$$\overline{V}_{\mathrm{S}} = (\alpha D_{\mathrm{S}}'/\nu_{\mathrm{S}})[(1 + X_{1\mathrm{S}}'X_{2\mathrm{S}}') + (X_{1\mathrm{S}}' + X_{2\mathrm{S}}')\coth \alpha l]^{-1} \times \{([\mathrm{S_R}] + [\mathrm{S_L}]) \tanh (\alpha l/2) + X_{1\mathrm{S}}'[\mathrm{S_R}] + X_{2\mathrm{S}}'[\mathrm{S_L}]\} \quad (53)$$

If R represents a reactant which is not rate determining, then:

$$D_{\mathrm{R}}' \,\mathrm{d}^2[\mathrm{R}]/\mathrm{d}x^2 = \nu_{\mathrm{R}} V \quad (54)$$

where ν_{R} is the corresponding stoicheometric coefficient. By the same procedure as above we may derive the following relations:

$$\left(\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}x}\right)_{x=0} = \frac{[\mathrm{R}_l] - [\mathrm{R}_0]}{l} + \gamma \left\{\frac{[\mathrm{S}_l] + [\mathrm{S}_0]}{l} + \left(\frac{\mathrm{d}[\mathrm{S}]}{\mathrm{d}x}\right)_{x=0}\right\} \quad (55a)$$

and

$$\left(\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}x}\right)_{x=l} = \frac{[\mathrm{R}_l] - [\mathrm{R}_0]}{l} + \gamma \left\{\frac{[\mathrm{S}_l] + [\mathrm{S}_0]}{l} + \left(\frac{\mathrm{d}[\mathrm{S}]}{\mathrm{d}x}\right)_{x=l}\right\} \quad (55b)$$

where $\gamma = (\nu_{\mathrm{R}}/\nu_{\mathrm{S}})(D_{\mathrm{S}}'/D_{\mathrm{R}}')$. Substitution of the expressions:

$$[\mathrm{R}_0] = [\mathrm{R_L}] + X_{1\mathrm{R}} \left(\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}x}\right)_{x=0} \quad (56a)$$

$$[\mathrm{R}_l] = [\mathrm{R_R}] - X_{2\mathrm{R}} \left(\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}x}\right)_{x=l} \quad (56b)$$

where $X_{1\mathrm{R}} = \delta D_{\mathrm{R}}'/D_{\mathrm{R}}$ and $X_{2\mathrm{R}} = X_{1\mathrm{R}} + dD_{\mathrm{R}}'/D_{\mathrm{R}}''$ produces the final relations:

$$\left(\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}x}\right)_{x=0} = \frac{[\mathrm{R_R}] - [\mathrm{R_L}] + lW_0 - X_{2\mathrm{R}}(W_l - W_0)}{X_{1\mathrm{R}} + X_{2\mathrm{R}} + l} \quad (57a)$$

and

$$\left(\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}x}\right)_{x=l} = \frac{[\mathrm{R_R}] - [\mathrm{R_L}] + lW_l + X_{1\mathrm{R}}(W_l - W_0)}{X_{1\mathrm{R}} + X_{2\mathrm{R}} + l} \quad (57b)$$

where:

$$W_0 = \gamma\{(1/l)([\mathrm{S}_l] + [S_0]) + (\mathrm{d}[\mathrm{S}]/\mathrm{d}x)_{x=0}\} \quad (58a)$$

$$W_l = \gamma\{(1/l)([\mathrm{S}_l] + [\mathrm{S}_0]) + (\mathrm{d}[\mathrm{S}]/\mathrm{d}x)_{x=l}\} \quad (58b)$$

Acknowledgment. This work was partially supported under Grant HL-12157 from the National Institute of Health, Public Health Service. It is a pleasure to dedicate this work to Dr. Maurice L. Huggins who, over the years, has made significant contributions to our understanding of polymer solution thermodynamics.

