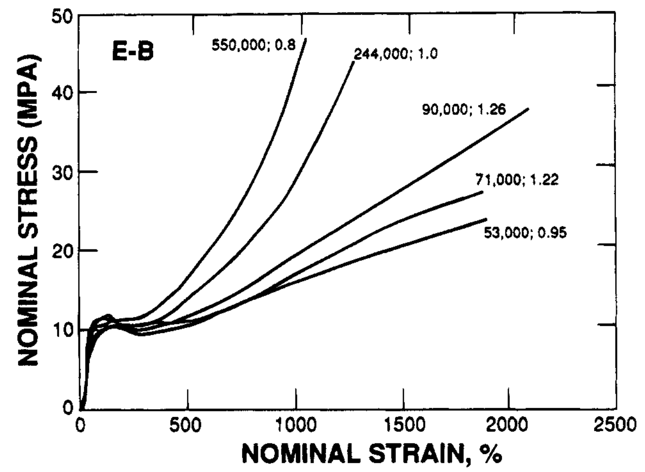

Figure 2. Nominal stress–strain curves for ethylene–butene copolymers illustrating changes with molecular weight at approximately the same branching concentration. The molecular weight and branching content are indicated for each curve.

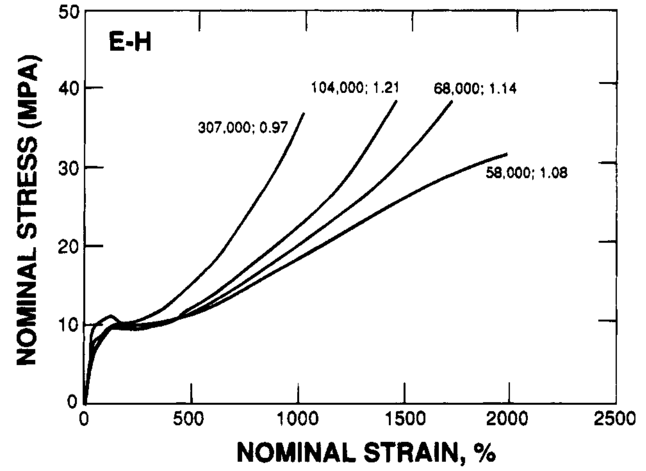

Figure 3. Nominal stress–strain curves for ethylene–hexene copolymers illustrating changes with molecular weight at approximately the same branching concentration. The molecular weight and branching content are indicated for each curve.

greater than about 30 000 with some modification for the co-unit content. During deformation an adiabatic heating process takes place. The magnitude of the temperature rise has been a matter of some argument.[3] A temperature rise of more than just a few degrees could affect some of the characteristics of the nominal stress–strain curve, particularly in cases where necking occurs. However the salient features in what follows and the major conclusions would not be altered.

Figures 2–5 give typical examples of nominal stress–strain curves as a function of molecular weight, for fixed co-unit content, for copolymers having different branch types. Beyond the yield region there is a marked effect of molecular weight on the stress-strain curves. In contrast to linear polyethylenes of comparable molecular weight the dominant feature in all of the curves is the development of significant strain hardening. This feature was pointed out by Capaccio and Ward in their study of very polydisperse ethylene–hexene copolymers[5] and was subsequently observed by others.[9,12,16] As a consequence, the region where the stress is independent of chain length is relatively narrow in the copolymers. For homopolymers the strain hardening region only becomes dominant at very high molecular weights M_w $\geq 10^6$. For all of the copolymer types, and beginning at relatively low molecular weights, the slope of the strain hardening region increases with chain length.

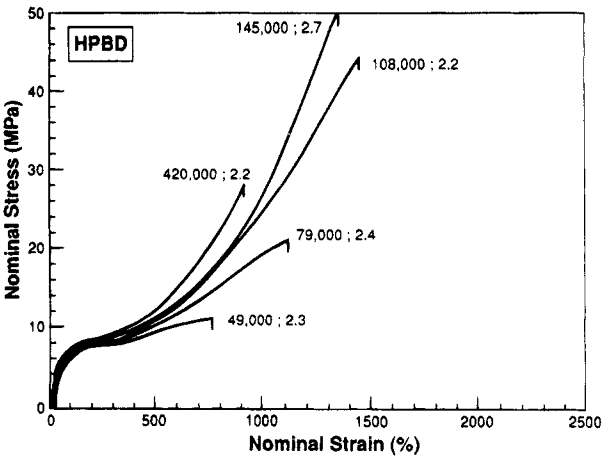

Figure 4. Nominal stress–strain curves for hydrogenated poly(butadienes) illustrating changes with molecular weight at approximately the same branching concentration. The molecular weight and branching content are indicated for each curve.

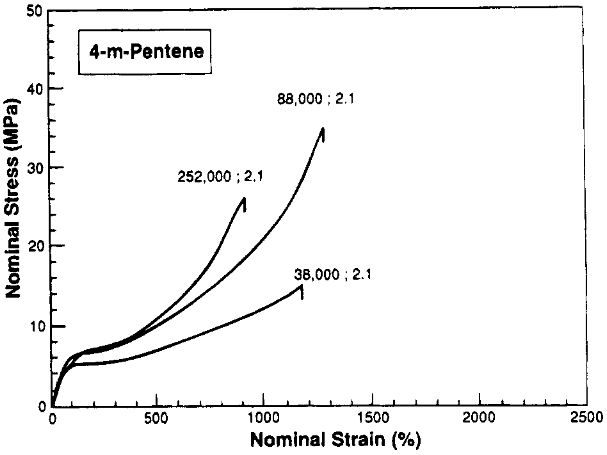

Figure 5. Nominal stress–strain curves for ethylene–4-methylpentene illustrating changes with molecular weight at approximately the same branching concentration. The molecular weight and branching content are indicated for each curve.

At a fixed composition the force–elongation curves of the copolymers with different co-units display a qualitatively similar pattern. However, as will be discussed in more detail subsequently, the actual shape of the stress–strain curves, at a given molecular weight and co-unit content, is dependent on the chemical nature of the branch. We can also deduce from these figures that the stress at failure passes through a broad maximum with increasing molecular weight at a fixed branching content.

In contrast to the above, in the low strain region only small differences are observed in the yield stress with molecular weight at a fixed co-unit content. This is mainly a reflection of the change in crystallinity level much with molecular weight for the copolymers. However, in all cases the nature of the yielding process is complex.[8,10,11,49,50] This observation is in contrast to the sharp yield point that is observed for linear polyethylenes of comparable molecular weights. The nature of diffuse and multiple yields that are observed in this class of copolymers, has been reported and discussed in detail.[51]

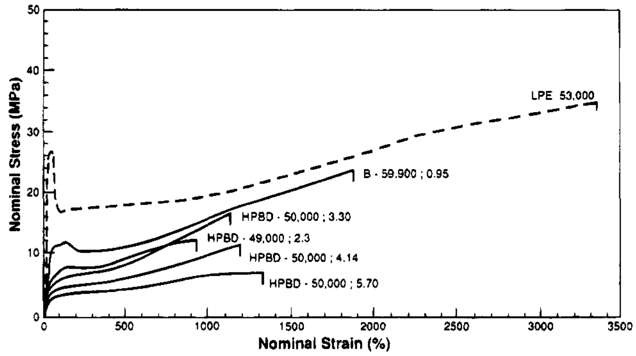

Figure 6. Nominal stress–strain curves for hydrogenated poly(butadienes) illustrating changes with branching concentration at approximately the same molecular weight of 50 000. The molecular weight and branching concentration are indicated for each curve. The dashed curve is for a linear polyethylene of comparable molecular weight.

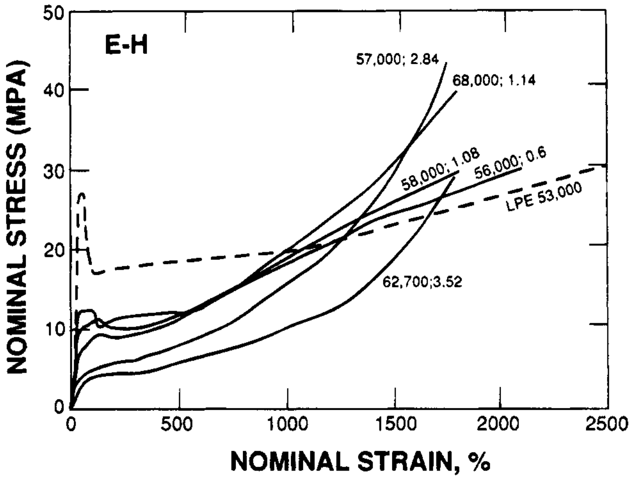

Figure 7. Nominal stress–strain curves for ethylene–hexene copolymers illustrating changes with branching concentration at approximately the same molecular weight of 60 000. The molecular weight and branching concentration are indicated for each curve. The dashed curve is for a linear polyethylene of comparable molecular weight.