References and Notes

(1) Address correspondence to this author.
(2) I. Prigogine, "Introduction to Irreversible Thermodynamics", 3rd ed, Interscience, New York, N.Y., 1967.
(3) L. W. Cunningham and C. S. Brown, *J. Biol. Chem.*, **221**, 287 (1956).
(4) M. L. Bender, *J. Am. Chem. Soc.*, **84**, 2583 (1962).
(5) M. L. Bender, G. E. Clement, F. J. Kézdy, and H. d'A. Heck, *J. Am. Chem. Soc.*, **86**, 3680 (1964).
(6) R. Goldman, O. Kedem, and E. Katchalski, *Biochemistry*, **7**, 4518 (1968).
(7) G. Kay and M. D. Lilly, *Biochim. Biophys. Acta*, **198**, 281 (1970).
(8) H. Yasuda, C. E. Lamaze, and A. Peterlin, *J. Polym. Sci., Part A-2*, **9**, 1125 (1971).
(9) A. Staverman, *Recl. Trav. Chim. Pays-Bas*, **70**, 344 (1951).
(10) A. Katchalsky and P. F. Curran, "Non-equilibrium Thermodynamics in Biophysics", Harvard University Press, Cambridge, Mass., 1967, p 119.
(11) G. V. Schulz and W. H. Kuhn, *Makromol. Chem.*, **29**, 220 (1959).
(12) J. Hine, *J. Am. Chem. Soc.*, **85**, 3239 (1963).
(13) M. K. Jain, "The Bimolecular Lipid Membrane: A System", Chapter 8, Van Nostrand-Reinhold, New York, N.Y., 1972.
(14) R. Goldman, O. Kedem, and E. Katchalski, *Biochemistry*, **10**, 165 (1971).
(15) C. Barnes, *Physics*, **5**, 5 (1934).
(16) B. Zerner and M. L. Bender, *J. Am. Chem. Soc.*, **86**, 3669 (1964).
(17) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structure", McGraw-Hill, New York, N.Y., 1968, p 306.

Molecular Relaxations in Partially Hydrogenated *cis*-1,4-Polybutadienes. A Guide to the Glass Transition Temperature of Amorphous Polyethylene

J. M. G. Cowie* and I. J. McEwen

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland.

Received April 11, 1977

ABSTRACT: A series of partially hydrogenated polybutadienes has been prepared by treating a sample of *cis*-1,4-polybutadiene with *p*-toluene sulfonhydrazide for varying lengths of time. The resulting polymers, which can be regarded as random copolymers of ethylene with acetylene, were examined by differential scanning calorimetry (DSC) and torsional braid analysis (TBA). The glass transition temperature (T_g) of amorphous polyethylene was estimated by plotting the T_g's of the copolymers, derived from DSC measurements, as a function of composition and extrapolating to 100% ethylene content. A value in the range 197–200 K was obtained using two extrapolation methods. Dynamic mechanical spectra exhibit a number of damping maxima for the copolymers, and attempts are made to identify these. The results suggest that the γ relaxation in polyethylene is not the glass temperature but is more likely to result from a crankshaft motion of short methylene sequences in the chain.

In spite of the vast amount of work reported on the relaxations observed in both linear and branched polyethylene, there is still no consensus on the precise temperature of the glass transition. Extensive reviews have been presented, most recently by Stehling and Mandelkern[1] and by Boyer[2] which highlight this problem, and each arrives at a different conclusion. It is now well established that polyethylene samples of medium crystallinity exhibit three major loss peaks in their dynamic mechanical spectra, at 145 ± 10 K, 240 ± 20 K and 340 ± 10 K, called respectively the γ, β, and α peaks. In high-density linear polyethylene the β peak tends to disappear and another damping maximum is found at temperatures of 390 ± 20 K called the α' peak.

Stehling and Mandelkern[1] have suggested that the glass temperature (T_g) for polyethylene is approximately 145 K and can be identified as the γ relaxation. This view is supported by Fischer and Kloos[3] from small-angle x-ray studies on linear polyethylene and by heat-capacity data reported by Beatty and Karasz.[4] From a study of the Raman spectra of rapidly quenched high-density polyethylene, Hendra et al.[5] have observed that the onset of crystallization takes place at temperatures near 190 K. They conclude that T_g must then lie near or below this temperature but were unable to identify a specific value. Boyer[1,6] has critically examined the evidence on which Stehling and Mandelkern base their conclusions and proposes instead that while the evidence supports the conclusion that the γ relaxation is associated with a relaxation in the amorphous phase, polyethylene actually exhibits two glass like relaxations neither of which is the γ relaxation. The two relaxations are identified as $T_g(\mathrm{L}) \approxeq 95$ K which is affected only slightly by crystallinity and $T_g(\mathrm{U})$ which is much more strongly influenced by the crystallinity of the sample but is located around 240 K for samples with fractional crystallinities between 0.4 and 0.75. Both $T_g(\mathrm{L})$ and $T_g(\mathrm{U})$ are considered to be coincident for the hypothetical amorphous polyethylene.