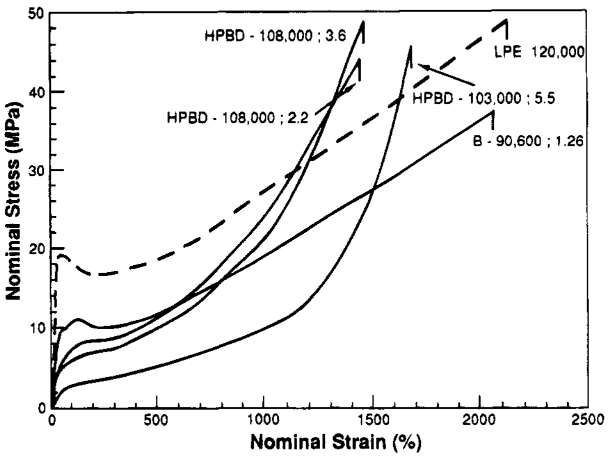

Figure 8. Nominal stress–strain curves for hydrogenated poly(butadienes) illustrating changes with branching concentration at approximately the same molecular weight of 100 000. The molecular weight and branching concentration are indicated for each curve. The dashed curve is for a linear polyethylene of comparable molecular weight.

Stress–Strain Curves: Influence of Branch Content. Figures 6–11 represents typical nominal stress–strain curves that were selected to illustrate the effect of branch content at a fixed molecular weight. Several different molecular weight intervals are given in this set of figures. A curve for a linear polyethylene fraction of comparable molecular weight is also included for reference purposes in each figure.[3]

Figures 6 and 7 are curves for hydrogenated poly(butadienes) (with one ethylene–butene sample included) and for ethylene–hexenes in the 50 000 molecular weight range. The mole percent of branch points ranges from 0.60 to 3.52 for the ethylene hexenes and from 0.95 to 5.70 for the ethyl-branched copolymers. In the low-strain and -yield region the stress–strain curves for both sets of copolymers are similar to one another. The reference homopolymer is characterized by a sharp, well-defined yield. With increasing co-unit content there is a continuous decrease in the yield stress with increasing co-unit content. Consequently, the yield region becomes progressively more diffuse. This behavior is clearly a reflection of the decreasing crystallinity level with mole percent of branch points (*cf. seq.*).

Major differences are observed, however, between these two copolymer types beyond the yield region. The invariant region is small in both cases. The nominal stress–strain curves for the ethyl-branched copolymers never intersect the one for the linear polymer of the same molecular weight for any composition. In contrast the curves for copolymers with larger size branches, in this same molecular weight range, intersect the reference curve of the linear polymer for all compositions, and the ultimate stress is always exceeded (Figure 7). There are also differences in the strain-hardening region between the two copolymer types. The strain hardening, based on the nominal stress and nominal strain, is reduced for the ethyl-branched copolymers relative to those with butyl branches. The ethylene–hexene copolymers with 0.6 and 1.0 mol % branch points have characteristics very similar to those of the ethylene–butenes. However, one begins to observe significant strain hardening for the copolymers that contain 1.14 and 2.84 mol % branch points. For these samples the nominal stresses exceed that of the linear polymer of corresponding molecular weight at the larger strains. The ethylene–hexene sample with the highest co-unit content, 3.52 mol % branch points, still displays well-defined strain-hardening regions. The deformation in this case begins to resemble a rubber elastic type. However, the stress level has been substantially reduced relative to the other copolymers and the homopolymer. If one takes the linear polymer as a reference, an incrase in stress level with co-unit content occurs initially followed by a substantial decrease at the higher co-unit content, so that an inversion occurs.

Figures 8–10 give nominal stress–strain curves for molecular weights in the 100 000 range. The copolymers illustrated are hydrogenated poly(butadienes), ethylene–butenes, and ethylene–octene, respectively. The copolymers in this molecular weight range behave very similar to the lower molecular weight samples in the low-strain regions. Irrespective of the branch type, the yield stress decreases as the co-unit content increases. In addition, the yield becomes progressively more diffuse. Just beyond yield, strain hardening is the predominant feature of all of the curves in this molecular weight range. The contrast in behavior with the lower molecular weights can be seen by comparing the results for the two sets of hydrogenated poly(butadienes) (Figures 6 and 8). The upsweep in the nominal stress–strain curves is quite dominant compared to the lower molecular weights of similar compositions. The curve

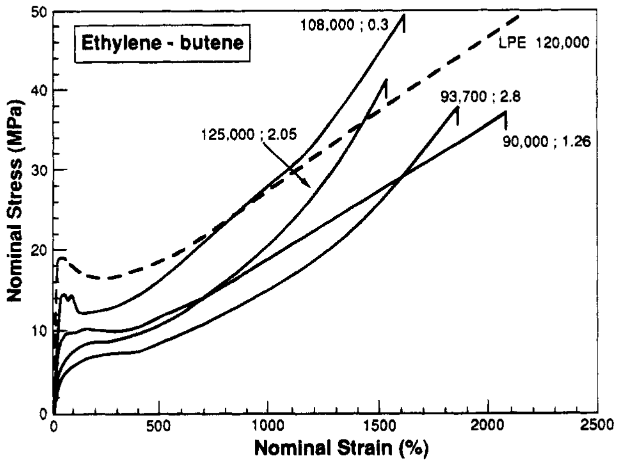

Figure 9. Nominal stress–strain curves for ethylene–butene copolymers illustrating changes with branching concentration at approximately the same molecular weight of 100 000. The molecular weight and branching concentration are indicated for each curve. The dashed curve is for a linear polyethylene of comparable molecular weight.

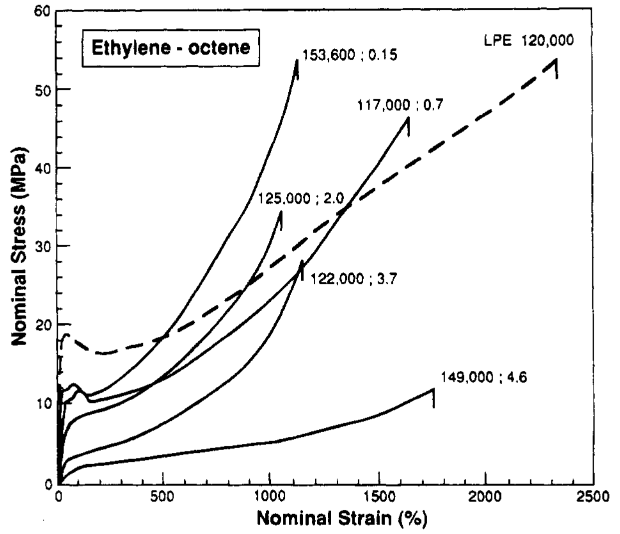

Figure 10. Nominal stress–strain curves for ethylene–octene copolymers illustrating changes with branching concentration at approximately the same molecular weight of 125 000. The molecular weight and branching concentration are indicated for each curve. The dashed curve is for a linear polyethylene of comparable molecular weight.

for the hydrogenated poly(butadene) sample with M = 103 000 and 5.5 mol % branch points is rather striking. The core crystallinity level is in the range 8–10% and the stress–strain curve resembles closely the deformation of a typical covalently cross-linked rubber-like system. For natural rubber the sharp upsweep in the stress can be attributed to strain-induced crystallization.[52]

Figures 9 and 10 demonstrate that strain-hardening develops, and predominates, at these molecular weights even at very low branch contents. This point is illustrated for the 0.3 mol % ethylene–butene copolymer. The dramatic change can be seen by comparing the nominal stress–strain curve of this copolymer with that of the linear polymer of comparable molecular weight. For both of these copolymers the predominance of strain hardening at higher co-unit contents is apparent. Thus, the introduction of just a small concentration of noncrystallizable co-unit drastically alters the stress–strain curves relative to the linear polymers of comparable molecular weights. The highest co-unit content ethylene–octene (Figure 10) appears to be an exception to this behavior. Since ethylene–octenes of similar as well as higher co-unit contents are not available, we cannot confirm whether this is a general result or peculiar to this particular sample. The curves for $M \sim 100\,000$ make quite evident that for all of the different types of branches the sharp upsweep, or strain hardening, is a characteristic feature. The results presented in Figures 8–10 substantiate the need to consider the molecular weight and co-unit content as independent variables.[18]

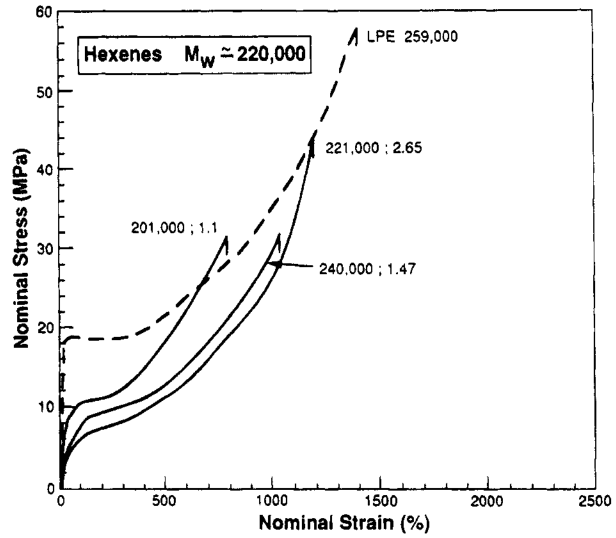

Figure 11. Nominal stress–strain curves for ethylene–hexene copolymers illustrating changes with branching concentration at approximately the same molecular weight of 250 000. The molecular weight and branching concentration are indicated for each curve. The dashed curve is for a linear polyethylene of comparable molecular weight.

Figure 11 gives a set of nominal stress–strain curves for ethylene–hexenes of varying branching contents in the molecular weight range of about 200–250 000. The corresponding curve for a homopolymer with M_w = 259 000, which has the same molecular weight distribution, is also given. At these higher molecular weights the copolymer curves are progressively shifted to lower stress levels with increasing branch content. The inversion with co-unit content that is observed at the lower molecular weights is no longer found. Strain hardening is again clearly the predominant feature. When compared to that of the reference homopolymer, the upsweep is much steeper and sets in at a much lower nominal strain.

Stress–Strain Curves: Influence of Branch Types. From the preceding discussion it is apparent that although the general patterns are quite similar the branch type influences the characteristics of a nominal stress–strain curve. We examine this effect in detail by directly comparing in Figures 12–15 stress–strain curves of copolymers with different types of co-units, chosen so as to have similar molecular weights and branching concentrations. Figure 12 gives a comparison of the nominal stress–strain curves for an ethylene–octene, an ethylene–hexene, and an ethylene–butene that have molecular weights of about 70 000 and 1.2 mol % branch points. The nature of the yield region and the magnitude of the yield stress are similar to one another for the three copolymers. This result is expected since the yield stress depends on the crystallinity level. In turn, the crystallinity level depends on the concentration of branch points.[18] However, this similarity disappears at elongations beyond the yield region.

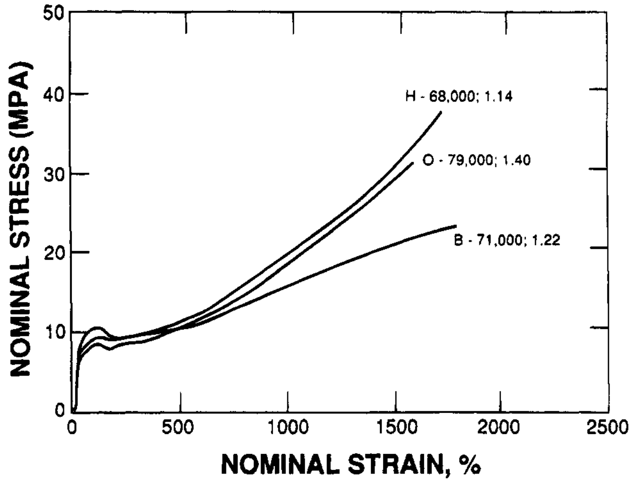

Figure 12. Nominal stress–strain curves for ethylene copolymers with similar molecular weights and co-unit concentrations but having chemically different co-units: B, ethylene–butene; H, ethylene–hexene; O, ethylene octene. The molecular weight and mole percent branch points are indicated for each curve.

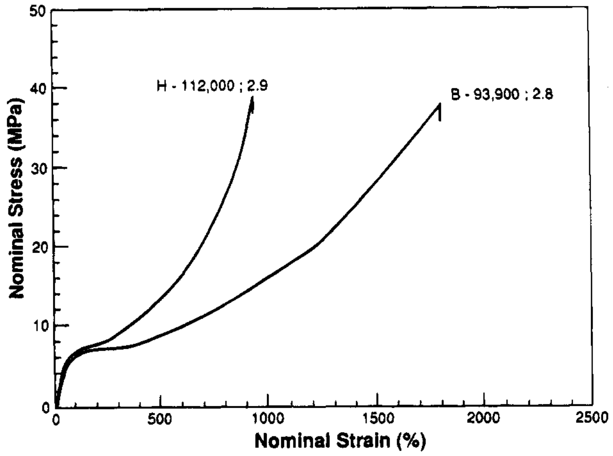

Figure 13. Comparison of nominal stress–strain curves of ethylene–butene and ethylene–hexene copolymers that have similar molecular weights and branching concentrations. The molecular weight and branching concentration are indicated for each curve.

Although the curves for the ethylene–octene and ethylene–hexene copolymers are very close to one another, they are quite different from the corresponding ethylene–butene copolymer. For the latter polymer the increase in the stress with strain is not nearly as great as found in the other two; i.e. the strain hardening is not nearly as dominant a feature. A general finding is that the ethylene–octenes, ethylene–hexenes, and ethylene–4-methylpentenes give similar stress–strain curves for specimens of the same molecular constitution.

The difference between the ethylene–butenes and the other copolymers is further demonstrated in Figure 13. Here, the comparison is made at slightly higher molecular weights and much greater co-unit contents than in Figure 12. The yield region is again very similar for the two copolymers. Beyond yield, the ethylene–butene copolymer now shows a greater increase in strain with stress, relative to the butene copolymer shown in Figure 12. However, for the hexene copolymer strain hardening sets in at smaller elongation and is much more marked.

Figure 14 illustrates how the differences in the nominal stress–strain curves of the butene and hexene

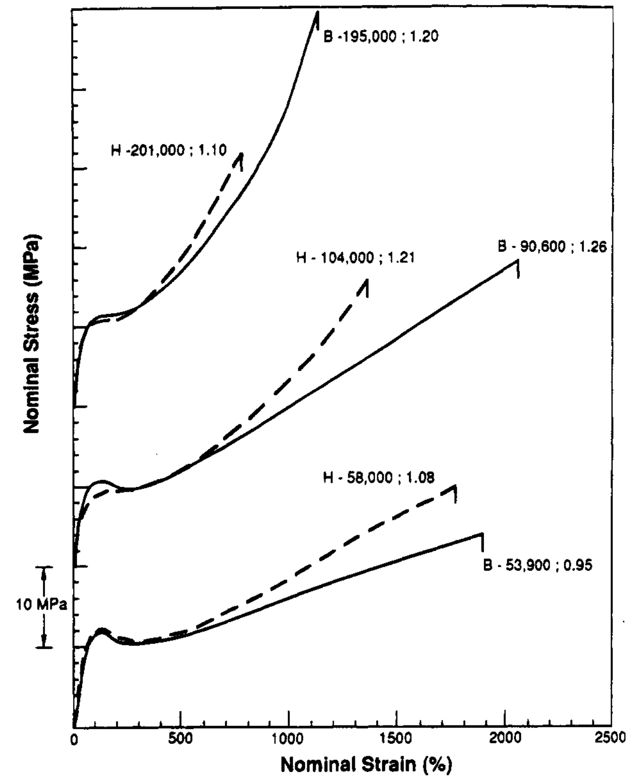

Figure 14. Comparison of nominal stress–strain curves for ethylene–butene and ethylene–hexene copolymers having approximately the same co-unit contents but varying molecular weights. The molecular weight and branching concentration are indicated for each curve.

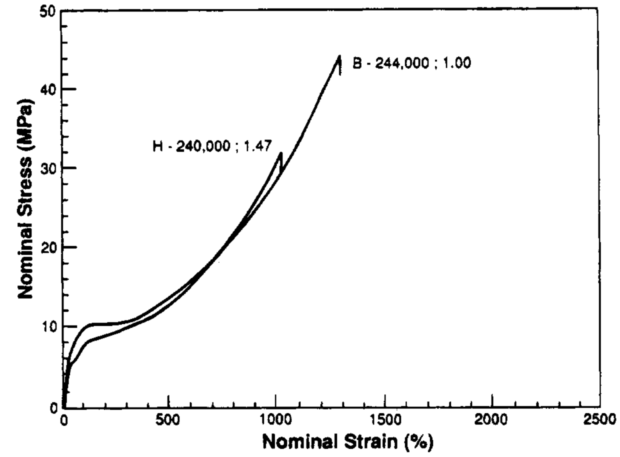

Figure 15. Comparison of nominal stress–strain curves for ethylene–butene and ethylene–hexene copolymers demonstrating that similar curves can be obtained. The molecular weight and mole percent branch points required are indicated.

copolymers depend on molecular weight for a fixed co-unit content. In this example all of the copolymers have about 1 mol % branch points and the molecular weight varies from about 50 000 to 200 000. The characteristics of the yield regions of each of the copolymer pairs are similar to one another. The differences in the nominal stress–strain curves assert themselves beyond yield. The disparity between pairs is greatest at the lower molecular weight. At the highest molecular weights the curves for the two copolymers are very close to one another. At still higher molecular weights, $M \approx 250\ 000$, the two stress–strain curves are virtually identical, as illustrated in Figure 15. The difference between the pairs at the lower molecular weights is a consequence of the development of significant strain hardening at