Polyethylene is normally highly crystalline and quenched samples crystallize too rapidly to permit examination of the amorphous phase; this makes direct measurement of T_g extremely difficult. Several workers have attempted to overcome this problem using copolymers containing ethylene and extrapolating the T_g data as a function of composition to obtain a value for pure polyethylene. A commonly used series is the ethylene–propylene copolymer and the results from a number of sources are reviewed by Maurer.[7] Data analysis shows that an extrapolated value of $T_g = 193$ K for polyethylene is obtained using the Gordon–Taylor equation,[8] when amorphous copolymers with ethylene contents of less than 60 mol % are used. It has been further noted that the sample crystallinity increases as the ethylene content rises beyond this value and that this is accompanied by an upswing in T_g. This second region can be treated independently and data extrapolate to $T_g = 240$ K for semicrystalline polyethylene. Not all ethylene copolymer systems extrapolate to precisely these values and temperatures lying in the range 163 to 198 K have been quoted.[9-14]

During a study of the hydrogenation of polydienes, a number of partially hydrogenated *cis*-1,4-polybutadienes were prepared and investigated. These can be regarded as either copolymers of ethylene and butadiene or alternatively ethylene and acetylene, depending on how one views the repeat unit in the chain. Their dynamic mechanical properties and behavior in the DSC have been examined and provide information which helps clarify aspects of the problem outlined above.

Experimental Section

Sample Preparation and Analysis. A sample of polybutadiene (Goodyear) was dissolved in toluene and filtered to remove any insoluble material. The solution was then fractionated to remove low molecular weight polymer and the top fraction was recovered. Viscometric measurement[14] showed the sample to have $M_v = 5 \times 10^5$, while infrared analysis[15] indicated a stereostructure of 94% cis-1,4, 4% trans-1,4 and 3% 1,2 units in the chain. Hydrogenation was carried out using the method outlined by Mango and Lenz,[16] in which polybutadiene is dissolved in toluene and refluxed under nitrogen in the presence of *p*-toluene sulfonhydrazide (TSH). Samples were withdrawn at intervals and isolated by precipitation with methanol. The extent of hydrogenation was determined by NMR analysis of solutions of the polymer in carbon tetrachloride (5–10% w/v) and the fraction of butadiene units hydrogenated (F) was calculated from

$$F = (1 - 2R)/(1 + 2R) \qquad (1)$$

where R is the total integral due to methylene groups (1.3 and 2.0 ppm) divided by the integral due to the protons on the remaining double bonds (5.4 ppm).

Torsional Braid Analysis (TBA). The dynamic mechanical response of each copolymer sample was determined, at a nominal frequency of 1 Hz, by a torsional braid technique.[17,18] A Model 100-B1 (Chemical Instruments Corp.) was used and measurements were extended over the temperature range 90 to 430 K. Composite samples were prepared by immersing glass fiber braids in a concentrated solution of the polymer (10% w/v). The braid was then suspended under tension (70 g) in a drying cell and the solvent was removed under vacuum. Glass braids were obtained from Jones Stroud Insulations and cleaned thoroughly in hot chromic acid before use.

After solvent removal was complete, the sample braid was introduced into the measuring chamber which was flushed by a constant stream of dry nitrogen. The sample and chamber were then cooled to about 90 K by circulating nitrogen gas, which had been precooled in liquid nitrogen passed through the cooling coils at a rate of 20 dm^3 min^{-1}. After equilibration at the lowest temperature for about 30 min, the rate of gas flow was slowly reduced. By adjusting this flow rate the sample could be warmed slowly at a controlled rate of about 1 K min^{-1}, during which time the dynamic mechanical response was recorded at 2 to 4 K intervals.

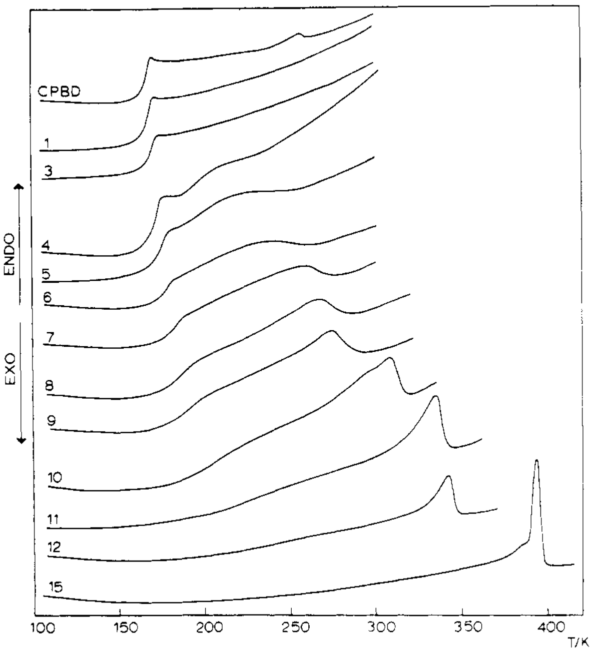

Figure 1. DSC thermograms for *cis*-1,4-polybutadiene (CPBD) and hydrogenated samples. Numbers correspond to those shown in Table I.

As the samples are in the form of a composite with indefinite geometry, only relative values of the mechanical response can be measured. The characteristic damping index ($1/n$), which is related to the logarithmic decrement, can be calculated from the number of oscillations (n) occurring between two fixed but arbitrary boundary amplitudes on the decay pattern. The data, displayed as $-\log(1/n)$ against temperature, show the damping response of the sample.

Differential Scanning Calorimeter (DSC). Transitions in the sample were detected by DSC using a Perkin-Elmer DCS-2 fitted with a low-temperature accessory. Samples were quench cooled from 400 K at a rate of 320 K min^{-1} and subsequent thermograms were obtained at a scan speed of 20 K min^{-1}. The glass transition temperature T_g was taken to be the point of intersection of the extrapolated baseline prior to a shift with the line of maximum slope encountered during the shift. Measurements were repeated until T_g values reproducible to ±0.5 K were obtained.

Results and Discussion

Structurally, *cis*-1,4-polybutadiene can be conveniently regarded as an alternating copolymer of ethylene and acetylene. Hydrogenation of the double bonds progressively converts this to more random copolymer structures of increasing ethylene content, ending finally as pure polyethylene. Examination of these intermediate structures can provide a means of estimating the glass transition temperature of amorphous polyethylene by extrapolating T_g as a function of copolymer composition for samples where T_g appears to be relatively unaffected by sample crystallinity.

The DSC thermograms for these copolymers, shown in Figure 1, exhibit two main features. In samples with less than 28% hydrogenation, only a T_g is obvious; when the hydrogenation exceeds about 65%, T_g becomes difficult to locate and a strong melting endotherm predominates. For samples in the intermediate range both T_g and a broad endotherm, suggesting some form of developing crystallinity, can be detected. The values of T_g are listed in Table I together with the

Table I
T_g and T_m Data from Differential Scanning Calorimetry Measurements on Samples of Hydrogenated *cis*-1,4-Polybutadiene

Sample	% hydrogenation	Wt % ethylene[a]	T_g, K	T_m, K (peak)
cis-1,4-Polybutadiene	0	53.8	164	256
1	12.8	58.2	164	
2	22.0	62.7	165	
3	28.0	65.7	166	
4	29.7	66.6	167	210
5	34.4	68.8	169	220
6	37.8	70.5	171	245
7	42.6	72.8	173	260
8	45.7	74.3	174	270
9	50.0	76.4	177	279
10	60.7	81.5	178	308
11	68.6	85.3	(185)	339
12	77.3	89.3		346
15	98.0	96.5		393

[a] Calculated using the model of an alternating copolymer to describe polybutadiene.

temperature of the endotherm maximum, designated T_m. The latter is a rather subjective choice when dealing with samples 4 to 7 where the endotherm is spread out over an extended temperature range which increases as the hydrogenation progresses.

The endothermic process begins to resolve, through samples 8 to 15, into a reasonably well-defined peak with a substantial low-melting tail. This would indicate that there is a gradual growth in the samples of small, imperfect crystallites which subsequently develop into well-defined crystalline regions as more of the molecule is transformed into a polyethylenic type structure. In the later stages the crystallinity becomes sufficiently pronounced to make detection of a T_g very uncertain (samples 11 to 15), if not impossible. In sample 15, with a percent hydrogenation of 98, T_m = 393 K, which is approximately 20 K lower than that expected for linear polyethylene. This could be due to the imperfections in structure introduced into the chain by the presence of the small proportion of 1,2 addition units in the original sample.