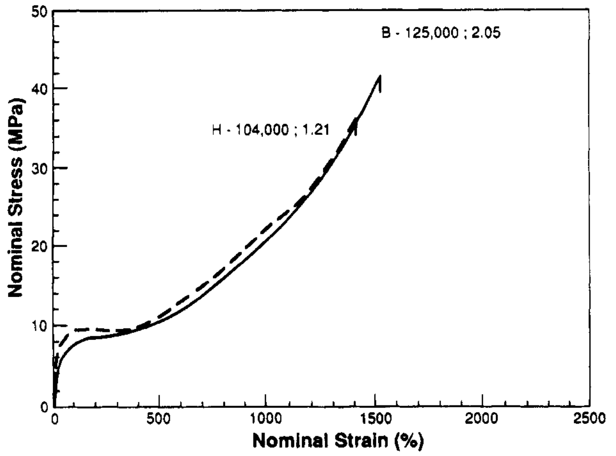

Figure 16. Comparison of nominal stress–strain curves for ethylene–butene and ethylene–hexene copolymers demonstrating that very similar curves can be obtained. The molecular weight and mole percent branch points required are indicated.

smaller elongations for the ethylene–hexene copolymers. At higher molecular weights, as has already been noted, the ethylene–butenes also display significant strain hardening. Among all the pairs, the strain at failure is greater for the ethylene–butene copolymers.

It is evident that for the same molecular weight and composition there are significant differences between the stress–strain curves of the ethylene–butenes and the other ethylene–1-alkene copolymers. On the other hand, the differences between the other copolymers, at the same molecular constitution, is relatively slight. However, the changes with molecular weight and copolymer composition in the character of the stress–strain curves for the ethylene–butenes are qualitatively similar to the others. Therefore, by selecting a unique molecular weight and branch content for each copolymer it should be possible to obtain similar stress–strain curves. This possibility is in fact realized. In Figure 16 we find that essentially identical stress–strain curves are obtained for ethylene–hexene and ethylene–butene copolymers of the same molecular weight. However, it is necessary for the butene copolymer to have 2.05 mol % branch points as compared to 1.21 for the hexene copolymer. Conversely, if the co-unit content is held constant, then, as is shown in Figure 17, very virtually identical stress-strain curves can be obtained by taking a higher molecular weight butene copolymer. In this case M equals 90 600 as compared to 58 000. These results are consistent with the nominal stress–strain curves that have been presented.

These results demonstrate that the molecular weight, copolymer composition, and branch type have to be considered as independent variables when stress–strain curves are analyzed. Although significant differences are observed between the ethylene–butenes and the other copolymers, similar curves can be obtained between the different type copolymers by matching appropriate molecular variables. Having analyzed the characteristics of the nominal stress–strain curves, we are now in a position to discuss the key tensile parameters in terms of the independent structural variables.

Initial Modulus. The initial modulus, E, is determined from the slope of the force–elongation curve in the limit of small strain. The initial portion of the force–length curve, to about 2–3% strain, is usually reversible. The deformation of the disordered interlamellar region is involved, and the lamellar structure

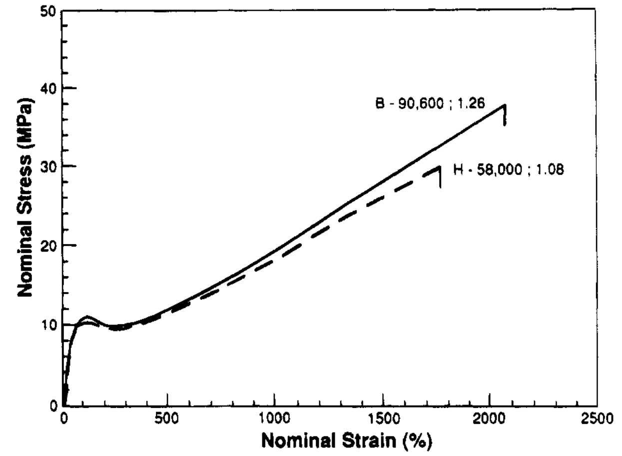

Figure 17. Comparison of nominal stress–strain curves for ethylene–butene and ethylene–hexene copolymers demonstrating that very similar curves can be obtained. The molecular weight and mole percent branch points required are indicated.

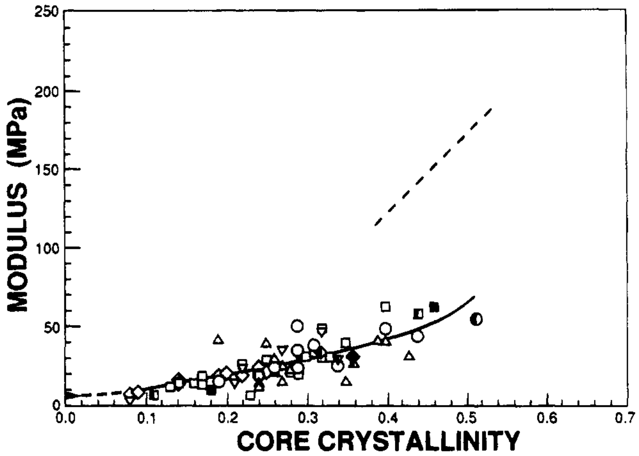

Figure 18. Plot of initial modulus against core crystallinity: hydrogenated poly(butadiene) (◇); ethylene–butene (○); ethylene–hexene (□); ethylene-4-methylpentene (△); ethylene–octene (▽); filled samples, brittle; half-filled symbols, transitional. The dashed line for linear polyethylenes is from ref 3.

remains essentially intact. Previous studies with unfractionated linear polyethylene[14] and random ethylene copolymers[6] have shown that it is difficult to interpret this modulus in terms of the basic molecular and structural parameters. Since the gauge length of the specimens being studied here is only 4 mm, the absolute values of the modulii cannot be compared with more conventional measurements where the gauge length is usually about 5 times larger.[4,6] This difference is due to the large radius of curvature, relative to the short gauge length, of the dogbone specimens that are used. However, the relative changes that are found in the values of the modulii with changes in structure and molecular constitution are significant.

In analyzing the influence of structural parameters we focus our initial attention on the crystallinity level. Figure 18 is a plot of E against the level of core crystallinity, α_c, for the different types of copolymers studied. The results for the different types of branches, as well as the branch concentration, delineate a single smooth curve. Comparison of the modulii results with the supermolecular structures in Table 1 as well as those reported for similarly constituted copolymers[21] makes clear that such structures do not influence the modulii. Examination of the data also indicates that there is no direct influence of molecular weight on E.

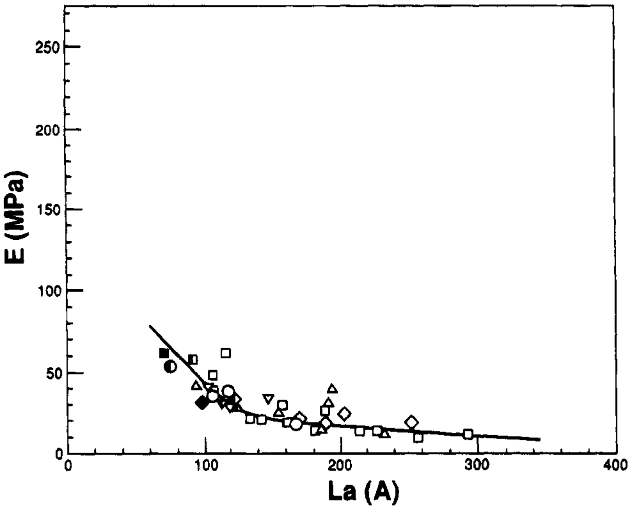

Figure 19. Plot of initial modulus against interlamellar thickness L_a. Symbols are the same as in Figure 18.

There is, however, an important indirect influence of the chain length by its control of α_c.[18] The moduli values in Figure 18 are in the range of about 4–70 MPa. These values are slightly lower than those reported for unfractionated copolymers.[6,14] The differences can be attributed to the small gauge length used here.

The smooth curves in Figure 18 extrapolate to an E value in the range 5–10 MPa for $\alpha_c = 0$. This range is typical of the modulus of a rubber-like substance. Several of the low-crystallinity copolymers (high co-unit content) give essentially the same moduli values. Such samples also display rubber-like stress–strain curves. Since the initial reversible portion of the force–length curve is involved, it would be expected to be governed in part, at least, by the noncrystalline portion of the system. This conclusion is consistent with the plot of Figure 18.