On the evidence obtained from the DSC thermograms, the developing crystallinity does not appear to affect the T_g until one reaches sample 11, consequently the T_g data for samples 1 to 10 were used to estimate the T_g of a hypothetical, amorphous sample of polyethylene. When the data were plotted using a Gordon–Taylor equation[8] a gentle curve resulted which could be extrapolated to give T_g(polyethylene) = 195 K. An alternative method proposed by Barton[19] was also used, where the equation has the form

$$T_g = n_{aa}'T_g(aa) + n_{bb}'T_g(bb) + (n_{ab}' + n_{ba}')T_g(ab) \quad (2)$$

and takes into account additional contributions from bonds between an "a" monomer and a "b" monomer. The T_g of the copolymer is related to T_g(aa) and T_g(bb), the glass temperatures of the respective homopolymers, and also to that of the alternating copolymer T_g(ab). The coefficient n_{ij}' is the mole fraction of rotatable bonds contained in an (ij) sequence and is weighted by the number of rotatable bonds in that sequence. While this form of equation is usually a more accurate representation of copolymer behaviour, lack of all relevant parameters forces us to simplify it. This can be achieved by treating polybutadiene as an alternating copolymer of acetylene (a) and ethylene (b); thus n_{aa}' = 0 and T_g(ab) is then the glass transition temperature of polybutadiene. The plot, shown in Figure 2, has a more extended linear portion of lower slope than the Gordon–Taylor treatment, which helps the extrapolation. The results are, however, much the same giving T_g(polyethylene) = 197–200 K. Both values are similar to the lower T_g(L) suggested by Boyer and are in close agreement with the extrapolated values of 193 and 196 K obtained using ethylene–propylene copolymers[7] and copolymers of ethylene with vinyl acetate and vinyl propionate,[9] respectively. An extrapolated value of T_g = 193 K has also been obtained by Lath[20] from ethylene–vinyl acetate copolymer samples.

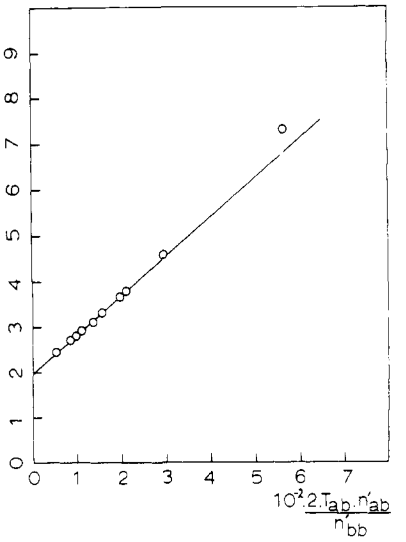

Figure 2. Glass transition temperatures of hydrogenated polybutadienes plotted according to eq 2 on the assumption that the samples are copolymers of ethylene and acetylene.

A wide variety of transitions have been reported by other workers. Thermal expansion measurements by Simha et al.[21] have revealed transitions at 148, 213, 251, and 273 K. Jain and co-workers[22] have found a strong transition at 152 K and a weaker one at 233 K for semicrystalline polyethylene. Stehling and Mandelkern[1] reported the existence of only one transition at 145 K and considered their thermal expansion data at higher temperatures were best represented by a curve. A reinterpretation of their data by Boyer[2] shows two additional transitions at 193 and 238 K.

The two temperatures most favored as the T_g for polyethylene are ~145 and ~195 K. Our DSC data support the latter value and the dynamic mechanical results, which follow, give further reasons for stating that the relaxation at 145 K is not the main glass temperature.