The dashed straight line in Figure 18 represents similar data for linear polyethylenes that have the same molecular weight distributions.[3] The modullii values for the linear polymers are about 1 magnitude greater than that of the copolymers. In a previous study it was found that a plot of E against density, for both linear and branched polyethylenes, resulted in an S-shaped curve.[14] The lower arm consisted of the copolymer data, while the upper one represented the linear polyethylene results. The present data behave in a qualitatively similar manner. Attempts to connect these data for chemically similar, but structurally different polymer systems, can lead to misleading conclusions. There are major differences in the lamellar structure and the interfacial and disordered regions between the homopolymer and copolymer. The problem involved is illustrated in the figure by the region of overlapping crystallinity for the two polymer types. Moduli data are available for both the linear and branched polymers in the range $\alpha_c = 0.4–0.5$. The moduli differ by factors of 2–3 over the same crystallinity range. Other factors, besides just the level of crystallinity, must be involved.

It was found previously that the thickness of the interlamellar region, L_a, has an important influence on the initial modulus of linear polyethylene.[3] The interlamellar thickness varied from about 40–200 Å. A discontinuity was observed at about 70 Å in a plot of E against L_a. This value serves as a demarcation between the ductile and brittle deformation regions. In the brittle region, L_a less than 70 Å, there is a large increase in E as L_a decreases. In contrast, in the ductile region the decrease in E with L_a is fairly modest. A similar plot of E against L_a for the copolymers is given in Figure 19. It should be borne in mind that L_a is calculated from the Raman spectra.[3,39] The calculation assumes a system of stacked lamellae, a condition that is not always fulfilled for the higher co-unit content random copolymers.[53,54a] Despite this limitation, similarities are observed between the copolymers and the linear polymers. At the higher values of L_a, which correspond to the lowest levels of crystallinity, there is only a slight decrease in E with L_a. At an L_a value of about 100 Å there is a sharp increase in E with decreasing L_a. In this region the copolymers include specimens that undergo ductile, brittle, or transitional type deformation. In contrast, the linear polymers only display brittle or transitional behavior in the corresponding region. It was also found (not shown here) that the modulus only depends slightly on the crystallite thickness. This behavior is similar to that of the linear polyethylenes that have the same molecular weight distribution.[3]

The reversibility of the deformation at very small strains is a strong indication that the structure of the interlamellar region must have a major influence on the modulus. The dependence of the modulus on the crystallinity level and on the interlamellar thickness supports this conclusion. The weak dependence of the modulus on crystallite thickness and its insensitivity to supermolecular structure are consistent with this concept. In this region of very small strain the deformation is primarily of the rubber-elastic type. This type of deformation depends on the structure of the disordered liquid-like region in terms of chain entanglements and other topological features that can serve as effective cross-links. Also important is the nature of the bounding crystallites. A comparison between the moduli of the copolymers and linear polymers, at comparably crystallinity levels (Figure 18) indicates that there are major structural differences between the two in this region.

Yield Stress. Many studies have shown that the nature of the yielding process and the value of the yield stress is intimately connected with the crystallinity level.[3,4,6,14] The stress-strain curves of Figures 6–11 show that the homopolymers of moderate molecular weight have sharp and well-defined yield points.[3] With the introduction of comonomers into the chain, and the concomitant decrease in crystallinity level, the yield stress decreases and the yield process becomes more diffuse. A detailed study of the yielding process for homopolymers and copolymers has recently been reported.[49] The necessary conditions for the existence of double yields has been described in terms of crystallinity level, temperature, and deformation rate. Possible reasons for the complex yielding were also discussed.

The yield stress is plotted against the core crystallinity, in Figure 20, for all of the copolymers studied. When multiple yields are observed, the largest yield stress was taken. The dashed line in the figure represents the previous results obtained for linear polyethylene over the crystallinity range of interest here.[3] Irrespective of the chemical nature of the branch, the data for all of the copolymers fall on the same curve. The yield stress is also independent of the molecular weight (except for its influence on α_c) and of the supermolecular structures. At the lower levels of crystallinity the yield stress is directly proportioned to α_c. However, a plateau is reached at $\alpha_c \simeq 0.4$ and 15

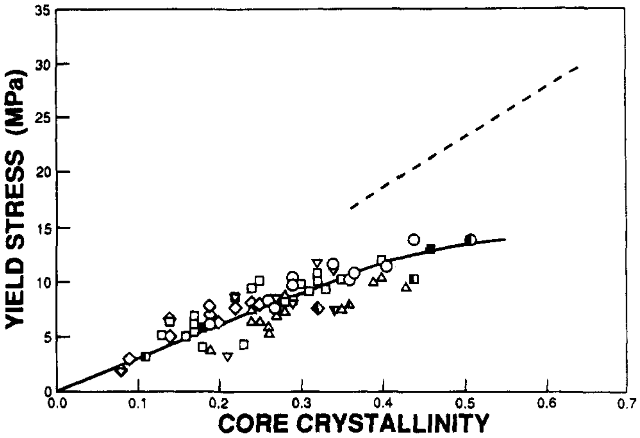

Figure 20. Plot of yield stress against core crystallinity. Symbols are the same as in Figure 18. The dashed line for linear polyethylenes is from ref 3.

MPa. These results only differ slightly from copolymers that are very polydisperse in molecular weight and composition.[14] From these results it would be expected that the yield stress would decrease with increasing co-unit content. A plot of the yield stress against mole percent branch points (not shown) confirms this expectation. In fact, a linear relation results.

The yield stresses of the linear polymers are significantly greater than those of the copolymers over the crystallinity range where a comparison can be made. The data for the homopolymers extrapolated linearly to the origin.[3] Therefore, at the very low levels of crystallinity it would be expected that not much difference would exist between the yield stresses of the two types. The yield stress of the linear polyethylenes reaches a plateau at about 32 MPa (not shown in figure) for the higher crystallinity levels. Thus, both the homopolymers and copolymer show qualitatively similar behavior with respect to the dependence of the yield stress on the core crystallinity level. The magnitude of the stresses involved and the crystallinity level at which changes occur are, however, different in the two cases.[54ab]

The strong dependence of the yield stress on the crystallinity level, independent of branch type or molecular weight, suggests that the crystallites, or associated regions, undergo some kind of structural change during the yielding process. Several different mechanisms have been suggested for yielding. Flory and Yoon[55] have proposed that a partial melting–recrystallization process is involved in the deformation process. Several studies have confirmed that a process of this type takes place during the yielding of linear polyethylene.[50,56,57] However, no direct experiments have tested this hypothesis for the yielding of copolymers.

Alternatively, it has been proposed that yielding in crystalline polymers in general, and the polyethylenes in particular, involves the thermal activation of screw dislocations with the Burgers vector parallel to the polymer chain direction.[4,58,59] From this model the dependence of the shear yield stress τ_y on the crystallite thickness, L_c, can be calculated. According to the theory developed, the free energy, ΔG, required to form a screw dislocation of a Burgers vector, b, located at a distance l from the edge of crystallite of thickness L_c is given by

$$\Delta G = \frac{kb^2L_c}{2\pi}\ln\left(\frac{l}{r_o}\right) - blL_c\tau_y \qquad (1)$$

Here k is a function of the shear modulus of the crystal; b, the magnitude of the Burgers vector has the value 2.54 Å, the c-axis dimension of the polyethylene unit cell; and r_o is the core radius of the dislocation thought to be the order of $2b$.[4,59] The critical value of l that is necessary to activate the dislocation, l_c, is obtained from the maximum in ΔG, and is given by

$$I_c = kb/2\pi\tau_y \qquad (2)$$

The corresponding activation energy for dislocation growth is given by

$$\Delta G_c = \frac{kb^2L_c}{2\pi}[\ln(l_c/r_o) - 1] \qquad (3)$$

From eqs 2 and 3 one obtains

$$\tau_y = \frac{k}{4\pi}\left[\exp\left(\frac{2\pi\Delta G_c}{kb^2L_c} + 1\right)\right]^{-1} \qquad (4)$$

Equation 4 directly relates the shear yield stress, τ_y to the crystallite thickness L_c and to the temperature through the quantity ΔG_c. ΔG_c is thought to be in the range between 40 and 80 kT.[59]

The tensile yield stress, σ_y, is the measured experimental quantity. It can be converted to the theoretical by the required shear yield stress, τ_y, needed to apply eq 4, by invoking the Tresca criteria, $\tau_y = \sigma_y/2$.[60a] This assumption implies that the yield takes place on crystal planes at 45° to the tensile axis.[60a] Young[59] has made the point that the "crystal" yield stress, τ_y^0, defined as

$$\tau_y^0 = \tau_y/\alpha_c \qquad (5)$$

is the proper quantity to use in conjunction with eq 4. Crist has given a similar theoretical analysis but used the unmodified τ_y in analyzing experimental data.[4]

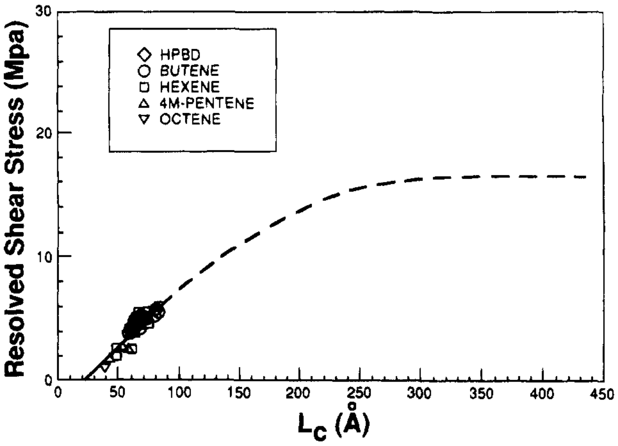

Figure 21. Plot of resolved shear stress against crystallite thickness L_c. The data points are for ethylene copolymers. Symbols describing each type are indicated in figure. The dashed curves are data for linear polyethylenes from ref 3.

The observed, resolved shear stress, τ_y, is plotted against the crystallite thickness in Figure 21. The solid straight line represents the plotted data for the copolymers, while the dashed curve is a reproduction of the results that were previously reported for linear polyethylene.[3] There is a continuity between the two curves, but it is not a linear one. The results for the copolymers can be represented by a linear relation over the restricted thickness range 50–100 Å that can be attained. This data set, therefore, could be interpreted as conforming to theory. However, this linearity is not

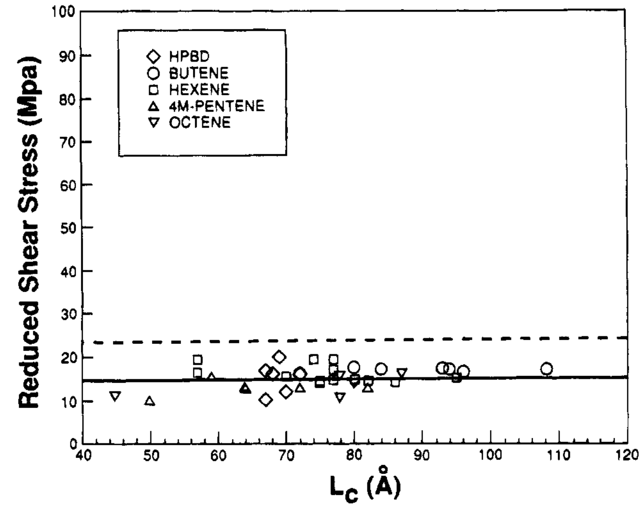

Figure 22. Plot of reduced shear stress against crystallite thickness, L_c for ethylene copolymers. Symbols are the same as in Figure 21. The dashed line gives data for linear polyethylenes from ref 3.

maintained for the larger crystallite thicknesses that are associated with the linear polymer. As was pointed out previously, in this case there is essentially no change in τ with crystallite thickness. Darras and Seguela[61] have examined the relation between the yield stress and crystallite thickness for a series of ethylene–butene copolymers that have very broad molecular weight and composition distributions. Their results for the samples crystallized from the pure melt are qualitatively similar to those reported here.

Young's suggestion is followed in Figure 22, where the reduced, resolved shear stress is plotted against the crystallite thickness. This quantity is independent of crystallite thickness for the copolymers. As is indicated by the dashed line in the figure, the same invariance was found for linear polyethylene.[3] The reduced shear stress of the linear polymer is substantially greater than the corresponding value of the copolymers. This result demonstrates that care needs to be taken when data from both types of polymers are analyzed together. It is also demonstrated that this method of analysis, i.e. using the reduced, resolved shear stress, gives results that are not in accord with theoretical expectations.

Despite the lack of quantitative agreement the dislocation theory predicts the correct order of magnitude of the yield stress. Perhaps modifying the theory, and using larger values of ΔG_c than have been postulated, would lead to better agreement. This possibility is suggested by the shape of the theoretical curves and their variation with ΔG_c (see Figure 9 of ref 3). It still remains to be established whether modification of the dislocation theory will quantitatively improve matters or whether future experiments will establish that a partial melting–recrystallization process also takes place in copolymers. It is not inconceivable that both types of mechanisms are involved.

Ultimate Properties. The discussion of ultimate properties will focus on certain key factors. These include the draw ratio after break, λ_B, the ultimate tensile strength, and certain characteristics of the strain-hardening region. The influence of molecular weight, co-unit type, and concentration on the transition from a brittle to ductile deformation will be detailed elsewhere.[48] Here, we are only considering the ductile type of deformation.

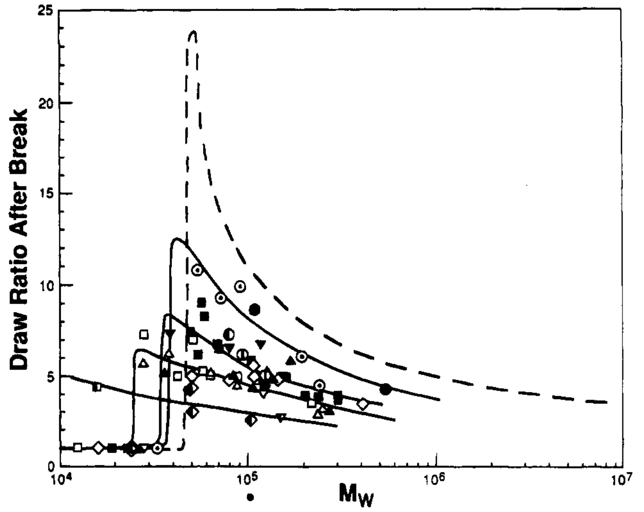

Figure 23. Plot of draw ratio after break against weight average molecular weight, M_W. Mole percent branch points: for ethylene–butene (●) <0.5, (⊙) >0.9 < 1.3, (◐) >1.3 < 2, (⊖) >2 < 3.7; for ethylene–hexene (■) <2, (□) >2 < 3.7, (■) > 3.7; for ethylene–4–methylpentene (▲) <2, (△) >2 < 3.7, (▲) >3.7; for ethylene–octene (▼) <2, (▽) >2 < 3.7, (▼) >3.7. The dashed curve gives data for linear polyethylenes from ref 3.

The draw ratio after break, λ_B, is plotted against M_W in Figure 23 for the different copolymer types and branching levels. A compilation of the results for linear polyethylene are given, as reference, by the dashed curve.[3,62] The shapes of the curves are similar. The transition from brittle ($\lambda \simeq 1$) to a ductile type deformation is sharp and well-defined in this plot. This transition between deformation types occurs with decreasing molecular weight as the co-unit content increases.

In the ductile region there is a definite decrease in λ_B with M_W, that is characteristic of the co-unit concentration. Except for the ethylene–butene copolymers that contain less than 1.3 mol % branch points, the results are independent of the chemical nature of the side groups. The ethylene–butene copolymers that have less than about 1.3 mol % of branch points have larger λ_B values as compared to the other type of copolymers. The values are closer to that of linear polyethylene. However, at higher co-unit contents the ethylene–butenes give the same values for λ_B as the others.

The dependence of λ_B on M_W becomes less pronounced as the branch content increases. For a branch content of about 4 mol % λ_B only depends slightly on chain length. We have previously reported that λ_B does not depend on molecular weight for random ethylene copolymers that have broad molecular weight and composition distributions.[6] Careful reanalysis of the data for two hydrogenated poly(butadienes), that were previously studied,[14] indicates a molecular weight dependence for λ_B similar to that found here.

A theoretical treatment of the ultimate properties focused attention on the liquid-like structure.[63–66] The observed dependence of λ_B on the molecular weight of linear polyethylenes agrees qualitatively with this concept. The observation that the λ_B values of ethylene–butene copolymers having less than 1.3 mol % branch point are greater than the other copolymers suggests that interactions in the melt differ between the short and longer length side groups at lower branch contents. Put another way, it can be postulated that the interactions between side groups in the melt are inherently greater for the larger size groups. However,

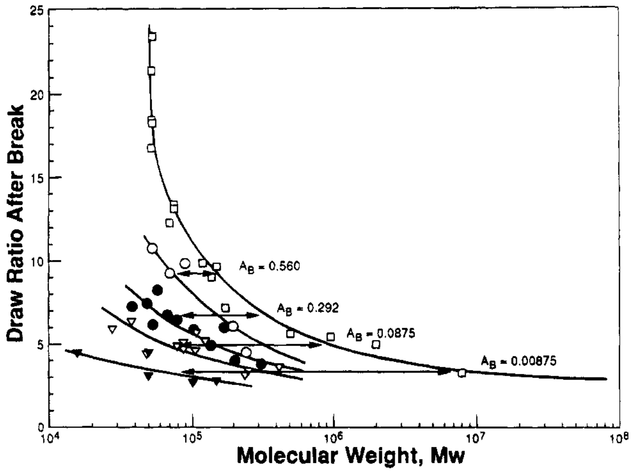

Figure 24. Schematic representation of shifting of data from Figure 25. Mole percent branch points: ethylene–butene 1.0. All others (●) 1.1, (▽) 2.2, (▼) >3.7, (□) linear polyethylene.