The transition at 145 K is usually called the γ relaxation in polyethylene, and it can be seen in some of the TBA spectra for the copolymers (Figures 3 and 4) that a peak in this temperature range first becomes obvious around 30% hydrogenation. The temperature of the peak stays essentially constant at ~150 K and it remains well resolved in all samples with ethylene contents in excess of 67 wt % through to polyethylene. It is reasonable to identify this damping peak in the copolymers with the γ relaxation in polyethylene. This damping maximum always remains identifiably separate from the damping peaks in the TBA spectra related to the T_g by comparison with DSC measurements. No evidence of a T_g in the region of 150 K could be found in the DSC thermograms. The temperatures of the damping maxima associated with the T_g are shown in Table II and are consistently higher than T_γ. It can also be seen that the TBA damping peaks which can be associated with the T_g occur at higher temperatures than those measured in the DSC. It is believed that this may in part be due to the fact that samples can be quenched rapidly then measured quickly in the DSC, thereby keeping crystalline

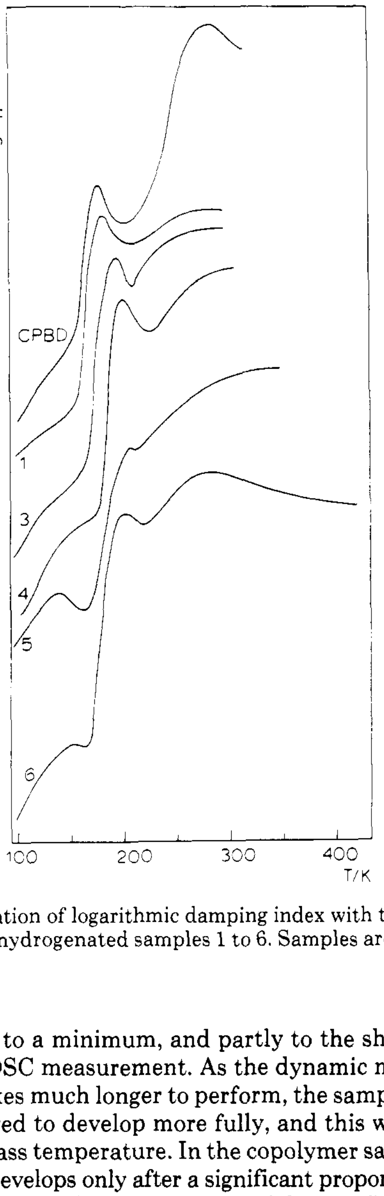

Figure 3. Variation of logarithmic damping index with temperature for CPBD and hydrogenated samples 1 to 6. Samples are numbered as in Table I.

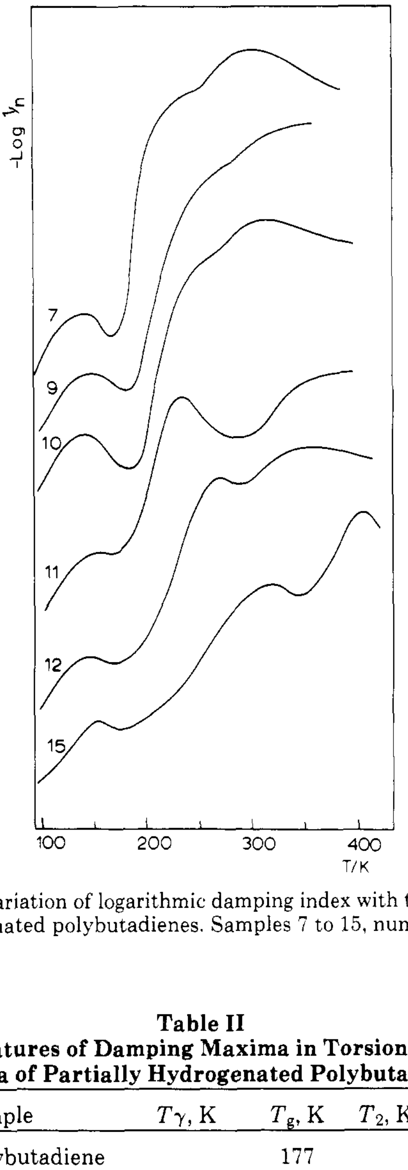

Figure 4. Variation of logarithmic damping index with temperature for hydrogenated polybutadienes. Samples 7 to 15, numbered as in Table I.

development to a minimum, and partly to the shorter time scale of the DSC measurement. As the dynamic mechanical technique takes much longer to perform, the sample crystallinity is allowed to develop more fully, and this will tend to elevate the glass temperature. In the copolymer samples, the γ relaxation develops only after a significant proportion of the chain is reduced, producing sequences of three to five ethylene units. Other work[23] has shown that the γ relaxation in polyethylene decreases with increasing sample crystallinity, and most workers agree that the relaxation arises from motion in the amorphous region of the polymer. This, together with the evidence presented here, suggests that the relaxation occurring around 145 K is more likely to be a result of limited crankshaft motion in the methylene sequences rather than a main glass transition temperature. This view is also held by MacKnight and co-workers.[24,25]