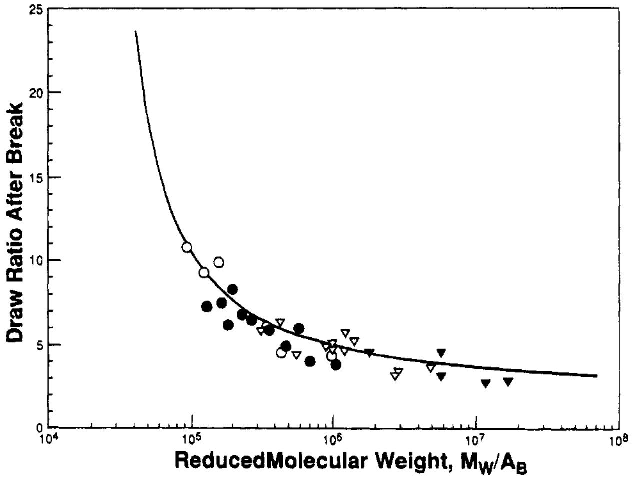

Figure 25. Result of shifting illustrated in Figure 24. Plot of draw ratio after break against reduced molecular weight. Symbols are the same as in Figure 24. The solid curve gives data for linear polyethylene.

with increasing branch concentration the differences are minimized. A similar postulate explains the differences in supermolecular structure that develop between the different types of copolymers.[21] It has been found that the ethylene–butene copolymers of low co-unit content yield much better developed supermolecular structures than the other copolymer types. However, at higher co-unit contents the structures formed are very similar to one another.

The fact that each curve in the ductile region has a similar shape, suggests that a master plot can be achieved by shifting each of the curves along the horizontal axis. This procedure is demonstrated in Figure 24. The shift factor A_B is defined as M_W/M_W^*, where M_W is the molecualr weight of the copolymer and M_W^* is that of linear polyethylene. Utilizing these factors, a single plot is obtained, as is indicated in Figure 25. The curve representing the highest branching content needs to be shifted the largest amount. The superposition illustrated in Figure 25 reflects the general observation that the copolymers behave as higher molecular weight linear polyethylenes.[22] Capaccio and Ward[5] have made a similar observation from their force–elongation studies: the greater the branching content, the higher the molecular weight of the corresponding linear polymer.

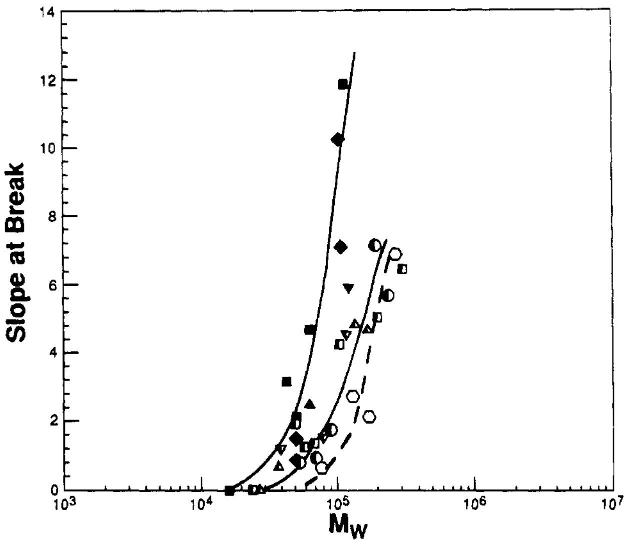

Figure 26. Plot of slope at break of nominal stress–strain curves against weight average molecular weight, M_W. Dashed curve and ○ linear show polyethylene having the most probable molecular weight distributions (from ref 3). Ethylene copolymers with mole percent branch points between 1.0–1.5: (◐) butenes; (◧) hexenes; (△) 4-methylpentene; (▽) octene. Ethylene copolymers with greater than 2.9 mol % branch points: (◆) hydrogenated poly(butadienes); (■) hexene; (▲) 4-methylpentene; (▼) octene.

As was pointed out earlier the force–elongation curves of the copolymers are dominated by strain hardening. The slopes of the nominal stress–strain curves at failure can be regarded, for present purposes, as representing the "intensity" of the strain-hardening portion of the deformation. In Figure 26, the slopes at break are plotted against M_W for different copolymer composition groupings. The results obtained for linear polyethylenes having the most probable molecular weight distributions are given as the dotted curve in the figure.[3] The shapes of the three curves are very similar. The very strong dependence of the slopes on molecular weight can be clearly seen. For a given molecular weight the slopes increase substantially with co-unit content. The curves are such that at the higher molecular weight and branch content the slopes can become very large. They are as much as 5-fold greater than those of the corresponding homopolymers of the same molecular weight. These plots reflect the domination of strain hardening in the postyield region as the molecular weight and co-unit content increases.

Another ultimate property of interest is the tensile stress at break. The ultimate tensile stress, UTS, which is based on the original specimen cross-section, is illustrated in Figure 27 for different composition groupings. The order of magnitude of the stress of the copolymers is similar to that found for the linear polyethylenes. The data in Figure 27a, for copolymers having less than or equal to 1 mol % branch points, appear to have a maximum at about $M_W \simeq 1.5 \times 10^5$. However, the scatter of the data at the higher molecular weights precludes a definite decision of this point. The maximum with molecular weight is, however, well-defined for the higher composition, as is illustrated in Figures 27b and c. However, the maximum appears to move to lower molecular weights as the branch content increases.

It would be physically more significant if the stress was based on the cross-section at break. Since this quantity is not available, the approximation is made

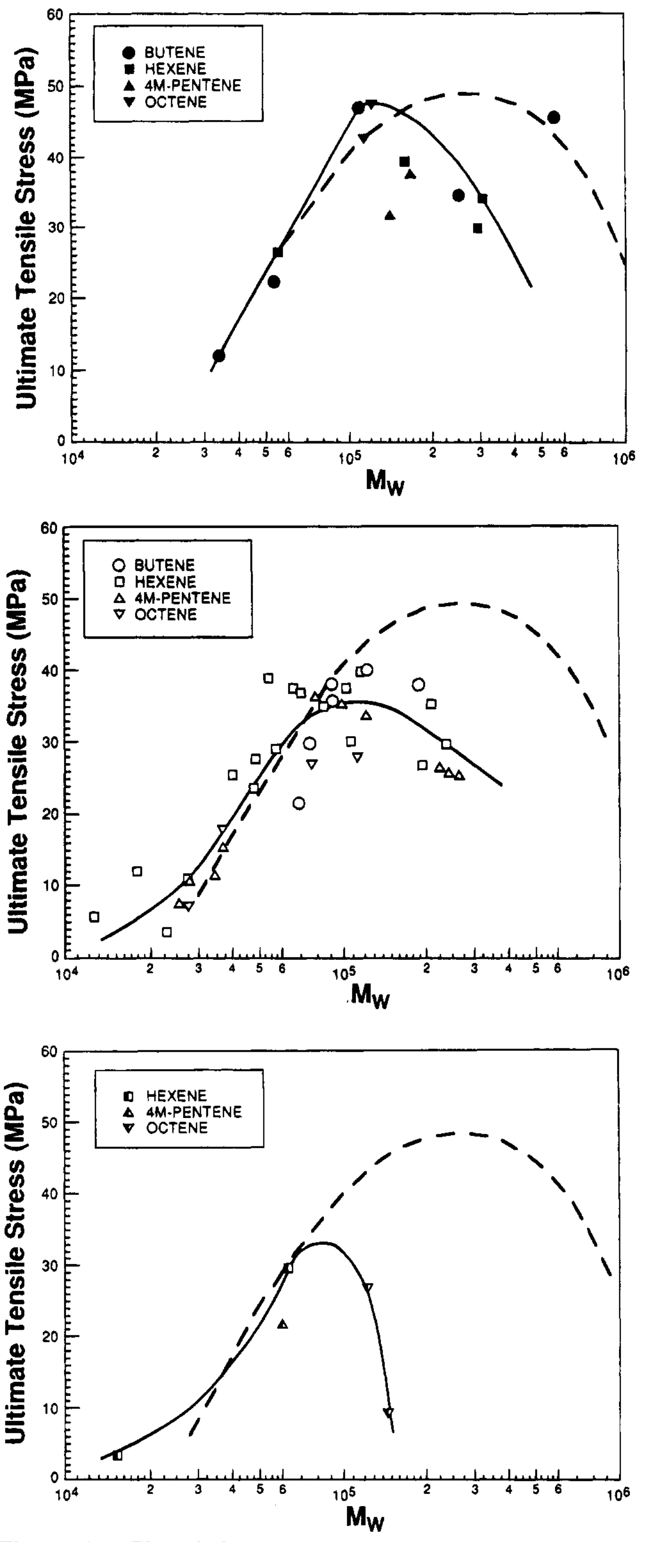

Figure 27. Plot of ultimate tensile strength against weight average molecular weight M_W. The dashed curves give data for linear polyethylene from ref 3. The copolymer type is indicated in each figure. (a, top) Mole percent branch points ≤1.0. (b, middle) Mole percent branch points >1 < 3.5. (c, bottom) Mole percent branch points >3.5.

that the deformation is uniform. The true ultimate tensile stress, TUTS, is then defined as UTS × λ_B. The results for TUTS are plotted in Figure 28. The curve representing linear polyethylene is also given. The maxima in the curves are well-defined. The maxima shift to lower molecular weights, and to lower values of the stress, as the co-unit content increases. The copolymer data at the different compositions, fall on the same curve at the left side of the maxima but describe separate curves for molecular weights on the right side of the maximum. The curves for the low co-unit content ethylene–butenes are again different. While the curves for the other co-unit types are the same, for a given composition, the data for the low co-unit content between are close to that of linear polyethylene. A major contribution to the character of these curves, relative to those for the UTS, is due to the changes in λ_B. The data for the hydrogenated poly(butadienes)(not illustrated) display a much sharper, well-defined maximum at $M_W \simeq 10^5$ than those for the 1-alkene copolymers of Figure 28. The true ultimate tensile strength of the hydrogenated poly(butadienes) is about 2 times greater than that of the copolymers of similar composition. Thus, in this aspect of the tensile properties there is a difference between a sharp fraction and a relatively narrow distribution.

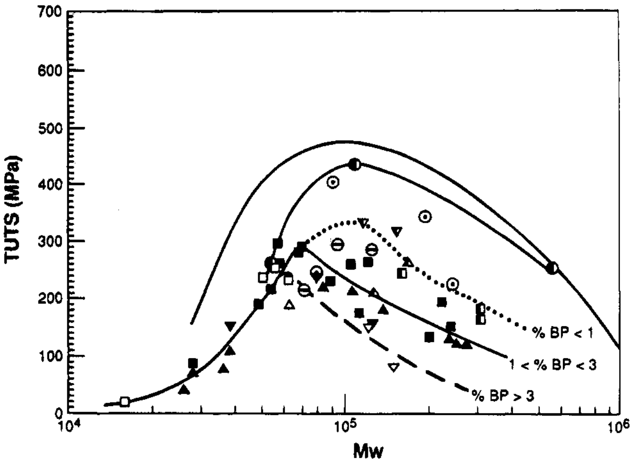

Figure 28. Plot of true ultimate tensile strength against weight average molecular weight. Mole percent branch points: for ethylene–butene (◐) < 1.0, (⊙) >1 < 1.5, (⊖) >1.5 < 3; for ethylene–hexene (◧) <1, (■) >1 < 3, (□) > 3; for ethylene–4-methylpentene (▲) <1, (▲) >1 < 3, (△) >3; for ethylene-octene (▼) <1, (▼) >1 < 3, (▽) >3.

Conclusions and Summary

Several major features have emerged from the present investigation of the tensile properties of the random ethylene copolymers that have the most probable molecular weight and narrow composition distribution. The experimental results have shown that the molecular weight, copolymer composition, and chemical constitution need to be treated as independent variables. The force–elongation curves for each of the branch types follow a qualitatively similar pattern when either the co-unit content is held fixed and the molecular weight is varied or the molecular weight is held constant and the composition is varied. The results for the copolymers having hexene, octene and 4-methyl pentene as comonomers are very similar to one another. However, the results for the ethylene–butenes are different. At the highest molecular weights studied the force–elongation curves of the different types of copolymers become similar to one another for the same co-unit content. Since the changes with molecular weight and composition follow a similar pattern, for each of the copolymer types, it is possible to select different compositions and molecular weights from among the two groupings that yield similar nominal stress–strain curves.

When compared with those for linear polyethylene,[3] the force–elongation curves of the copolymers behave as though they were of much higher molecular weight. This behavior has been observed in the study of other properties of random ethylene copolymers.[22] Therefore, except for low molecular weights, ≤50 000, strain hardening dominates the postyield deformations. A qualitatively similar result has been reported by Seguela and Rietsch[67] for a set of ethylene–butene copolymers that were very polydisperse with respect to both molecular weight and copolymer composition. Although the ethylene–butenes display the same general characteristics, the effects are not as great as those of the other copolymers.

The basic mechanism, or mechanisms, causing strain hardening have not as yet been clearly elucidated. The major influence is found in very high molecular weight linear polyethylene and in the ranom copolymers. Both of these type species have in common the fact that their core crystallinity levels are relatively low, ≤0.40. Therefore, potentially crystallizable units exist in these systems. Thus, the distinct possibility exists that strain-induced crystallization can take place during the tensile deformation. The upsweep in the stress–strain curve of naturally result. Here it has been shown that the large upsweep that is observed in the stress–strain curve is caused by strain-induced oriented crystallization.[52] Whether this process is operative in homopolymers and copolymers of relatively low levels of crystallinity still remain to be established. This is an important aspect of the problem that needs to be investigated.

Another possible mechanism for strain hardening resides in the elastic response of the disordered interlamellar region to the applied force. Although the density of entanglements of linear polymers is independent of molecular weight, their number per molecule increases with chain length. As a chain moves, or slips, through the impediment of entanglements, its apparent modulus will be affected and will increase with molecular weight. Thus, at a sufficiently higher molecular weight the apparent modulus will also be high and will be reflected in the observation of an enhanced strain hardening. It has been postulated that in copolymers the entanglement density increases with co-unit content.[5] If this were so, then these changes in the noncrystalline region would make a contribution to strain hardening at a lower molecular weight than the corresponding homopolymers. However, Carella *et al.*[68] found that the plateau modulus of hydrogenated poly(butadiene) decreases with increasing co-unit content. Consequently, following conventional arguments the entanglement density will accordingly decrease.[68] Therefore, on this basis the entanglement argument cannot explain the enhanced strain hardening of random copolymers at lower molecular weights. There are, therefore, at least two mechanisms that can qualitatively explain strain hardening and its predominance in copolymers.

We next consider the influence of the specificity of the commonomer on the general characteristics of the nominal stress–strain curves and on the ultimate properties. In the case of ethylene–propylene copolymers, not studied here, the directly bonded methyl groups enter the crystal lattice on an equilibrium basis.[19,20] Consequently, it is not surprising that the nominal stress–strain curves for this copolymer are similar to those of the linear polymer of comparable molecular weight.[5] The co-unit of the copolymers studied here does not enter the crystal lattice.[19,69] However, as we have noted in the preceding discussion, there is a major difference in the tensile properties between the ethylene–butenes and the others. In addition, the molecular weight analogy that has been made between the linear polymers and copolymers is not as marked with the butene copolymers. The thermodynamic properties and phase structure are the same for the different branch types, when compared at the same molecular weight and co-unit content, with the exception of the ethylene–octenes.[18] The only difference is that the interfacial content and thicknesses of the ethylene–octenes are slightly higher than the others. Therefore, the differences in tensile properties cannot be caused by the crystallite and associated structures. They must reside in the residual, noncrystalline portion of the semicrystalline polymer. The interactions and dynamics that cause the copolymers to behave as higher molecular weight linear polymers are not as strong with the ethylene–butene copolymers. The interaction involved could depend on the size of the side groups. Since we are concerned with a time-dependent phenomenon, the size of the side groups could also be influencing the elastic response.

In contrast to deformation in the postyield region the observed yield stress only depends on the crystallinity levels and is independent of the chemical nature of the co-unit. Thus, the crystallite and associated regions are involved in the process. In the range of crystallinity levels where there is an overlap between the copolymers and homopolymers, there is a significant difference in the yield stress between the two. Since the crystallographic structure is the same in both cases, yielding must involve more than just displacement of atoms within the crystallite interior. In addition the character of the yielding process itself is dependent on the crystallinity level. It has been reported that cross-linking linear polyethylene, by high-energy ionization radiation, causes a substantial increase in the yield stress.[70] In this case the crystallinity level remains about the same, or decreases slightly. These results indicate that yielding must involve more than just deformation within the interior of the crystallite.

The crystallinity levels of the copolymers that were studied here are much less than 50% in most cases. Thus, a substantial portion of the system is not in the ordered state but is still involved in the deformation. One of the main problems in understanding the molecular basis of the tensile properties of crystalline polymers is to establish the role of the different structural regions on the different aspects of the deformation process.

In this paper we have presented the major features of the tensile properties of a set of random ethylene–1-alkene copolymers. The general character of the nominal stress–strain curves and of key tensile properties has been described in terms of the molecular constitution of the chains, the structural quantities that define the crystalline state of polymers, and the chemical nature of the co-unit. A complete molecular understanding of the total deformation process is not yet at hand. However, these results, as well as those reported for fractions, and well-characterized linear polyethylenes, should serve as a basis and aid further developments in this understanding.

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