The dynamic mechanical spectra exhibit other damping peaks. In the original sample of *cis*-polybutadiene, two major damping maxima appear at 177 and 282 K. While the temperatures differ somewhat from the DSC measurements, these can be correlated with respectively the T_g and a small melting endotherm detected at about 256 K in the DSC thermograms. The spectra for the copolymers become much more complex and the temperatures of the main damping maxima are summarized in Table II. The glass transition is a prominant damping peak up to sample 6 but becomes less distinct when the ethylene content exceeds 71 wt %. Whereas the DSC thermograms display unmistakable glass transitions up to sample 10, the thermomechanical spectra show an increasingly complex damping pattern in an adjacent but higher temperature range which appears to result from the developing crystallinity in the samples. This seems to submerge the T_g peak and makes resolution of the separate processes difficult. Thus samples 6 to 10 exhibit a strengthening of the damping peaks in the range 280–330 K, apparently absorbing the T_g process as a shoulder. The broad, ill-defined nature of these peaks may result from several overlapping relaxation mechanisms involving different amorphous regions associated with imperfect crystalline domains. The T_g is more readily resolved for these samples in the DSC thermograms, but pronounced melting endotherms with substantial low melting regions can also be seen. These broad endotherms cover a temperature range of ~200 to 280 K and correspond to the damping observed in the TBA spectra in the temperature span 200–350 K. They also indicate a steady growth in sample crystallinity and crystallite size as the ethylene content increases.

Table II
Temperatures of Damping Maxima in Torsional Braid Spectra of Partially Hydrogenated Polybutadienes

Sample	T_γ, K	T_g, K	T_2, K	T_1, K
cis-1,4-Polybutadiene		177		282
1		181		
2		195		
4	(shoulder)	200		
5	140	205		
6	150	202		290
7	140		(215)	300
9	149		(234)	330
10	145		(240)	315
11	150		233	330
12	150		270	350
15	153		320	405

The compound damping peaks eventually resolve above

69% hydrogenation (sample 11) into two distinct maxima which shift to higher temperatures as the ethylene content increases. These are listed as T_1 and T_2 in Table II. In sample 11, T_2 is found in the temperature range normally associated with the β relaxation in polyethylene, but this moves rapidly into a position (sample 15) near where the α relaxation is detected in polyethylene. There is now no distinct baseline shift, characteristic of T_g, in the DSC thermogram for sample 11, but the melting endotherm is quite pronounced and becomes increasingly so through to sample 15. The β relaxation is usually thought to be a consequence of a relaxation involving branch points in low-density polyethylene. The original *cis*-polybutadiene sample had less than 3% 1,2-addition units present so that the contribution from branch points should be similar to low-density polyethylene, but because the branches are shorter it would appear more likely that the T_2 peaks arise from relaxation processes involving the amorphous regions of small imperfect crystallites.

The spectrum of sample 15 is similar to that of a high-density polyethylene sample in which an α and an α' peak are resolved. Both are attributed to molecular motion believed to originate in the crystalline regions.[26]

Conclusions

On the basis of the evidence presented here it is concluded that the glass transition temperature of completely amorphous polyethylene would lie in the region 190–200 K and that the γ relaxation, while associated with amorphous regions in the polymer, is not the major glass transition temperature. As the rate of crystallization of polyethylene is much too rapid to allow direct measurements on a stable amorphous sample, the significance of T_g in polyethylene remains somewhat academic.

References and Notes

(1) F. C. Stehling and L. Mandelkern, *Macromolecules*, **3**, 242 (1970).
(2) R. F. Boyer, *Macromolecules*, **6**, 285 (1973).
(3) E. W. Fischer and F. Kloos, *J. Polym. Sci., Part B*, **8**, 685 (1970).
(4) C. L. Beatty and F. E. Karasz, *Bull. Am. Phys. Soc.* **16**, Ac-12 (1971).
(5) P. J. Hendra, H. P. Jobic, and K. Holland-Moritz, *J. Polym. Sci., Part B*, **13**, 365 (1975).
(6) R. F. Boyer, *J. Macromol. Sci., Phys.*, **8**, 503 (1973).
(7) J. J. Maurer, *Rubber Chem. Technol.*, **38**, 979 (1965).
(8) M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**, 493 (1952).
(9) R.-H. Illers, *Kolloid Z. Z. Polym.*, **190**, 16 (1963).
(10) E. G. Kontos and W. P. Slichter, *J. Polym. Sci.*, **61**, 61 (1962).
(11) I. Baldi and R. Zannetti, *Mater. Plast. Elastomeri*, **31**, 1309 (1965).
(12) L. E. Nielsen, *J. Polym. Sci.*, **42**, 357 (1960).
(13) C. A. F. Tuijnman, *J. Polym. Sci., Part C*, **16**, 2379 (1967).
(14) M. Takeda and R. Endo, *Rep. Prog. Polym. Phys. Jpn.*, **6**, 37 (1963).
(15) J. L. Binder, *Appl. Spectrosc.*, **28**, 17 (1969).
(16) L. A. Mango and R. W. Lenz, *Makromol. Chem.*, **163**, 13 (1973).
(17) A. F. Lewis and J. K. Gillham, *J. Appl. Polym. Sci.*, **6**, 422 (1962).
(18) J. K. Gillham, *Crit. Rev. Macromol. Sci.*, **1**, 83 (1972).
(19) J. M. Barton, *J. Polym. Sci., Part C*, **30**, 573 (1970).
(20) D. Lath, personal communication.
(21) (a) J. L. Zakin, H. C. Hershey, and R. Simha, *J. Appl. Polym. Sci.*, **10**, 1455 (1966); (b) S. Lee and R. Simha, *Macromolecules*, **7**, 909 (1974).
(22) R. K. Jain, R. N. Gupta, and V. S. Nanda, *J. Macromol. Sci., Phys.*, **11**, 411 (1975).
(23) D. E. Kline, J. A. Sauer, and A. E. Woodward, *J. Polym. Sci.*, **22**, 455 (1955).
(24) R. Sanui, W. J. MacKnight, and R. W. Lenz, *Macromolecules*, **7**, 101 (1974).
(25) T. R. Earnest, Jr., and W. J. MacKnight, *Macromolecules*, **10**, 206 (1977).
(26) N. G. McCrum, B. E. Reid, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York, N.Y., 1967.

Neutron Scattering Studies on the Molecular Trajectory in Polyethylene Crystallized from Solution and Melt[†]

D. M. Sadler* and A. Keller

H. H. Wills Physics Laboratory, University of Bristol, Royal Fort, Bristol BS8 1TL, England.

Received May 10, 1977

ABSTRACT: A comparative survey was carried out on the trajectory of polyethylene chains within their own crystal environment in the case of solution- and melt-crystallized samples by means of low-angle neutron scattering using the isotope miture method. The issue of prime concern was the manner of fold re-entry as assessed by the arrangement of the straight segments. However, to ensure molecular dispersion of the labeled minority species total scattering mass and radius of gyration were also studied to a lesser extent, the full range of measurements extending over the rather wide angular range from 1400 to 16 Å equivalent Bragg spacing. The principal result was that in solution-grown crystals the chains form sheets consistent with adjacent fold re-entry, confirming earlier claims,[15] in sharp contrast to samples crystallized from a cooling melt where the effectively random arrangements of stems imply random fold re-entry. It is believed these two cases are extremes of a general behavior pattern. Scattering effects in the lowest angular range were interpretable in terms of enrichment of the labeled species along the periphery of large-scale morphological units, as opposed to molecular associations, where very low levels of enrichment sufficed to account for the observed effects. How far effects of this kind permit or limit the interpretation of neutron diffraction data in wider angular ranges has been evaluated and discussed. Other discussions are concerned with a number of effects observed relating to variations in molecular weight, crystallization temperature, concentration of the labeled species, and the significance of the findings in general.

General Background

The basic issue underlying this paper is the nature of chain folding in crystalline polyethylene: specifically what is the manner of re-entry and how this is affected by crystallization conditions, in particular when crystallization from solution and melts are compared. These have been long-standing problems which can now be approached from a new angle thanks to the recently introduced method of neutron scattering from isotopically tagged molecules. Deuterated molecules are mixed in small concentrations with the protonated version of the same species, or vice versa, when, owing to the largely differing scattering amplitudes of H and D, the mi-

---

[†] Dedicated to the 80th birthday of Professor Maurice L. Huggins.